Investigation of Three-Way (TWC), Lean NOx Trap (LNT) and Selective Catalytic Reduction (SCR) Catalysts For Control of NOx Emissions from Lean-Burn Engines

Christopher Dominic DiGiulio

University of South Carolina

Follow this and additional works at: https://scholarcommons.sc.edu/etd

Part of the Chemical Engineering Commons

Recommended Citation

This Open Access Dissertation is brought to you by Scholar Commons. It has been accepted for inclusion in Theses and Dissertations by an authorized administrator of Scholar Commons. For more information, please contact dillarda@mailbox.sc.edu.
INVESTIGATION OF THREE-WAY (TWC), LEAN NOₓ TRAP (LNT) AND
SELECTIVE CATALYTIC REDUCTION (SCR) CATALYSTS FOR
CONTROL OF NOₓ EMISSIONS FROM LEAN-BURN ENGINES

by

Christopher D. DiGiulio

Bachelor of Science
University of Oklahoma, 2008

Submitted in Partial Fulfillment of the Requirements
For the Degree of Doctor of Philosophy in
Chemical Engineering
College of Engineering and Computing
University of South Carolina
2013

Accepted by:
Dr. Michael D. Amiridis, Major Professor
Dr. Oleg S. Alexeev, Committee Member
Dr. A. Jochen Lauterbach, Committee Member
Dr. Donna A. Chen, Committee Member
Dr. Todd J. Toops, Committee Member
Dr. John W. Weidner, Chemical Engineering Department Chair
Dr. Lacy K. Ford, Vice Provost and Dean of Graduate Studies
DEDICATION

TO MY WIFE RACHEL…

THIS IS BUT ONE CHAPTER IN THE REST OF OUR LIVES TOGETHER

LOVE ALWAYS,

CHRIS
ACKNOWLEDGEMENTS

First and foremost, I would like to acknowledge my advisor Dr. Michael Amiridis, who made all of this possible. I would like to thank him for accepting me into his group, even though he had already made commitments to other students. I would like to thank him for allowing me the freedom to pursue my own ideas and avenues of research. I would like to thank him for making time for me, even though he has an exceptionally busy schedule and for inviting me into his home to share a holiday meal with his family. Lastly, I would like to thank him for his invaluable insight and perspective. He is someone that I could never predict, but who always offered the best advice. I learned something every time we met. I hope that as I continue to grow in my career and as a person, I develop the long-sighted perspective that he so clearly possesses.

I would like to acknowledge Dr. Oleg Alexeev for all of his time and support, especially when I first arrived in Dr. Amiridis’ research group. He, more than anyone, deserves the credit for teaching me the proper way to design equipment and perform experiments. Dr. Alexeev’s un-compromising principles in pursuit of the truth taught me to be patient and focus on performing scientifically valid experiments, even when I desperately needed to make progress.

I would like to acknowledge Dr. John Monnier for the integral role he played in shaping my education. I am sincerely thankful, that instead of retiring, Dr. Monnier’s love for catalysis brought him to the University of South Carolina to a lab with no windows across the hall from mine. He became a resource that any student would be lucky to have. I would to like thank him
for welcoming my questions, even when they were not related to his area of emphasis, and for allowing me to use his equipment. I would also like to thank him for allowing me to work on one of his projects and challenging me to learn and advance my education every time we spoke. Most importantly, I would like to thank Dr. Monnier for all of the advice he provided me and all of the stories he shared. They will stay with me forever.

I would like to acknowledge Dr. Donna Chen for her overt excitement and charisma for the field of Surface Science, but also for her love of education and the pursuit of knowledge in general. I would like to thank her for being such an exceptional teacher and for helping guide my research, especially during the early stages. She is easily one of my favorite professors.

I would like to acknowledge Dr. Lauterbach for allowing me to become a de facto member in his research group and attend weekly meetings to learn from him and his other students. I would also like to thank him for the critical role he played in re-directing my dissertation research. Lastly, I would also like to thank him for offering his time, equipment and expertise in pursuit of my research goals.

I would like to acknowledge Dr. Toops, Dr. James Parks II, Dr. Jae-Soon Choi, Dr. Miyoung Kim and Josh Phil for accepting me into the group at Oak Ridge National lab and for the integral role they all played in helping me complete my dissertation research. Under their guidance, my view of automotive catalysis matured from a very specific examination of NSR catalysts into a much more comprehensive perspective of the entire field. I would specifically like to thank Dr. Miyoung Kim for her patience and time when teaching me how to operate the bench reactor at ORNL. I would like to thank Josh Pihl for helping me when I had experimental difficulties and for all of the work he did behind the scenes to make sure that my efforts were not in vain. I would like to thank Dr. Jae-Soon Choi for volunteering time on his reactor and for
being understanding when things were accidentally broken. I would like to thank Dr. James Parks II for approving my inclusion into the group and for all of the advice he provided from an engines perspective. Lastly, I would like to thank Dr. Todd Toops for mentoring me while at ORNL and for becoming yet another valued professional advisor and joining my PhD committee.

In summary, I am sincerely thankful for having the opportunity to interact and learn from so many skilled and successful professionals. I feel that my experience has not been typical and that I am truly lucky to have worked with all of you. I am also thankful that while you all were exceptional mentors and teachers, to me, you feel more like my close friends.

Additionally, I would like to thank all of the administrative/technical staff that helped along the way, specifically: Marcia Rowen, Loretta Hardcastle, Vernon Dorrell, Brian Loggans, Chuck Holland and Pam Olszewski. Thank you all.

Funding from the National Science Foundation and the Department of Energy, which made all of this research possible – and therefore my PhD possible, was also immensely appreciated.

Lastly, I would like to acknowledge my family, especially my parents, for their love and support and for encouraging me to reach for my dreams and providing me with the tools to achieve my goals. Thank you for always emphasizing the value of education, even when I was too immature to listen. Now, begrudgingly following your advice has made all the difference in the world. I will never be able to truly repay you for the difference you have made. All I can say is:

Thank you,

Chris
ABSTRACT

Lean-burn gasoline engines are approximately 10% more fuel efficient than conventional, stoichiometric-burn ones. Although relatively modest, if implemented across the entire U.S. automotive fleet, this improvement in fuel economy could have far-reaching implications on the amount of gasoline imported in the country on an annual basis. However, the development of a cost-effective catalytic converter catalyst capable of meeting emission regulations for lean-burn vehicles still represents a major technical challenge. Currently, lean NO\textsubscript{X} trap (LNT) and selective catalytic reduction (SCR) catalysts are used for this purpose, but both systems suffer from significant drawbacks. For example, LNT catalysts generally require high platinum group metal (PGM) loadings and are highly susceptible to sulfur poisoning. SCR catalysts require a costly urea-dosing system for delivery of urea as the reducing agent into the exhaust stream, as well as a secondary “fuel” tank for on-board storage of urea.

LNT catalysts are typically favored for smaller gasoline engines and are designed for periodic operation in lean and rich environments. NO\textsubscript{X} is stored on the LNT system during a longer (e.g., 60 – 120 s) lean period and rapidly reduced during a much shorter (e.g., 1- 5 s) rich period. The mechanism for NO\textsubscript{X} storage is fairly well understood, but the NO\textsubscript{X} reduction mechanism is still the subject of considerable debate. Lean/rich cycling monitored by \textit{in situ} Fourier Transform infrared spectroscopy (FTIR) confirmed the presence of surface isocyanate (NCO) species during reduction. Quantification of the FTIR results confirmed that surface NCO species could account for as much as 30% of the N\textsubscript{2} formed during the rich period. Hydrolysis of the NCO species to NH\textsubscript{3} in the presence of water vapor could also play a significant role. The
effect of the lean/rich cycle timing on NH$_3$ formation over a commercial LNT catalyst was also considered. At low temperatures, both the release and reduction of stored NO$_X$ was kinetically limited and longer rich periods favored increased NO$_X$ conversion and NH$_3$ formation. At elevated temperatures, the opposite was true and shorter rich periods favored increased NO$_X$ conversion and NH$_3$ formation. The effects of cycle timing were most pronounced in the 250 – 400 °C temperature range, where optimization of the cycle timing could potentially decrease the PGM requirements of the LNT, especially in a coupled LNT-SCR system.

SCR catalysts are typically favored for heavy-duty applications, but General Motors (GM) recently developed a urea-less, passive-NH$_3$, three way catalyst SCR approach (TWC-SCR) for lean-gasoline vehicles. This TWC-SCR approach also relies on lean/rich cycling, but in this case NH$_3$ is intentionally formed over a TWC during rich periods and stored on a downstream SCR catalyst. The stored NH$_3$ is then used during a subsequent lean period to reduce lean-NO$_X$. NH$_3$ generation over TWCs under steady and cycling conditions was investigated. The temperature, catalytic formulation and reductant concentration all affected NH$_3$ formation. Storage of NH$_3$ on the downstream SCR catalyst was also considered. At low temperatures, the selective reduction of NO$_X$ by stored NH$_3$ was favored over a Cu-zeolite SCR catalyst. Above 350 °C, NH$_3$ oxidation was favored over NO$_X$ reduction. Recent bench reactor screening using a two-reactor, bench-core reactor configuration demonstrated the viability of the TWC-SCR configuration and NO$_X$ conversions exceeding 98% were measured.
# TABLE OF CONTENTS

DEDICATION ........................................................................................................................................... III

ACKNOWLEDGEMENTS............................................................................................................................... IV

ABSTRACT ................................................................................................................................................ VII

LIST OF TABLES ........................................................................................................................................ XI

LIST OF FIGURES ....................................................................................................................................... XII

CHAPTER 1. INTRODUCTION, MOTIVATION, LITERATURE REVIEW AND REAL SYSTEMS .............. 1

1.1 INTRODUCTION..................................................................................................................................... 1

1.2 MOTIVATION AND SIGNIFICANCE ................................................................................................. 1

1.3 LITERATURE REVIEW ....................................................................................................................... 4

1.4 REAL SYSTEMS..................................................................................................................................... 61

CHAPTER 2. In situ FTIR INVESTIGATION OF THE ROLE OF SURFACE ISOCYANATES IN THE REDUCTION OF NOX BY CO AND C3H6 OVER MODEL Pt/BA/Al2O3 AND RH/BA/Al2O3 NOX STORAGE AND REDUCTION (NSR) CATALYSTS ........................................................................... 71

2.1 PREFACE ............................................................................................................................................. 71

2.2 INTRODUCTION................................................................................................................................. 72

2.3 EXPERIMENTAL ............................................................................................................................... 74

2.4 RESULTS AND DISCUSSION ............................................................................................................. 79

2.5 CONCLUSIONS .................................................................................................................................. 106

2.6 ACKNOWLEDGEMENTS .................................................................................................................. 107

CHAPTER 3. NH3 FORMATION OVER A LEAN NOX TRAP (LNT) SYSTEM: EFFECTS OF LEAN/RICH CYCLE TIMING AND TEMPERATURE ......................................................................................... 108

3.1 PREFACE ............................................................................................................................................. 108
LIST OF TABLES

Table 1†. Typical Operating Conditions for NSR Catalysts. .............................................................. 7
Table 2. FTIR Band Assignments for Nitrite/Nitrate Species on Ba/Al$_2$O$_3$ NSR Catalysts............ 34
Table 3. FTIR Peak Assignments for C and S containing Species on Ba/Al$_2$O$_3$ NSR Catalysts .... 36
Table 4. Typical Exhaust composition for several common commuter vehicles, Kaspar et al. [279]. ........................................................................................................................................ 67
Table 5. Characterization of the catalysts used in this investigation. ........................................... 75
Table 6. FTIR band assignments. .................................................................................................. 82
Table 7. OSC values measured for the LNT catalyst at different temperatures. ....................... 117
Table 8. Calculated reductant concentrations for the cycle timing protocols used in this investigation in the 150 – 400 ºC range (OSC = 1.6% CO). ................................................................. 117
Table 9. Elemental composition of the LNT catalyst used in this investigation. ....................... 118
Table 10. Summary of the cycling performance of the LNT catalyst at 300 ºC (60 s lean/5 s rich) ........................................................................................................................................ 123
Table 11. Elemental compositions of the four catalysts used in this investigation. ................. 150
Table 12. Reaction conditions for the steady-state catalytic evaluation of TWCs, with calculated AFRs and $\lambda$ values. ......................................................................................... 154
Table 13. Reaction conditions for lean/rich cycling evaluation of TWCs, with calculated AFRs and $\lambda$ values. ........................................................................................................ 155
LIST OF FIGURES

Figure 1. Progression of emissions standards in the US for light-duty, gasoline fueled vehicles, recreated from Faiz et al. [14], where (*) represents uncontrolled emissions from a 1968 light-duty vehicle and (†) denotes that no NO\textsubscript{X} regulations were in place from 1970 to 1972. ............................................................................................................................ 3

Figure 2. Conversion efficiency of CO, NO\textsubscript{X} and HCs over a TWC, Farrauto and Heck [15]. .... 4

Figure 3. (A) Schematic showing proposed surface chemistry and timing occurring during storage/reduction, (B) Corresponding reactor profiles obtained during storage/reduction, Roy and Baiker [4]. ................................................................................................................. 7

Figure 4. Mechanism of NO storage in the presence of oxygen, where (A) represents the “nitrite” route and (B) represents the “nitrate” route, Forzatti et al. [42]................................. 9

Figure 5. Mechanism of NO\textsubscript{X} storage in the absence of oxygen, Fanson et al. [43]. .............. 9

Figure 6. Possible reaction pathways for the reduction of stored NO\textsubscript{X} by H\textsubscript{2}, Clayton et al. [67]. ............................................................................................................................................... 12

Figure 7. Schematic of NO\textsubscript{X} storage (shaded), \textsuperscript{15}NO\textsubscript{X} isotopic exchange (dots) and reduction on a Pt/BaO/Al\textsubscript{2}O\textsubscript{3} catalyst where (a) A pristine surface, (b) After NO\textsubscript{X} storage, (c) After \textsuperscript{15}NO\textsubscript{X} exchange and (d) After reduction, Kumar et al. [66]................................................................. 14

Figure 8. NO oxidation (a) and reduction (b) over (◊) 4 \% Pt, (□) 2 \% Pt, (Δ) 2 \% Pt - 1\% Rh, (▽) 1 \% Pt – 0.5 \% Rh, and (○) 1 \% Rh catalysts containing equimolar amounts of BaO as a function of sulfur exposure, Amberntsson et al. [141]......................................................... 27

Figure 9. NO\textsubscript{X} storage capacity and hydrocarbon conversion measurements for some alkali and alkaline earth elements including: Cs, K, Na, Ba, and Mg, Takeuchi and Matsumoto [160]. ............................................................................................................................................... 29

Figure 10. Pictorial representation of the chemical nature of Ba on Al\textsubscript{2}O\textsubscript{3} at different loadings, Piacentini et al. [161]........................................................................................................................................... 31

Figure 11. The effect of temperature on the morphology of BaO/Al\textsubscript{2}O\textsubscript{3} NSR catalysts, Szanyi et al. [192,193]............................................................................................................................... 35

Figure 12. The effect of water on the morphology of BaO/Al\textsubscript{2}O\textsubscript{3} NSR catalysts, Szanyi et al. [187,191]. ...................................................................................................................................................... 35
Figure 13. NO₂ evolution profiles for Ba and/or K supported on Al₂O₃ where (a) Pure Al₂O₃, (b) 6.7 wt % Ba/Al₂O₃, (c) 1.6 wt K/Al₂O₃, and (d) 6.7 wt % Ba and 2.7 wt % K/Al₂O₃, Park et al. [164].................................................................................................................................. 40

Figure 14. In situ DRIFTS spectra of Pt/K/TiO₂-ZrO₂ after exposure to 400 ppm NO + 5% O₂ for 10 min at temperatures of 100, 200, 300, 350, 400 and 500 °C, Liu et al. [206]. ........... 40

Figure 15. CO₂ evolution profiles of BaCO₃ decomposition formed during calcination at 500 °C of the Ba(Ac)₂ precursor for varying loadings of Ba on different supports where (A) Pt-Ba/CeO₂, (B) Pt-Ba/ZrO₂ and (C) Pt-Ba/Al₂O₃. Pt-Ba/SiO₂ not shown, Piacentini et al. [161,228]. .............................................................................................................................. 46

Figure 16. (A) Theoretical concept describing differences in aggregation phenomena for a physical mixture of Al₂O₃ and ZrO₂-TiO₂ vs. a nanocomposite of Al₂O₃ and ZrO₂-TiO₂, (B) FE-TEM micrograph for nanocomposite of Al₂O₃ and ZrO₂-TiO₂ after calcination at 1173 K and (C) FE-TEM micrograph for physical mixture of Al₂O₃ and ZrO₂-TiO₂ after calcination at 1173 K, Imagawa et al. [215]. ........................................................................................... 51

Figure 17. Preparation of hydrotalcite-like catalysts for NOₓ storage/reduction/decomposition applications, Yu et al. [252]. ......................................................................................................................... 53

Figure 18. Schematics showing early catalytic converter systems, Faiz et al. [14]...................... 63

Figure 19. Effect of the AFR, advanced on-board diagnostics (OBD) and oxygen storage capacity (OSC) on the operation of TWC systems, Kaspar et al. [279]............................................................................ 64

Figure 20. Two examples comparing the location and size of close-coupled TWCs [15] ........ 65

Figure 21. Close-coupled TWC, under-floor LNT configuration, as present on the BMW 120i (Model Year, 2009). ...................................................................................................................... 68

Figure 22. Close-coupled TWC, under-floor LNT + SCR configuration. (Further discussed in Chapter 3.)............................................................................................................................ 68

Figure 23. Layout of the passive-NH₃, urea-less TWC + SCR approach, Li et al [282]. (Further discussed in Chapter 4.) ........................................................................................................ 69

Figure 24. Layout of the emissions system for a light-duty diesel vehicle containing a diesel oxidation catalyst (DOC) and LNT + SCR configuration and a diesel particulate filter (DPF), McCabe et al. [283] ........................................................................................................... 69

Figure 25. Layout of the modern medium- or heavy-duty DPF-SCR system (based on urea), Johnson et al. [284]..................................................................................................................... 70

Figure 26. STEM images and corresponding EDX analyses of two different regions of the Pt/Ba/Al₂O₃ catalyst used in this investigation. ................................................................. 81
Figure 27. In situ FTIR spectra of a Pt/Ba/Al₂O₃ catalyst during exposure to (A) 1000 ppm NO/5% O₂ in He and (B) 1000 ppm CO in He mixtures at 350 °C (Spectra shown at 0, 0.5, 1, 2, 3, 5, 10 and 20 min of exposure) ................................................................. 84

Figure 28. NOₓ storage capacity of ( ) Pt/Ba/Al₂O₃ and ( ) Rh/Ba/Al₂O₃ in a 1000 ppm NO/5% O₂ in He mixture at 350 °C (obtained by integration of FTIR bands in the 1050 - 1650 cm⁻¹ region) .......................................................................................................................... 85

Figure 29. A 3D plot showing the in situ spectra collected during three lean-rich phases of NOₓ storage-reduction cycling on Pt/Ba/Al₂O₃ using CO as the reducing agent at 350 °C .......... 86

Figure 30. In situ spectra collected during NOₓ storage-reduction cycling on Pt/Ba/Al₂O₃ at 250 °C. Panes (A) and (C) display spectra collected during the first lean periods (conditions: 1000 ppm NO/5%O₂/He); panes (B) and (D) display spectra collected during the rich periods (conditions: 9000 ppm CO/He). Spectra in panes (A) and (B) were collected during dry cycling; spectra in panes (C) and (D) were collected in the presence of 1% H₂O........... 88

Figure 31. In situ spectra collected during NOₓ storage-reduction cycling on Pt/Ba/Al₂O₃ at 350 °C. Panes (A) and (C) display spectra collected during the first lean periods (conditions: 1000 ppm NO/5%O₂/He); panes (B) and (D) display spectra collected during the rich periods (conditions: 9000 ppm CO/He). Spectra in panes (A) and (B) were collected during dry cycling; the spectra in panes (C) and (D) were collected in the presence of 1% H₂O.... 91

Figure 32. Concentrations of surface NCO species formed on Pt/Ba/Al₂O₃ under different conditions: ( ) 350 °C in the absence of H₂O, ( ) 350 °C in 1% H₂O ( ) 250 °C in the absence of H₂O and ( )250 °C in 1% H₂O (Lean: mixture of 1000 ppm NO/5% O₂/He; Rich: mixture of 9000 ppm NO/5% O₂/He) ........................................................................................................ 94

Figure 33. In situ spectra collected during NOₓ storage-reduction cycling on 1Pt/17Ba/Al₂O₃ at 350 °C. Panes (A) and (B) display spectra collected during rich periods (conditions: 1000 ppm C₃H₆/He). Spectra in pane (A) were collected during dry cycling; the spectra in pane (B) were collected in the presence of 1% H₂O. ........................................................................ 96

Figure 34. Comparison between the amounts of NCO species formed on ( ) Pt/Ba/Al₂O₃ and ( ) Rh/Ba/Al₂O₃ at 350 °C in the absence of H₂O (Lean: mixture of 1000 ppm NO/5% O₂/He; Rich: pane (A) 9000 ppm CO/He; pane (B) 1000 ppm C₃H₆/He). .......................................................... 98

Figure 35. Spectra collected during exposure of a Pt/Ba/Al₂O₃ catalysts at the end of the rich phase to (A) He or (B) 1000 ppm O₂/He at 350 °C ................................................................. 101

Figure 36. Normalized integrated intensity of NCO bands observed on ( ) Ba/Al₂O₃, ( ) Pt/Ba/Al₂O₃ and ( ) Rh/Ba/Al₂O₃ during exposure at the end of the rich phase to (A) He, (B) 1000 ppm O₂/He, (C) 1000 ppm NO/He and (D) 1000 ppm H₂O in He at 350 °C. ........... 102

Figure 37. N₂ profiles (m/z = 28) obtained during the reaction of stored NOₓ with ¹³CO and the subsequent reaction of residual NCO species with (A) He, (B) 1000 ppm O₂/He or (C) 1000 ppm NO/He on Rh/Ba/Al₂O₃ at 350 °C. ......................................................................................... 104
Figure 38. OSC measurement performed at 550 °C over the LNT catalyst (See experimental section for conditions). ................................................................. 116

Figure 39. EPMA map for Ba in a washcoat corner of the front section of the LNT catalyst brick. White dashed lines separate the three apparent layers of the washcoat. ............... 119

Figure 40. SEM image of the washcoat cross-section. .......................................................... 120

Figure 41. Approximate elemental compositions in weight percentage of the two primary phases in the washcoat as measured by EDS (carbon signal originating from the mounting epoxy). ........................................................................................................ 120

Figure 42. A 60 s lean/5 s rich cycling experiment performed at 300 °C, where the NO\(_X\), ( ) NO\(_2\), ( ) N\(_2\)O, ( ) NH\(_3\) and (x) CO concentrations are plotted as a function of cycle time. 123

Figure 43. Cycle averaged NO\(_X\) conversions obtained for the LNT catalyst as functions of temperature for different lean/rich cycle timing protocols ........................................ 125

Figure 44. Cycle averaged NO\(_X\) conversions obtained for the LNT catalyst for different lean/rich cycle timing protocols at 250 and 500 °C. ...................................................... 126

Figure 45. Cycle averaged CO (A) and C\(_3\)H\(_6\) (B) conversions obtained for the LNT catalyst as functions of temperature for different lean/rich cycle timing protocols ......................... 129

Figure 46. Cycle averaged CO conversion obtained for the LNT catalyst in comparison to the amount of NO\(_X\) stored and the WGS equilibrium conversion as a function of temperature (60 s lean / 5 s rich). ............................................................... 130

Figure 47. Cycle averaged NH\(_3\) yield and NO\(_X\) slip from the LNT catalyst as functions of temperature and lean/rich cycle timing. .............................................................................. 133

Figure 48. Cycle averaged NH\(_3\) selectivity obtained for the LNT catalyst as a function of temperature and lean/rich cycle timing. .............................................................. 134

Figure 49. Cycle averaged N\(_2\)O yield (A) and selectivity (B) obtained for the LNT catalyst as functions of temperature and lean/rich cycle timing. ................................................. 135

Figure 50. Cycle averaged NH\(_3\) and N\(_2\)O yields obtained for the LNT catalyst for different lean/rich cycle timing protocols at 250 and 500 °C. ..................................................... 137

Figure 51. LNT reactor effluent profiles for NO, NO\(_2\), NH\(_3\), CO, N\(_2\)O and C\(_3\)H\(_6\) observed during a 5 s rich cycle following a 60 s lean cycle at different temperatures. .................. 142

Figure 52. Effluent gas concentrations for ( ) NO\(_X\), ( ) NH\(_3\) (X) N\(_2\)O, ( ) CO and ( )C\(_3\)H\(_6\) over (A) HPGM, Pd-only TWC and (B) LPGM, Pd/Rh TWC, respectively. (S.V. 75,000 hr\(^{-1}\), Inlet Temp. = 250 °C, Reaction conditions shown in Table. 12). ........................................ 158
Figure 53. Effluent gas concentrations for ( ) NO\textsubscript{X}, ( ) NH\textsubscript{3} (X) N\textsubscript{2}O, ( ) CO and ( )C\textsubscript{3}H\textsubscript{6} over (A) Dual-Zone TWC and (B) LNT as TWC, respectively. (Same conditions as Fig. 52). 159

Figure 54. Quantified NH\textsubscript{3} yield as a function of catalyst temperature for AFRs of (A) 14.0, (B) 14.2 and (C) 14.4. …………………………………………………………………………………………………………………………………………………………….. 164

Figure 55. Quantified NH\textsubscript{3} yield over the HPGM, Pd-only TWC as a function of the AFR and temperature. …………………………………………………………………………………………………………………………………………………………….. 166

Figure 56. Lean/rich cycling over the HPGM, Pd-only TWC at 250 and 500 °C, respectively. (Reaction conditions shown in Table 13: Lean/Rich2 – AFR=14.2). ................................. 169

Figure 57. The cycle averaged $\alpha$ as a function of temperature for rich period AFRs of 14.4 and 14.2, respectively. …………………………………………………………………………………………………………………………………………………………….. 172

Figure 58. Lean/rich cycling over the LPGM, Pd/Rh TWC at 250 and 500 °C, respectively. (Same conditions as Fig. 56). …………………………………………………………………………………………………………………………………………………………….. 175

Figure 59. Lean/rich cycling over LNT as TWC at 250 and 500 °C, respectively. (Same conditions as Fig. 56) …………………………………………………………………………………………………………………………………………………………….. 176

Figure 60. Typical temperature exotherms observed the HPGM, LPGM, Dual-Zone and LNT catalysts during cycling at 250 and 500 °C, respectively. (Rich period AFR = 14.2). ……… 178

Figure 61. The cycle averaged $\alpha$ as a function of temperature for the HPGM, LPGM, Dual-Zone and LNT catalysts. (Rich period AFR = 14.2). …………………………………………………………………………………………………………………………………………………………….. 180

Figure 62. The cycled averaged NO\textsubscript{X}, CO and C\textsubscript{3}H\textsubscript{6} conversion as a function of temperature for the HPGM, LPGM, Dual-Zone and LNT catalyst. (Rich period AFR = 14.2). …………… 182

Figure 63. The cycled averaged N\textsubscript{2}O yield as a function of temperature for the HPGM, LPGM, Dual-Zone and LNT catalyst. (Rich period AFR = 14.2)………………………………………………………………………………………………………………………………………………………….. 187
CHAPTER 1. INTRODUCTION, MOTIVATION, LITERATURE REVIEW AND REAL SYSTEMS

1.1 INTRODUCTION

Lean-burn gasoline engines have attracted the attention of automobile manufacturers because operation in an oxygen-rich (i.e., lean) environment leads to higher engine efficiency, which translates into better fuel economy and lower emissions of CO$_2$. For example, Heck and Farrauto [1] reported that lean-burn engines could achieve engine efficiencies 20 – 30% higher than conventional ones. However, the three-way catalysts (TWCs) commonly employed for removal of emissions from stoichiometric-burn engines cannot reduce NO$_X$ in the presence of excess O$_2$, which stimulated significant research activity into the development of new catalytic converter catalysts for application in lean-burn engine exhaust systems.

Selective catalytic reduction by hydrocarbons (HC-SCR) and ammonia (NH$_3$-SCR) were suggested as promising solutions. Initially, HC-SCR catalysts were the most attractive solution because the hydrocarbon reductants necessary for NO$_X$ reduction were already available on the vehicle (as gasoline) and a urea/NH$_3$ storage tank would not need to added, filled or maintained for this catalyst to be commercially implemented [2,3]. Unfortunately, HC-SCR catalysts generally suffer from poor activity in a narrow temperature range, poor thermal stability and especially poor hydrothermal stability [2–5]. Therefore, NH$_3$-SCR catalysts seemed to be the better alternative at the time because they had already been implemented for stationary sources and a considerable amount of information regarding these catalytic systems was known [2–
4,6,7]. However, NH$_3$-SCR catalysts for mobile sources requires on-board storage of NH$_3$/urea, which can limit the practicality of this system, especially for smaller passenger cars [2–4,6].

In the mid 1990’s, researchers at Toyota introduced an innovative solution to compete with HC-SCR and NH$_3$-SCR catalysts, which they referred to as, NO$_X$ storage and reduction (NSR) catalysts [8]. These catalysts were designed to function in periodic lean/rich environments. In this case, NO$_X$ was stored during lean phases and then reduced to N$_2$ by intermittent rich periods. Early NSR catalysts were capable of NO$_X$ conversions as high as 90%, but were highly susceptible to sulfur poisoning and required ultra-low sulfur fuels for commercial implementation [8].

The following literature review summarizes the general operation features, reaction mechanisms and the highlights the function of each catalytic component present on NO$_X$ storage and reduction catalysts. A brief review of real-world catalytic converter systems and how NSR catalysts fit into this larger framework is also discussed.

1.2 Motivation and Significance

In the 1970s, the Clean Air Act was passed by Congress to improve air quality in the United States. This gave the Environmental Protection Agency (EPA) the authority to write and enforce regulations regarding criteria pollutants [9]. Currently, six criteria pollutants are regulated by the EPA and include: ground level ozone, particulate matter, carbon monoxide, nitrogen oxides, sulfur dioxide and lead. In 2006, mobile sources were responsible for approximately 35% of volatile organic compounds (VOCs), 58% of NO$_X$ and 78% of CO emitted into the atmosphere. VOCs contain known carcinogens (e.g., benzene) and can additionally react with NO$_X$ in the presence of sunlight to form ground level ozone - an eye and throat irritant that can potentially cause respiratory tract problems and/or lung damage [10,11].
Similarly, nitrogen dioxide ($\text{NO}_2$) contributes to acid rain and smog formation and is also a respiratory irritant. Carbon monoxide (CO) exposure can lead to reduced mental alertness, heart attacks, cardiovascular diseases, impaired fetal development and death [11].

Since automobiles account for a significant portion of the criteria pollutants released, the EPA has steadily implemented more and more stringent regulations to minimize the amount of toxic pollutants emitted by automobiles each year, as shown in Fig. 1, with mandated emission decreases for approaching 2 orders of magnitude (by 2004) in comparison to an uncontrolled vehicle operating in 1968. This triggered a massive search for catalytic materials in the 1970s capable of operating under harsh emission environments. In response, so called three way catalysts (TWCs) were developed and typical formulations consisted of Pt-Rh bimetallic particles deposited on a $\text{CeO}_2$ modified $\text{Al}_2\text{O}_3$ support. TWCs are capable of simultaneously oxidizing carbon monoxide and hydrocarbons to $\text{CO}_2$ and $\text{H}_2\text{O}$ and reducing $\text{NO}_X$ to $\text{N}_2$, but only when operated in a very narrow regime near stoichiometric conditions (air-to-fuel ratio $\approx 14.67:1$), as shown in Fig. 2.

More recently, a 2007 assessment report generated by the Intergovernmental Panel on Climate Change (IPCC) stated warming of the climate to be, “unequivocal, as evident from observations regarding increases in global air and ocean temperatures, widespread melting of snow and ice and rising global sea levels” [12]. Anthropogenic greenhouse gases (GHG) were attributed to the observed changes in global climate. In April of 2007, the Supreme Court concluded that greenhouse gases meet the clean air definition of an air pollutant, which gave the EPA authority to regulate greenhouse gas emissions. On April 1, 2010 the EPA and the National Highway Traffic Safety Administration (NHTSA) finalized a rule that harmonized greenhouse gas emissions and fuel economy standards for light-duty vehicles for model years 2012 through
The regulation requires an estimated combined average of 250 g CO₂/mi, which is equivalent to 35.5 mi/gal if met through fuel economy improvements alone.

**Figure 1.** Progression of emissions standards in the US for light-duty, gasoline fueled vehicles, recreated from Faiz et al. [14], where (*) represents uncontrolled emissions from a 1968 light-duty vehicle and (†) denotes that no NOₓ regulations were in place from 1970 to 1972.
Figure 2. Conversion efficiency of CO, NO\textsubscript{X} and HCs over a TWC, Farrauto and Heck [15].

As previously mentioned, one obvious way to increase the fuel efficiency of the internal combustion engine and decrease CO\textsubscript{2} emissions is to run the engine lean. If you examine Fig. 2 however, it becomes clear that the traditionally used TWC-only systems (1970s – present) will not be able to remove NO\textsubscript{X} under these conditions. Thus, additional catalytic technologies in combination with the TWC need to be implemented in order to meet the emission regulations shown in Fig. 1.

1.3 Literature Review

The primary focus of this dissertation was on NO\textsubscript{X} Storage and reduction catalysts (i.e, Chapters 2 and 3), so an in-depth review of these materials is warranted. Following the literature review, real-world catalytic converter systems are discussed, only some of which include an NSR catalyst.
1.3.1 General Features of NO\textsubscript{X} Storage and Reduction Catalysts

As previously discussed, NO\textsubscript{X} storage and reduction catalysts are designed for periodic operation in lean and rich environments from 100 to 400 °C, but the optimum temperature is approximately 350 °C [3]. Commercial NSR formulations are based on a Pt/Ba/Al\textsubscript{2}O\textsubscript{3} catalyst promoted using Rh and/or CeO\textsubscript{2}. The platinum loading typically varies from 1 to 2.5 wt %, while the Ba loading usually ranges from 8 to 30 wt %. The Rh loading is always substantially lower than the Pt loading, but CeO\textsubscript{2} loadings can be quite high and may even exceed the Ba loadings. Typical exhaust gas concentrations for NSR cycling conducted in laboratory investigations are shown in Table 1.

The lean period duration typically ranges from 60 to 120 s, while the rich period only lasts 1 to 5 s [16–20]. A short rich period is a necessary feature of NSR catalyst operation because longer rich periods would result in a more substantial fuel penalty and negate the benefits of lean-burn operation. Fig. 3 provides a simplified schematic of the NSR surface chemistry (Fig. 3A) and the expected NO\textsubscript{X} reactor profile (Fig. 3B) obtained during cycling. As shown in Fig. 3A, NO is oxidized to NO\textsubscript{2} over precious metals during the lean period. The NO\textsubscript{2} then spills over onto the storage component and is stored in the form of a nitrite/nitrate [21,22]. During rich periods, the nitrates are reduced to N\textsubscript{2}, but N\textsubscript{2}O and NH\textsubscript{3} can also be produced. While the mechanism for NO\textsubscript{X} storage is widely accepted, the mechanism for reduction of stored nitrates is still unclear and seems to be dependent on the reductant [23,24]. Hydrocarbons (HCs), CO and H\textsubscript{2} were included as possible reductants in Fig. 3A, but H\textsubscript{2} is commonly cited to be the most effective reductant during laboratory investigations. Generally, the activity for reductants is as follows: H\textsubscript{2}≥CO>C\textsubscript{3}H\textsubscript{6}>>C\textsubscript{3}H\textsubscript{8}, where CO and H\textsubscript{2} have been reported to show similar activity if H\textsubscript{2}O is included in the feed [25–28]. In Fig. 3B, NO\textsubscript{X} storage is indicated by an outlet
NOX concentration lower than the inlet NOX concentration. As storage elapses, the storage component becomes saturated with NOX and the outlet NOX concentration eventually approaches the inlet concentration. At this point, the rich period begins and the NOX concentration drops considerably. During the rich period, the stored NOX is reduced to N2 and the storage component is regenerated. After the storage component has been regenerated, the reductant is removed from the feed and storage resumes.

In some investigations H2O has been reported to increase the activity of CO as a reductant [28], but Epling et al. [29] reported that addition of H2O and CO2 negatively influenced storage capacity of NSR catalysts. H2O was proposed to interact with hydroxyl groups on Al2O3 and render these sites incapable of NOX storage. CO2 and NO2 were proposed to compete for the same storage sites on BaO. Since CO2 and H2O will always be present in actual engine exhausts, it is critical to understand how these species interact with the catalyst surface. SO2 exposure results in irreversible adsorption during typical reaction conditions and prolonged exposure can lead to complete loss of the NSR activity [30].

In summary, NOX storage and reduction catalysts are designed for periodic operated in 60 s lean, 5 s rich periods. The optimum temperature is approximately 350 °C. H2 and CO are the best reducing agents and storage occurs most readily for feeds containing NO + O2 or NO2. Both H2O and CO2 can be detrimental to storage capacity, but the effect is reversible. SO2, on the other hand, can completely deactivate the catalyst.
Table 1†. Typical Operating Conditions for NSR Catalysts.

<table>
<thead>
<tr>
<th></th>
<th>NO</th>
<th>O₂</th>
<th>C₃H₆</th>
<th>CO</th>
<th>H₂O</th>
<th>CO₂</th>
<th>N₂/He</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rich</td>
<td>0.07%</td>
<td>0.60%</td>
<td>0.2%</td>
<td>0.50%</td>
<td>10%</td>
<td>14.50%</td>
<td>bal</td>
</tr>
<tr>
<td>Lean</td>
<td>0.70%</td>
<td>4.00%</td>
<td>0.80%</td>
<td>0.10%</td>
<td>10%</td>
<td>12.70%</td>
<td>bal</td>
</tr>
</tbody>
</table>

†Reproduced from Takahashi et al. [8].

Figure 3. (A) Schematic showing proposed surface chemistry and timing occurring during storage/reduction, (B) Corresponding reactor profiles obtained during storage/reduction, Roy and Baiker [4].
1.3.2 The Mechanism of NO\textsubscript{X} Storage and Reduction

1.3.2.1 NO\textsubscript{X} Storage

Many investigations have been performed in an attempt to understand the mechanism for NO\textsubscript{X} storage [21,22,27,31–38]. Initially, Bogner et al. [38] proposed that storage occurred as nitrites, where oxidation of NO to NO\textsubscript{2} over Pt was necessary before storage could occur. However, Sedlmair et al. [31] observed storage in the form of nitrites and nitrates when a Pt/Ba/Al\textsubscript{2}O\textsubscript{3} catalyst was exposed to mixtures of NO and O\textsubscript{2} and reported that the amount of surface nitrites on Ba reached a maximum at 18 min and declined thereafter. This led the authors to conclude that nitrites were intermediates in the formation of nitrates. Several other authors have also suggested the formation of nitrites to be an intermediary step [21,22,33,39]. Alternatively, Prinetto et al. [40] proposed that storage of NO\textsubscript{2}, which was not promoted by Pt, occurred through a disproportionation reaction that led to a stored nitrate and release of gas phase NO. Other researchers have also reported storage via this mechanism [38,41], but Cant and Patterson [32] reported an initial, short-lived phase involving storage of NO\textsubscript{2} without the evolution of gas phase NO. Again, this observation supports the intermediacy of nitrites, as more clearly seen for disproportionation reaction mechanism as shown in Eqns. 1, 2 and 3 [4].

\begin{align*}
BaO + NO\textsubscript{2}(g) &\rightarrow BaO - NO\textsubscript{2} \\
BaO - NO\textsubscript{2} &\rightarrow BaO\textsubscript{2} + NO(g) \\
BaO\textsubscript{2} + 2NO\textsubscript{2}(g) &\rightarrow Ba(NO\textsubscript{3})\textsubscript{2}
\end{align*}

In a later study, Forzatti et al. concluded that NO\textsubscript{X} storage could occur via two routes, as shown in Fig. 4 [42]. The “nitrite” route (A) involves oxidation of NO on Pt sites and subsequent storage as nitrites on neighboring Ba sites, which can later be oxidized to nitrates.
The “nitrate” route (B), also known as the disproportionation route, proceeds through oxidation of NO to NO$_2$ on Pt and subsequent storage on neighboring Ba sites as nitrates with the evolution of gas phase NO. Under typical reactions conditions, the nitrite route was expected to be the dominant route for NO$_X$ storage.

![Figure 4](image.png)

**Figure 4.** Mechanism of NO storage in the presence of oxygen, where (A) represents the “nitrite” route and (B) represents the “nitrate” route, Forzatti et al. [42]

![Figure 5](image.png)

**Figure 5.** Mechanism of NO$_X$ storage in the absence of oxygen, Fanson et al. [43].

Fanson et al. [43] proposed a different mechanism involving the direct adsorption of NO on BaO as a surface nitrite, which was subsequently oxidized by another adsorbed nitrite species to a monodentate nitrate, as shown in Fig. 5. The oxidation of NO to NO$_2$ over Pt did not appear
to be a critical step in this work because the authors observed significant storage even in the absence of oxygen. They cited the primary role of Pt to be adsorption of gas phase $O_2$, which then spills onto nearby BaO sites. This conclusion contradicts other studies, which assert that the primary method of storage occurs through interaction of NO$_2$ with BaO [38, 41, 44–46].

Recently another adsorption mechanism has been discussed involving co-adsorption or cooperative adsorption of nitrite-nitrate pairs on BaO [47–54]. Several theoretical studies have predicted the formation of nitrite-nitrate pairs on MgO and BaO [47, 53, 54] and Yi et al. [49] experimentally confirmed the presence of these nitrite-nitrate pairs on a thick BaO model surface upon admission of NO$_2$ at 90 K. In a later work, Yi and coworkers [48] suggested the simultaneous monotonic increase and saturation of peaks at 1240 and 1300-1500cm$^{-1}$ to be indicative of nitrite-nitrate ion pairs when BaO films were exposed to NO$_2$ at 300 K. Alternatively, Desikusumastuti et al. [51] observed the formation of nitrites followed by nitrates when BaO was exposed to NO$_2$ at 100 K, but simultaneous formation of nitrites and nitrates at 300 K. They proposed a cooperative mechanism that operates at low temperatures that switches to a non-cooperative mechanism at higher temperatures. In summary, these mechanistic pathways have been developed to describe NO$_X$ adsorption on BaO and the operating mechanism could largely be dependent on the source of NO$_X$ available, the Ba loading and the temperature of exposure.

Considering that oxidation of NO to NO$_2$ has been reported as a key step in the storage mechanism, it is worth mentioning that two kinetic models have been proposed for NO oxidation on Pt. Olsson et al. [55] proposed a Langmuir-Hinshelwood model and observed that adding BaO to the support decreased the rate of NO oxidation. The basic nature of BaO was used to explain this observation, where BaO may donate electron density to the platinum. A more
electron rich Pt surface would then be expected to favor the formation of oxides [55–57]. Crocoll et al. [58] proposed Eley-Rideal kinetics and O\textsubscript{2} dissociatively adsorbed on the surface of Pt, while gas phase NO reacted with O\textsubscript{ads} to form NO\textsubscript{2}. A negative order was observed with respect to NO\textsubscript{2}, which implied that NO\textsubscript{2} inhibited oxidation of NO. Oxidation of Pt\textsuperscript{0} to Pt\textsuperscript{+δ} by NO\textsubscript{2} has previously been reported [56]. Interestingly, both kinetic reports mentioned deactivation due to formation of oxides.

1.3.2.2 Reduction

The reduction mechanism for stored NO\textsubscript{X} has not been investigated nearly as thoroughly as the storage mechanism, possibly because the duration of the rich period makes it much more difficult to investigate [16]. For example, Nova et al. previously reported that the possible mechanisms for the reduction of NO\textsubscript{X} in a rich environment are fairly well established from research on TWCs, but the mechanism for NO\textsubscript{X} release from the storage component is still open to debate [59,60]. Currently multiple release mechanisms have been proposed including: 1.) thermal release enabled by heat generated from oxidation of reductants, 2.) a decrease in gas phase oxygen, which destabilizes stored nitrates due a shift in the storage equilibrium, 3.) spillover and reduction of NO\textsubscript{2} on Pt sites, 4.) establishment of a net reducing environment that decreases the stability of nitrates, 5.) direct reaction of the reductant (or activated reductant molecule spilled over from Pt) with stored nitrates [59–62]. Nova et al. [60] concluded that the main mechanism for decomposition of stored nitrates did not proceed via thermal decomposition, but instead proceeded through one of the following pathways: 1.) activation of H\textsubscript{2} on Pt site, followed by spillover of the H\textsubscript{2} onto the alumina support and migration towards a nitrate adspecies, which is then either decomposed to gas-phase NO\textsubscript{X} that re-adsorbs on Pt to be reduced or directly reduced on the support 2.) surface diffusion of NO\textsubscript{X} adspecies toward reduced Pt and
subsequent reduction. Further reports by Nova and coworkers [23,63,64] favor the two-step reduction mechanism involving activation of H$_2$ on a Pt site, followed by spillover onto the alumina support and surface diffusion towards the nitrate adspecies, which are then decomposed to NO$_X$ and released into the gas phase. These species are then further reduced over Pt sites to form NH$_3$. The NH$_3$ can then react with stored nitrates to produce N$_2$. Mulla et al. [65] also predicted the formation of NH$_3$ as an intermediate, when H$_2$ was used as the reductant. If CO was used as the reductant, in the absence of water, the mechanism was proposed to proceed via cyanate/isocyanate species that react with nitrates to produce N$_2$ [24,64]. In the presence of water, the cyanate/isocyanate species could be hydrolyzed to form NH$_3$, which would then reduce stored NO$_X$, as previously discussed. Lastly, CO and water mixtures could undergo the water gas shift (WGS) reaction to produce hydrogen, where H$_2$ would then reduce nitrates via the already described mechanism. Kumar et al. performed isotopic labeling experiments and again concluded that NH$_3$ was an important intermediate in the reduction of stored NO$_X$ [66]. The reduction of NO$_X$ by hydrogen can be summarized according to Fig. 6, where path 1 is direct reduction of NO$_X$ to N$_2$, path 2 is reduction of NO$_X$ to ammonia, path 3 is reduction of stored NO$_X$ by ammonia, path 4 is oxidation of NH$_3$ to N$_2$, and path 5 is decomposition of NH$_3$ to N$_2$ [67]. However, the reduction of NO$_X$ by CO, CH$_4$, C$_3$H$_6$, C$_3$H$_8$ and other small hydrocarbons has not been investigated nearly as thoroughly, but the direct reduction by CO and hydrocarbons and indirect reduction via steam reforming and water gas shift have been suggested [4].

![Figure 6](image)

**Figure 6.** Possible reaction pathways for the reduction of stored NO$_X$ by H$_2$, Clayton et al. [67].
1.3.2.3 The Effect of the Pt-BaO Interface

One factor known to influence both the mechanism for storage and reduction of NO\textsubscript{X} is the Pt-BaO interface and several different types of storage sites have been mentioned in the literature [21,29,68–70]. Mahzoul et al. [46] initially proposed two types of Pt sites, one close to barium, which was responsible for the storage of nitrates, and one far from barium responsible for the oxidation of NO to NO\textsubscript{2}. In a later study, Cant et al. [68] observed a five-fold increase in the NO\textsubscript{X} storage-reduction rate for a Pt/BaO/Al\textsubscript{2}O\textsubscript{3} over a physical mixture of Pt/SiO\textsubscript{2} and BaO/Al\textsubscript{2}O\textsubscript{3} when a system comprising a Pt/SiO\textsubscript{2} catalyst, solely for oxidation of NO to NO\textsubscript{2}, was placed upstream of a Ba/Al\textsubscript{2}O\textsubscript{3}. The authors concluded that co-loading of both Pt and Ba was essential for efficient NO\textsubscript{X} storage and reduction. Lindholm et al. [69] attributed the idea of different storage sites to one of several possibilities including: 1.) aluminum and barium storage sites, 2.) surface and bulk barium sites, and 3.) barium close and far from the noble metal. Bhatia et al. [70] also defined two different storage sites in their modeling efforts of the NSR process. “Fast” sites corresponded to a location close to the Pt/BaO interface – where storage was most likely to occur according to the nitrite route shown in Fig. 4. “Slow” sites represented storage in locations far from the Pt/BaO interface – where storage was most likely occurring according to the nitrate route described in Fig. 4. Sakamoto et al. [71] demonstrated using a thin film of BaO on a Si (100) that NO\textsubscript{X} adsorbed more readily near the Pt/BaO interface. The decomposition of Ba(NO\textsubscript{3})\textsubscript{2} was also suggested to occur most rapidly near the Pt/BaO interface. The authors suggested that this preferential adsorption explained observations by others in the literature that only 20% of the NSR catalyst is utilized [72]. Recently, Kumar and coworkers [66] used isotopic labeling studies to investigate storage near-to and far-from the Pt/Ba interface.
Fig. 7 summarizes their results, where (a) is a pristine surface, (b) is after exposure to NO, (c) is after NO-\(^{15}\)NO isotopic exchange, and (d) is after reduction. Notice that the authors have only shown significant reduction near the Pt/BaO interface, whereas the rest of the surface remains partially saturated with NO\(_X\). Lastly, many groups have stressed the importance of the Pt/Ba interface for optimization of both the storage and reduction cycles in NSR catalysts [8,21,29,46,73,74].

![Figure 7](image.png)

**Figure 7.** Schematic of NO\(_X\) storage (shaded), \(^{15}\)NO\(_X\) isotopic exchange (dots) and reduction on a Pt/BaO/Al\(_2\)O\(_3\) catalyst where (a) A pristine surface, (b) After NO\(_X\) storage, (c) After \(^{15}\)NO\(_X\) exchange and (d) After reduction, Kumar et al. [66].

1.3.3 **IMPORTANT CATALYST COMPONENTS**

NO\(_X\) storage and reduction catalysts are usually comprised of the following constituents: 1.) a noble metal, which provides both NO oxidation and reduction activity, 2.) a storage component, which mainly provides NO\(_X\) storage capacity, but may also act as a promoter for other reactions (e.g. Ba has been suggested as a promoter for the water gas shift reaction [75], 3.) a support, which provides a high surface area substrate on which the storage component and
noble metal are dispersed. Additionally, a variety of promoters have been investigated to increase the thermal stability of the support or stabilize precious metal dispersion, increase sulfur tolerance, enhance storage capacity and improve reduction efficiency or selectivity. The following sub sections summarize the compounds used and their currently proposed/accepted role in the NO\textsubscript{X} storage and reduction catalytic system.

1.3.3.1 \textit{Noble Metals}

The impact of noble metals on NSR activity can be divided into four main subdivisions including: 1.) oxidation of NO to NO\textsubscript{2}, 2.) reduction of stored NO\textsubscript{X} to N\textsubscript{2} and 3.) resistance to sulfur tolerance. In the following subsections, each of these issues will be addressed regarding the specific metals commonly used in NSR catalysts.

\textbf{Platinum}

Pt has been extensively used in automotive catalysis because it is an excellent oxidation catalyst [7]. Therefore, it should not be surprising that Pt is the most commonly used noble metal in NSR catalysts. As mentioned, the loading typically varies from 1-2.5 wt % with a dispersion ranging from 3 to 80\% [76–81]. For NSR catalysts, one of the most important aspects of Pt is its ability to oxidize NO to NO\textsubscript{2}. Clayton et al. [77] reported that conversion of NO to NO\textsubscript{2} reached a maximum between 270 to 330\degree C, where the catalyst with 20 \% dispersion of Pt was most active, followed by 50 \% dispersion, 8 \% dispersion and lastly, 3 \% dispersion. This is in agreement with a study by Kim et al. [82] where smaller Pt particles were reported to offer better NO\textsubscript{X} storage activity. However, Lee et al. [83] determined that a sample with 4\% dispersion had a turn over frequency (TOF) 100 times greater than a sample with 82\% dispersion, which is also in agreement with other reports in the literature [84]. This led Xue et al. [84] and others to propose that NO oxidation over Pt was a structure sensitive reaction since
NO oxidation occurred more readily over larger particles [83]. Olsson and Fridell [56] similarly argued that smaller Pt particles were less active for NO oxidation, but argued the difference was due to increased susceptibility of oxidation. XPS measurements conducted on Pt/Al₂O₃ and Pt/Ba/Al₂O₃ samples confirmed the presence of both PtO and PtO₂ phases, but the Pt/Ba/Al₂O₃ catalyst generally formed more PtO₂ than Pt/Al₂O₃. The authors explained the increased formation of Pt oxides on Pt/Al₂O₃ using the electrophilic nature of the alumina support, where Pt was expected to donate electron density to the Al₂O₃ support. To form Pt oxide, Pt must be able to transfer electrons to the oxygen, but when Pt is supported on an electrophilic support electron donation from the Pt to the support suppresses formation of Pt oxides [57]. The basic nature of BaO influences Pt in the opposite way and higher amounts of Pt oxides were observed.

When a Pt/Al₂O₃ and Pt/BaO/Al₂O₃ catalyst were exposed to pulses of NO in the absence of oxygen during temporal analysis of products (TAP) experiments, both NO decomposition and adsorption/storage were observed [85]. NO decomposition was proposed to occur through Reactions 4 – 10. Over the reduced Pt catalyst, the first pulses of NO produced nearly stoichiometric amounts of N₂, but as the number of pulses increased, oxygen accumulated on the surface and inhibited NO bond scission. As the surface become more crowded, N₂O was observed. The N₂O yield reached a maximum at the same time as breakthrough of NO was observed. Over Pt/Ba/Al₂O₃, NO breakthrough was delayed because storage and decomposition could occur simultaneously. Under these conditions, storage could occur either through spillover of oxygen from Pt onto the Ba, where a BaO₂ site could then directly react with gas phase NO, or direct formation of NO₂ over the Pt, which then reacts with BaO.

\[ NO + Pt \leftrightarrow NO - Pt \]
\begin{align*}
NO - Pt & \leftrightarrow N - Pt + O - Pt \quad 5 \\
2N - Pt & \leftrightarrow N_2(g) + 2Pt \quad 6 \\
2NO - Pt & \leftrightarrow N_2O(g) + Pt + O - Pt \quad 7 \\
NO - Pt + N - Pt & \leftrightarrow NO_2(g) + 2Pt \quad 8 \\
NO - Pt + O - Pt & \leftrightarrow NO_2(g) + 2Pt \quad 9 \\
O - Pt + O - Pt & \leftrightarrow O_2(g) + 2Pt \quad 10
\end{align*}

Anderson et al. [86] observed a dramatic increase in NO\textsubscript{X} storage for Pt/Ba/Al\textsubscript{2}O\textsubscript{3} over Ba/Al\textsubscript{2}O\textsubscript{3}, which further supported the crucial role of Pt in NSR catalyst formulations. Pt has also been reported to catalyze the transition from Ba nitrites to Ba nitrates [22,86]. Schmitz et al. [87] determined that NO oxidation over Pt was influenced by the following factors (in order of importance): support > pretreatment > loading > calcination atmosphere > calcination temperature > precursor salt. The reduction of NO on Pt does not seem to be nearly as dependent on particle size, but could be related to the strength of the Pt–NO bond or could also be structure sensitive, as is the case for Pd and Rh [83,84,88–92].

As demonstrated by Fridell et al. [62], Pt also plays an important role in the reduction of stored NO\textsubscript{X}. For example when BaO/Al\textsubscript{2}O\textsubscript{3} was cycled between lean and rich periods, no appreciable NO\textsubscript{X} storage was observed during lean periods and only minor NO\textsubscript{X} reduction occurred during rich phases. A Pt-Rh/Al\textsubscript{2}O\textsubscript{3} catalyst was able to completely reduce NO\textsubscript{X} during rich phases, but no NO\textsubscript{X} storage was observed during lean periods. Su et al. [22] also reported that Pt was necessary for activation of hydrocarbons. Currently, NO reduction over Pt is explained by one of two mechanisms including: (1) NO decomposition on reduced Pt sites, where the main role of the reductant is to scavenge surface oxygen from Pt and keep the Pt in a
reduced state so the NO dissociation can occur, or (2) the direct reaction between released NO\textsubscript{X} and adsorbed reductants on Pt sites [5,60,93]. In a series of publications, Abdulhamid et al. [25–27] demonstrated that Pt was an effective metal for reduction of stored NO\textsubscript{X} using H\textsubscript{2} and CO for temperatures between 250°C and 350°C. C\textsubscript{3}H\textsubscript{6} was reported to be somewhat less efficient and C\textsubscript{3}H\textsubscript{8} showed no NO\textsubscript{X} reduction capability. Although CO was initially an effective reductant, the authors reported deterioration of the reduction efficiency with increased cycling. Lower temperatures also reduced the reduction efficiency for CO. The observed loss was attributed to either poisoning of Pt by strongly adsorbed CO or through the formation of isocyanate species on alumina or barium in the Pt/BaO interfacial region, which would prevent NO\textsubscript{X} spillover from the storage component to the precious metal. The authors attributed CO accumulation on the surface Pt sites to be the main cause of deactivation from 150 to 250°C due to the high heat of adsorption of CO on Pt. However an FTIR band at 2117 cm\textsuperscript{-1} (assigned to a cyanide species on Pt) was observed and was stable under both lean and rich conditions, which was assigned to a stable cyanide species that blocked NO\textsubscript{X} spillover from the storage sites to Pt.

The location of Pt, synthetic route, method of deposition and type of precursor used also affect the catalytic performance [76,80,81,94–96]. Elizundia et al. [81] reported that deposition of the Ba precursor before the Pt precursor led to a more active catalyst. In their case, preparation of a 1.3%Pt-15.7%Ba/Al\textsubscript{2}O\textsubscript{3} (w/w) sample was accomplished using sequential wet impregnations of tetraammineplatinum nitrite [Pt(NH\textsubscript{3})\textsubscript{4}(NO\textsubscript{2})\textsubscript{2}] and barium acetate [Ba(CH\textsubscript{3}COO)\textsubscript{2}]. After each impregnation, samples were dried and then calcined at 650°C for 4 h. The dispersion of Pt ranged from 0.6 – 5.5%. The authors attributed the increased catalytic activity of samples where Ba had been impregnated first to increased Pt/Ba interfacial contact. Lindholm et al. [95] reported higher storage capacity and reduction efficiency for samples where
Pt was deposited before Ba. Preparation of monolithic 3%Pt/20.7%Ba/Al2O3 samples was accomplished using incipient wetness impregnation of platinum nitrite, Pt(NH3)4(NO2)2, and dip coating of barium nitrate, Ba(NO3)2. After each impregnation, samples were dried at 80°C for 12 h and then calcined at 550°C for 2 h. The dispersion of Pt ranged from 18 – 25%. Lindholm et al. [95] hypothesized that the higher activity of Al/Pt/Ba was caused by better dispersion of Ba on the support, which led to better interfacial contact between Pt and Ba. Interestingly, both Elizundia et al. [81] and Lindholm et al. [95] linked the catalytic activity to the degree of contact between Pt and Ba, but observed opposite results in terms of impregnation order. Dawody et al. [94] compared samples prepared from hexachloroplatinic acid [H2Pt(Cl)6], tetraammineplatinum hydroxide [Pt(NH3)4(OH)2], diammineplatinum nitrite [Pt(NH3)2(NO2)2] and platinum nitrate [Pt(NO3)2] and found that samples derived from platinum nitrate were the most active for NOX storage and reduction followed by tetraammineplatinum hydroxide. The resulting dispersions and activity differences were explained by electrostatic interactions and/or ion and ligand exchange between the Pt complex and the BaO/BaCO3/Al2O3 support. Pereda-Ayo et al. [96] similarly reported that tetraammineplatinum hydroxide to be a better Pt precursor than hexachloroplatinic acid when used for synthesis of NSR materials. Buchel et al. [97] synthesized NSR catalysts using the flame spray pyrolysis method [98,99], with Pt selectively on Al2O3 or BaCO3 and found that Pt located on Al2O3 exhibited better NO oxidation activity, but Pt located on Ba showed greater reduction activity. Above 350 °C, the location of Pt insignificantly influenced storage and reduction.

Pt, like Ba, is susceptible to sulfur poisoning and the formation of Pt sulfides, which could block potential NO oxidation sites, have been observed [35,36,100–102]. Sedlmair et al. reported a higher reduction temperature for Pt during TPR after the catalyst had been sulfided.
and hypothesized that decreased activity during cycling might be explained by the higher Pt reduction temperatures [36]. Amberntsson et al. [103–106] alternatively reported an increase in NO oxidation activity for Pt-containing catalysts after exposure to SO$_2$, which they explained by reaction of Pt-O with SO$_2$ to form sulfites and sulfates. The sulfided Pt was hypothesized to remain in a reduced state during NO oxidation, which explained the higher activity. Fridell et al. [106] also proposed that exposure to SO$_2$ leads to sintering of the Pt particles, which enhanced the oxidation activity because larger particle were less likely to be oxidized and also exhibited higher TOFs. This rational was explained in a previous work by Olsson et al. linking dispersion and the presence of BaO to differences in flow reactor studies [56], Pt with a higher dispersion or in the presence of BaO was more likely to be oxidized, which then decreased NO oxidation activity. During lean conditions, Pt has been reported to catalyze the oxidation of SO$_2$ to SO$_3$, which facilitates the formation of bulk BaSO$_4$ [107], but Su et al. [22] observed nearly-identical spectra after SO$_2$ + O$_2$ exposure for a Ba/Al$_2$O$_3$ and Pt/BaO/Al$_2$O$_3$ catalyst and concluded that Pt did not play a significant role during poisoning by SO$_2$. During rich conditions, Pt can also form Pt-S bonds, as observed by Kim et al. and others [35,108]. The formation of BaS has also been reported [109,110]. During subsequent lean periods, Pt-S and BaS species could be re-oxidized to form bulk/surface barium and aluminum sulfates [35,36]. Re-oxidation of reduced sulfur compounds is thought to preferentially poison sites near the Pt/BaO interface [35,36,71,102,111].

**Palladium**

In recent publications, Pd has been suggested as a viable alternative to Pt for NSR catalysts because of its high activity during both lean and rich periods and its ability to activate saturated hydrocarbons [25,27,112,113]. Facile interconversion between Pd$^{2+}$ and Pd$^{0}$ during lean and rich cycling has also been suggested as another advantage of Pd over Pt [4]. Salasc et
al. [113] demonstrated that a Pd/BaO/Al₂O₃ catalyst stored more NOₓ than Pt/BaO/Al₂O₃ at 300°C, but the Pt containing catalyst stored slightly more at 400°C. The Pd/BaO/Al₂O₃ sample was also able to completely reduce all stored NOₓ at 300°C, while the Pt-based catalyst exhibited incomplete reduction. Salasc et al. [113] also demonstrated the beneficial role of BaO during reduction; where the Pt/Al₂O₃ and Pd/Al₂O₃ catalysts slowly deactivated during extended rich periods, but the Pt/Ba/Al₂O₃ and Pd/Ba/Al₂O₃ reduced most of the gas phase NOₓ at 400°C. Pt/BaO/Al₂O₃ in comparison to Pd/BaO/Al₂O₃ showed more significant deactivation during extended rich periods, which led the authors to conclude that Pd was less susceptible to self poisoning mechanisms. Migration of NOₓ species originating from decomposition of barium nitrate to noble metal sites or spillover of hydrocarbons to the BaO or interactions between the precious metal and storage component could explain why BaO has such a positive effect on the sustained NOₓ reduction activity of NSR materials. Lastly, Pd²⁺ and Pd⁰ were observed during lean and rich cycling for Pd/BaO/Al₂O₃, but only metallic Pt was observed for Pt/Ba/Al₂O₃. Recently, Weiss et al. [114,115] proposed that NO oxidation on Pd was also affected by the size of the particles, which was discussed in the previous section regarding Pt. In that case, NO oxidation turnover rates were insensitive to oxidative or reductive pretreatments because PdO was formed rapidly and is thermodynamically favored for NO oxidation conditions. Instead, the strength of the Pd-O bond determined NO oxidation turnover rates. Smaller particles have stronger bonds and fewer vacancies on the surface for NO oxidation to occur.

Abdulhamid et al. [25] demonstrated that a Pd-based NSR catalyst stored more NOₓ than a Pt based catalyst when CO, C₃H₆ and C₃H₈ were used as model reductants, but the Pt-based catalyst stored more NOₓ when H₂ was used. Additionally, Pd was the only precious metal tested that showed activity for reduction when C₃H₈ was used as a model reductant. While Pd
may seem more active, it is important to note that dispersion of Pt was 4%, while the dispersion of Pd was 15% and this may have affected the results by changing Pd/BaO and Pt/BaO interfacial contact areas, respectively. In another study by Abdulhamid et al. [27], Pd and Pt were compared using in-situ DRIFTS and reactor studies. Again, Pd seemed to be more active when CO or C₃H₆ was used as the reductant. Again however, differences in precious metal dispersion made elucidation of the results more complicated (5% for Pt and 12% for Pd). In both cases, the reduction of stored NOₓ occurred through the formation of isocyanates, where higher concentrations of isocyanates were formed on Pd samples. In this case, the authors concluded that the lower NOₓ storage and reduction properties were related to lower metal dispersion and/or lower metal/Ba interfacial area and not to inherent differences in the precious metals themselves. In a later study, Su et al. [112] reported that a Pd/BaO/Al₂O₃ catalyst had higher overall NOₓ reduction efficiency than Pt/BaO/Al₂O₃ catalyst between 250 and 375 °C, but the performance was almost identical above 375 °C. The improvement in efficiency was related to higher activity for the oxidation/activity of propylene and higher activity for the formation of surface nitrite species. In this case, the metal dispersions were approximately the same (around 40%), but the molar concentration of Pd was approximately 2 times higher than Pt. Desikusumastuti et al. [52] also observed strong nitrite features for Pd containing catalysts and concluded that the highest concentration of surface nitrites will be present in samples with a strong Pd/BaO interaction. The sulfur resistance of Pd containing NSR materials has not been investigated, but Pd/Al₂O₃ diesel oxidation catalysts have been reported to be susceptible to sulfur poisoning [116]. Kolli et al. [116] observed losses of precious metal dispersion and decreased activity for oxidation reactions. The supports containing Pd exhibited higher total
sulfur than alumina samples alone, which further demonstrated the catalytic role of Pd in sulfur oxidation and storage on to the support.

**Rhodium**

Very few studies have been performed using monometallic Rh as the precious metal for NSR systems [16,25,27,117,118]. Abdulhamid et al. [25] found Rh/BaO/Al₂O₃ to have poor NOₓ storage capacity, but high reduction ability in comparison to Pt and Pd. The authors suggested the poor activity of supported Rh catalysts was due to lack of NOₓ spillover from Rh to BaO. Rh also had the lowest activity for NH₃ formation, which could be explained by an increased ability to dissociate NO on the metal surface. This is in agreement with a study done by Breen et al. where Rh containing samples produced the smallest amount of ammonia [119]. In a later study, Breen et al. suggested that spillover from Rh to BaO may not be limiting storage-reduction activity and suggested that Rh may simply be a poor oxidation catalyst [16,120]. Alternatively, Huang et al. [117] observed better storage-reduction properties for Rh/CaO/Al₂O₃ over Pt or Pd supported on CaO/Al₂O₃, which demonstrates that NSR properties could be both a function of precious metal and storage component. Vijay et al. [118] observed similar storage amounts for Pt/BaO/Al₂O₃ and Rh/BaO/Al₂O₃ if long cycle times were used. Therefore, discrepancies on the role of Rh exist and further study is warranted, especially since many commercial catalysts contain mixtures of Pt and Rh. While the role of Rh in NOₓ storage and reduction chemistry may still be unclear, Mahzoul et al. observed Rh to inhibit sulfur formation, which is a desirable attribute for NSR catalysts [121].

Other monometallic metals investigated include: Cu, Co, Fe, and Ag. HC-SCR systems commonly employ a Ag/Al₂O₃ catalyst and can achieve NOₓ conversions as high as 79% [122,123]. Along these lines, Mihalova et al. [124] compared a Ag/BaCO₃/Al₂O₃ and
Pt/BaCO$_3$/Al$_2$O$_3$ catalyst and observed a maximum NO$_X$ conversion of approximately 50% at 500 °C for Ag based samples, but 90% conversion at 350 °C for Pt based samples. While the Pt based sample initially had much higher activity, they were much more susceptible to sulfur poisoning. After sulfur exposure, the Ag sample was more active when compared to the Pt samples. In a series of publications, Vijay et al. [118,125,126] studied Co-containing NSR materials. They found that a 5%Co/15% Ba on alumina and 1%Pt/15% Ba on alumina stored equivalent amounts of NO$_X$ when the catalysts were exposed to lean environments at 375 °C. XRD confirmed that Co was present as a highly oxidized Co$_3$O$_4$ phase. In comparison to Co, Pt was still a better oxidizing metal, but Co is much cheaper and could therefore be used in much higher amounts. Co was also more uniformly distributed on the support, which was thought to lead to better interfacial contact between the oxidizing metal and storage component. Unfortunately, Co exhibits poor reduction activity and another noble metal, most likely Rh, would need to be included to reach high conversions. Park et al. [127] also observed NSR activity for Co containing NO$_X$ storage catalysts. Monometallic Fe samples were studied by Hendershot et al. [128,129] using high throughput experimentation and the presence of Fe was found to affect the performance significantly less than the Pt and Ba weight loadings. Wang et al. [130,131] synthesized a Cu/K$_2$Ti$_2$O$_5$ NSR catalyst because Cu is capable of simultaneous removal of SO$_2$ and NO$_X$ in flue gases and they hoped to extend some of these desirable properties to NSR catalysts. They observed storage and reduction activity at higher temperatures (500 – 600 °C), but observed poor reduction activity at lower temperatures (200 – 400 °C). Ir based catalysts have been suggested to be highly active for SCR and DFT calculation have implied Pt/Ir to be an interesting bi-metallic system, but no experimental investigations have been performed using Ir to date [132–134].
Most of the model NSR catalysts considered only contain Pt and Ba supported on Al\textsubscript{2}O\textsubscript{3}, but commercial catalysts consist of complex mixtures involving differing combinations of the following elements: Pt, Pd, Rh, Ba, K, Ce, La, Zr, Mg, Ti, and Al\textsubscript{2}O\textsubscript{3} [31,45,102,135–138]. Sedlmair et al. used a Pt-Rh/BaO-BaCO\textsubscript{3}/Al\textsubscript{2}O\textsubscript{3} commercial catalyst in their studies [31,102]. Others have used formulations including Mg, Al, Ce, Zr, Ba, Pt, Pd, Rh, La, Fe, and Ti [136,139,140] or Pt, Rh, Ba, Ce and Al [138]. While many investigations have used either model or commercial bi-metallic catalysts [31,46,62,75,102,104,105,121,135–139,141–156], only a small number of these investigations have been devoted to understanding the specific role each metal plays on the observed catalytic performance [16,46,75,121,141,153]. Commercial catalysts typically contain a large number of elements because the addition of multiple promoters can increase activity, selectivity or improve catalyst lifetime. For example, Choi et al. [135] investigated sulfur poisoning on an industrial sample containing Pt, Pd and Rh, in addition to many other component. The reasoning for addition of three different metals could be as follows: Pt for the oxidation of NO to NO\textsubscript{2} [55,115], Pd for activation of saturated hydrocarbons [25,27,112,113], and Rh for its high reduction activity and low selectivity to ammonia [27,119]. However, the addition of multiple metals does not necessarily infer additive properties as observed during monometallic studies. Therefore, bimetallic and tri-metallic interactions must be carefully considered in order to determine if the additional metals provide increased catalytic performance. Otherwise, the higher costs associated with incorporation of additional precious metals is unwarranted. This section focuses strictly on Pt-Rh supported on BaO containing substrates. No literature was available for Pd containing bimetallic samples. The addition of
other elements will be discussed in section 1.3.4.3 on supports (MgO, TiO₂, ZrO₂ and La₂O₃) or section 1.3.4.4 on promoters (mainly Co, Fe and CeO₂).

Initially, Mahzoul et al. [46,121] observed that washcoat samples containing Pt, Rh, Ba, La, and Al stored more NOₓ at saturation conditions than other standard washcoat formulations containing only Pt, Ba and Al₂O₃. The authors also determined that Rh inhibited the formation of sulfates. Amberntsson et al. [141] performed a detailed study on NO oxidation and reduction as a function of Pt and Rh loading. The NOₓ storage capacity was observed to decrease as follows: 4% Pt > 2% Pt ≈ 2% Pt-1% Rh > 1% Pt-0.5% Rh > 1% Rh for samples containing equimolar amounts of BaO on alumina. The samples containing monometallic Pt performed much better when oxidation of NO to NO₂ was examined. To help understand why Rh negatively affected NO oxidation, the authors conducted XPS studies and found the surface coverage of Pt decreased by 70% in oxidizing conditions compared to reducing conditions. Conversely, Rh surface concentration increased by 35%. This inferred that the bimetallic samples consisted primarily of Rh on the surface during lean conditions, which helped explain the poor performance, since Rh has been reported to be a poor NO oxidation catalyst [16,120].

While initial inspection of Pt-Rh bimetallic catalysts inferred a negative influence for Rh incorporation, Amberntsson et al. [141] demonstrated that Pt-Rh bimetallic samples sustained much higher conversions when SO₂ was present in the exhaust gas. The bimetallic samples were not susceptible to deactivation like their monometallic counterparts, as seen in Fig. 8. NO oxidation on monometallic Rh samples deactivated very quickly, but monometallic Pt and Pt-Rh samples were stable during the time frame of the experiment. Conversely, NO reduction on monometallic Pt samples deactivated very quickly, whereas bimetallic Pt-Rh and monometallic Rh samples were stable. The authors concluded that addition of Rh was essential for good
overall performance of NSR catalysts even though the amount of NO\textsubscript{X} stored was lower. Similarly, Schmeißer et al. and Kim et al. have found the incorporation of Rh leads to improved performance due to its high NO\textsubscript{X} reduction ability even though it suppresses NO\textsubscript{X} storage capacity [75,152].

![Figure 8](image)

**Figure 8.** NO oxidation (a) and reduction (b) over (◊) 4 % Pt, (□) 2 % Pt, (Δ) 2 % Pt - 1% Rh, (☑) 1 % Pt – 0.5 % Rh, and (○) 1 % Rh catalysts containing equimolar amounts of BaO as a function of sulfur exposure, Amberntsson et al. [141].

Conversely, Breen et al. [16] performed a study using fast transient techniques and determined that the addition of Rh does not have a beneficial effect in NSR catalysts. Their investigation employed realistic 60 s lean periods followed by 1.2 s rich periods and they found that NSR activity to decreased as follows: 1.6 wt % Pt > 0.5 wt % Pt – 0.8 wt % Rh > 1.1 wt % Rh > 0.5 wt % Pt. However if the data was corrected for the percentage of metal atom exposed, the activity decreased as follows: 0.5 wt % Pt > 0.5 wt % Pt – 0.8 wt % Rh > 1.1 wt % Rh. The authors explained these results by introducing operational regimes, where NSR performance could either be storage limited catalysts or reduction limited. The 1.6 Pt and 0.5 Pt – 0.8 Rh samples were reduction-rate limited catalysts because they were incapable of completely
regenerating the storage component during rich periods and so conversion decreased with cycling time. The monometallic Rh catalyst was the only sample with a high enough reduction activity to completely regenerate the catalyst, but was limited by the storage-rate during lean phases. In this case, conversion of NO\textsubscript{X} was low but remained constant with cycling time. While the study by Breen et al. [16] indicated low activity for Rh containing NSR catalysts, it should be noted that the authors excluded the role of sulfur and the bimetallic catalyst tested contained a molar ratio of 0.84 for Pt:Rh, respectively. The low ratio of Pt to Rh could exacerbate surface enrichment of Rh on the surface of Pt during lean periods, as observed by Amberntsson and coworkers [141]. Several surface science investigations reported diffusion of Rh into Pt particles even at room temperature [157–159], which further demonstrates that interconversion between Pt rich and Rh rich surfaces in different environments may be facile and should be considered when designing bimetallic catalysts. The ratio of Rh to Pt was also quite high in comparison to formulations typically employed for commercial catalysts [139].

1.3.3.2 Storage Materials

The storage component is usually selected from alkali metals and/or alkaline earth metals. Matsumoto [8,160] demonstrated that NO\textsubscript{X} storage increased as the electronegativity decreased, but hydrocarbon conversion increased as the electronegativity increased. Fig. 9 demonstrates the inverse relationship between the NO\textsubscript{X} storage ability and hydrocarbon (HC) conversion as a function of electronegativity.
Figure 9. NO$_X$ storage capacity and hydrocarbon conversion measurements for some alkali and alkaline earth elements including: Cs, K, Na, Ba, and Mg, Takeuchi and Matsumoto [160].

For these reasons, considerable efforts have been devoted to Ba as a storage component because it has desirable properties when examining both the lean and rich phases of NSR operation [21,22,32,39,61,73,94,100,161–163]. Recently, there has been interest in K because it may offer higher storage capacity [160], help stabilize stored nitrogen oxide species [164] and have better interaction with Pt [165]. Other storage materials include Li [166,167], Mg [163,167–170], Ca [167,169,170], Sr [169,171–173], and Na [167,174–177]. When considering these different storage materials, primary questions of concern include: (i.) Which storage material offers the best performance when sulfur resistance, thermal stability, NO$_X$ storage capacity, HC conversion, and selectivity to N$_2$ are all considered? (ii.) What is the optimum loading of that storage material and what is the nature of the storage material therein? (iii.) How strongly does the storage material store NO$_X$ and what types of species are present on the surface? (iv.) How does the metal-storage material interface affect the storage? The following two subsections will focus on the current understanding of these questions.

**BA CONTAINING NSR MATERIALS**

Ba represents the most commonly used element as a NO$_X$ storage material. The optimum Ba loading has been reported as 6-12 wt % Ba [178], 16-23 wt % Ba [179] and 23 wt % Ba [73].
Generally higher amounts of Ba are capable of storing more NO$_X$, but loadings higher than 10 wt% can negatively affect noble metal dispersion [73,179]. Unfortunately, direct comparison between studies can be difficult because a wide range of loadings have been used: e.g., 8 wt% BaO/BaCO$_3$ [31], 8.3 wt% Ba [29], 9 wt% Ba [32], 13 wt% BaO [94], 16.3 wt% Ba [61], 17 wt% Ba [21], 18 wt% BaO [94], 20 wt% BaO [22], and concentrations up to 30 wt % Ba [73]. These samples will most likely exhibit different distributions and dispersions of Ba and/or differences in morphology of the Ba present on the surface. For example, Piacentini et al. [161] performed a study using XRD and TPD to examine the effect of varying the Ba loading from 4.5 to 28 wt % and concluded that the chemical nature of Ba was dependent on loading. They observed no evolution of CO$_2$ during TPD for Ba loadings of 4.5 wt %., but saw evolution of CO$_2$ in all samples with loadings of 9 wt % or higher. Fig. 10 depicts the observed changes in the chemical nature of Ba as a function of loading, where LT-BaCO$_3$ corresponds to desorption temperatures of 400-800°C and HT-BaCO$_3$ corresponds to bulk-like BaCO$_3$ with desorption temperatures approaching 1050°C. XRD patterns indicative of crystalline BaCO$_3$ were observed in samples with loadings of 16.7 wt % and higher.

Lietti et al. [39] also observed diffraction patterns indicating the presence of both monoclinic and orthorhombic BaCO$_3$ after calcination of a Pt/Ba/Al$_2$O$_3$ (1/20/100 w/w) at 500°C, but noticed with subsequent lean-rich cycling (lean: NO+O$_2$; rich: H$_2$) BaCO$_3$ was exchanged for BaO and/or Ba(OH)$_2$. In summary, researchers have reported that NSR catalysts contain only BaO [100,162], only BaCO$_3$ [27] and mixtures of BaO and BaCO$_3$ [163,180]. Differentiating between Ba phases is important because thermodynamic calculations infer BaCO$_3$ to be a relatively inactive storage component due to the higher stability of barium carbonates over barium nitrates, if bulk-like properties are assumed [44]. However, these
calculations do not account for support interactions with the dispersed compounds. As shown previously, these interactions can be significant, especially at lower loadings of Ba [161]. Cant and Patterson [32] concluded that CO$_2$ has no effect on NO$_2$ uptake, but others [29,44,45,181–183] reported a negative effect for CO$_2$ on the storage of NO$_X$. Since the active storage component is most likely BaO [44,47,184,185], but the catalyst may also contain significant amounts of BaCO$_3$ [27,39,161,163,180], it is important to establish a mechanism by which NO/NO$_2$ interacts with BaCO$_3$ to form BaO and/or Ba(NO$_3$)$_2$, especially in the presence of excess CO$_2$ because CO$_2$ is always going to be present in exhaust environments. Broqvist et al. [47] attempted to do so in a DFT study and they demonstrated decarbonation of the surface to be promoted by the presence of NO$_2$ and argued that forming a NO$_3^{2-}$ species significantly reduces the energy cost for CO$_2$ desorption. Conversely, Sedlmair et al. [31] only noticed decarbonation of the surface if NO was present and NO$_2$ was not observed to facilitate decomposition of supported barium carbonates.

![Figure 10. Pictorial representation of the chemical nature of Ba on Al$_2$O$_3$ at different loadings, Piacentini et al. [161].](image-url)
In summary, characterization of calcined Pt/BaO/Al₂O₃ samples using XRD and FTIR have repeatedly shown the presence of a “bulk-like” BaCO₃ phase [34,37,161,179]. However, Frola et al. [179] and others have demonstrated that this phase undergoes a morphological transformation during NSR cycling treatments, in the absence of additional gas phase CO₂, leading to the formation of highly dispersed BaO [21,34,45,65]. Zhou et al. [186] demonstrated that calcining supported Ba(NO₃)₂ in air leads to the formation of BaCO₃, which indicates the reversibility of the exchange between barium nitrate and barium carbonate.

Storage of NOₓ on BaO/BaCO₃ occurs through the formation of surface nitrites, surface nitrates and bulk-like nitrates depending on the NOₓ source (i.e., NO, NO+ O₂, or NO₂), time of exposure, temperature and the presence of water [21,22,31,33,34,43,187]. For example, Seldmair et al. [31] exposed a Pt/BaO/Al₂O₃ (1/8/100 w/w) to NO at 50°C and observed formation of linear and bridging nitrites; increased exposure time led to formation of peaks corresponding to N-coordinated nitrites on alumina (1537 cm⁻¹), monodentate nitrites (1340 and 1440 cm⁻¹), linear nitrites on Ba (1422 cm⁻¹) and hyponitrites (1380 cm⁻¹). Exposure to NO₂ at 50°C resulted in the formation of linear barium nitrites (1419 cm⁻¹), bidentate nitrites (1203 and 1332 cm⁻¹), chelating bidentate surface nitrates on Al₂O₃ (1564 cm⁻¹), and monodentate nitrates on BaO (1429 and 1332 cm⁻¹). Nova et al. [21,34,40] did not observe the formation of nitrites when a Pt/Ba/Al₂O₃ (1/20/100 w/w) was exposed to NO₂ at 350°C, but many others observed the formation of both nitrites and nitrates upon exposure of NO₂ [27,31,33,41]. Exposure of a Pt/BaO/Al₂O₃ (1/8/100 w/w) to NO + O₂ at 50°C led to the formation of surface nitrites on Ba (1200 cm⁻¹), linear Ba nitrites (1419 cm⁻¹), bridging bidentate nitrates on Al oxide (1619 cm⁻¹), chelating bidentate surface nitrates (1561 and 1290 cm⁻¹), linear nitrites on Al (1479 cm⁻¹), and monodentate nitrates on BaO (1424 and 1332 cm⁻¹) [31]. The thermal stability of the adsorbed
NO\textsubscript{X} species increased as follows: Al nitrites (linear, N-coordinated) < Ba nitrites (linear, monodentate) < Al nitrates (bridging bidentate, chelating bidentate) < Ba hyponitrites < Ba nitrates (monodentate). Therefore, under realistic exhaust conditions the stored species are most likely in the form of bidentate nitrates on alumina, monodentate nitrites on alumina, monodentate nitrates and nitrites on barium, and bridge bonded bidentate nitrites over barium [21,22,27,33,34,41,112], as summarized in Table 2.

Additionally, Szanyi et al. [188] demonstrated that both bidentate (surface: 1300 and 1574 cm\textsuperscript{-1}) and ionic (bulk: 1320 and 1420 cm\textsuperscript{-1}) nitrates are formed in BaO-containing samples and that the relative intensity of the ionic nitrates increase with BaO coverage. They also observed a transition from bidentate nitrates to ionic nitrates with increasing temperature in a 20 wt % BaO/Al\textsubscript{2}O\textsubscript{3} sample. Conversely, a decrease in ionic nitrates was observed for the case of an 8 wt % BaO sample. Desikusumastuti et al. [50] also observed the formation of bulk Ba(NO\textsubscript{3})\textsubscript{2} from surface nitrites and nitrates at elevated temperatures. The study was performed using varying sizes of BaAl\textsubscript{2}xO\textsubscript{1+3x} particles, which have previously been regarded as a source of deactivation for the BaO [162]. The authors demonstrated that Ba\textsuperscript{2+} ions could be extracted from the larger barium-aluminate particles to form Ba(NO\textsubscript{3})\textsubscript{2} and deactivation due to the formation of BaAl\textsubscript{2}O\textsubscript{4} could be reversible. Hodjati et al. [189,190] also mentioned BaAl\textsubscript{2}O\textsubscript{4} particles to be a viable NO\textsubscript{X} storage material because they are unable to interact with CO\textsubscript{2} and may have some resistance to sulfur poisoning. Another factor known to affect the size of these particles is the presence of water. Szanyi et al. [187,191] demonstrated using TPD, XRD and FTIR that nitrated (NO\textsubscript{2} exposure) samples exposed to water form crystalline Ba(NO\textsubscript{3})\textsubscript{2} particles, which decomposed to highly dispersed BaO in the range of 640-940 K. Figs. 11 and 12 demonstrate the influence of water and temperature on stored NO\textsubscript{X}. 
Table 2. FTIR Band Assignments for Nitrite/Nitrate Species on Ba/Al$_2$O$_3$ NSR Catalysts

<table>
<thead>
<tr>
<th>Structure</th>
<th>Assignment</th>
<th>Wavenumber (cm$^{-1}$)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Adsorbed on Al</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{Al}^+\text{O} \equiv \text{N-O}$</td>
<td>Bridging bidentate nitrate</td>
<td>1627-1619, 1180 - 1260</td>
<td>[31,33,34]</td>
</tr>
<tr>
<td>$\text{Al}^+\text{O} \equiv \text{N-O}$</td>
<td>Chelating bidentate nitrate</td>
<td>1569-1561, 1180-1290</td>
<td>[31,33,34]</td>
</tr>
<tr>
<td>$\text{Al}^+\text{O} \equiv \text{N-O}$</td>
<td>Linear nitrite</td>
<td>1537, 1480*, 1083</td>
<td>[31,33]</td>
</tr>
<tr>
<td>$\text{Al}^+\text{O} \equiv \text{N-O}$</td>
<td>Bridged bidentate nitrite</td>
<td>1300, 1200-1230</td>
<td>[31,33,34]</td>
</tr>
<tr>
<td>$\text{Al}^+\text{O} \equiv \text{N-O}$</td>
<td>Bridged N-coordinated nitrite</td>
<td>1522, 1160</td>
<td>[31,33]</td>
</tr>
<tr>
<td>$\text{Al}^+\text{NO}_3^-$</td>
<td>Bulk Nitrate</td>
<td>1397</td>
<td>[33]</td>
</tr>
<tr>
<td>$\text{Al}^+\text{NO}^-$</td>
<td>Hyponitrite</td>
<td>1343</td>
<td>[33,34]</td>
</tr>
<tr>
<td>Adsorbed on Ba</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{Ba}^+\text{N}$</td>
<td>Monodentate nitrite</td>
<td>1440, 1340</td>
<td>[31,33,34]</td>
</tr>
<tr>
<td>$\text{Ba}^+\text{O} \equiv \text{N-O}$</td>
<td>Monodentate nitrate</td>
<td>1429-1422, 1332</td>
<td>[31,33]</td>
</tr>
<tr>
<td>$\text{Ba}^+\text{O} \equiv \text{N-O}$</td>
<td>Linear nitrite</td>
<td>1422-1419</td>
<td>[31,33]</td>
</tr>
<tr>
<td>$\text{Ba}^+\text{O} \equiv \text{N-O}$</td>
<td>Bridged bidentate nitrite</td>
<td>1300, 1230</td>
<td>[31,34]</td>
</tr>
<tr>
<td>$\text{Ba}^+\text{NO}^-$</td>
<td>Hyponitrite</td>
<td>1316</td>
<td>[33,34]</td>
</tr>
</tbody>
</table>
Interaction of CO\textsubscript{X} on Ba has also been studied because CO\textsubscript{X} and NO\textsubscript{X} could be competing for the same storage sites [37,179]. Epling et al. [37] studied Pt/BaO/Al\textsubscript{2}O\textsubscript{3} - (2/20/100 w/w) exposed to CO\textsubscript{2} at room and observed formation of surface Al- and/or Ba-bicarbonates (1232, 1448 and 1650 cm\textsuperscript{-1}), bidentate carbonates (1349 and 1598 cm\textsuperscript{-1}), CO bound to Pt (2030 cm\textsuperscript{-1}) and adsorbed CO\textsubscript{2} (2347 cm\textsuperscript{-1}). Heating led to a decrease in the peaks corresponding to bicarbonates, while the peak at 1448 cm\textsuperscript{-1} remained the same. This indicated that a stable, bulk-like barium carbonate phase had formed. A new peak at 1402 cm\textsuperscript{-1} also appeared and was assigned to unidentate carbonates. Exposure to CO + O\textsubscript{2} at RT led to a prominent band at approximately 2067 cm\textsuperscript{-1}, but the rest of the spectrum remained fairly clean. Heating resulted in formation of bidentate carbonates and bulk-like barium carbonate and closely resembled the spectra for the CO\textsubscript{2} adsorption experiments. At higher temperatures, the primary surface species formed were Ba-formates (1359, 1369 and 1585 cm\textsuperscript{-1}). Exposure to CO at higher temperatures resulted in substantially lower carbonate formation than in the case of CO\textsubscript{2} and CO + O\textsubscript{2}, but formation of bulk like species was still observed, which demonstrated the tendency for BaO to form bulk like carbonates. H\textsubscript{2}O was observed to facilitate interconversion between the
adsorbed species. In a room temperature study by Frola et al. [179], exposure of CO$_2$ led to bands assigned to surface carbonates, bridged carbonates on Ba and Al, bridged, chelating and a relatively small amount of monodentate carbonates on Ba sites, with relative intensities related to Ba loading. Interestingly, Frola et al did not notice the reformation of the bulk-like or orthorhombic BaCO$_3$ in the time scale of their experiments, which could point to an active phase comprised mainly of less stable surface carbonates. Table 3 depicts FTIR band assignments for carbon and sulfur containing species on Ba.

**Table 3. FTIR Peak Assignments for C and S containing Species on Ba/Al$_2$O$_3$ NSR Catalysts**

<table>
<thead>
<tr>
<th>Assignment</th>
<th>Wavenumber (cm$^{-1}$)</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Carbon Containing Species</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Unidentate carbonate</td>
<td>1747, 1403</td>
<td>[37]</td>
</tr>
<tr>
<td>Bicarbonate</td>
<td>1656, 1448, 1238</td>
<td>[37]</td>
</tr>
<tr>
<td>Bridged carbonate</td>
<td>1620, 1280</td>
<td>[179]</td>
</tr>
<tr>
<td>Bidentate carbonate</td>
<td>1598-1530, 1350</td>
<td>[37,179]</td>
</tr>
<tr>
<td>Formate</td>
<td>1585, 1398-1357</td>
<td>[37]</td>
</tr>
<tr>
<td>Monodentate carbonate</td>
<td>1460, 1320</td>
<td>[179]</td>
</tr>
<tr>
<td>Isocyanates</td>
<td>2169, 2230</td>
<td>[37,179]</td>
</tr>
<tr>
<td>Adsorbed CO$_2$</td>
<td>2350</td>
<td>[37]</td>
</tr>
<tr>
<td><strong>Sulfur Containing Species</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hydrogen-bonded sulfites</td>
<td>3638, 3570, 972</td>
<td>[35]</td>
</tr>
<tr>
<td>Tri- co-ordinated sulfates on alumina</td>
<td>1318, 1040</td>
<td>[22,35,36]</td>
</tr>
<tr>
<td>Bulk barium sulfate</td>
<td>1249 1168</td>
<td>[22,35,36]</td>
</tr>
<tr>
<td>Surface bidentate barium sulfate</td>
<td>1107, 1060</td>
<td>[22,35,36]</td>
</tr>
</tbody>
</table>

One disadvantage of using Ba as a storage component is its high susceptibility to sulfur poisoning [6]. Mahzoul et al. [121] reported that BaO, alumina and ceria exposed to SO$_2$ formed various sulfate species, which in the case of BaSO$_4$ did not decompose until approximately
1000°C. Engstrom et al. [105] observed the degree of deactivation to be proportional to the amount of sulfur exposed. Fridell et al. and others have observed sulfur deactivation to be more severe during the rich phase [35,56,103,194–196]. Sedlmair et al. [36,102] demonstrated the appearance of bands at 1120 and 1060 cm⁻¹ after 1 min of exposure, which were assigned to the S-O stretching vibrations of bidentate sulfates on BaO. After 5 min, bands at 1350 1248, 1155 and 1040 cm⁻¹ appeared in addition to the bands in the range 1060-1000 cm⁻¹. The bands at 1248 and 1155 were assigned to bulk barium sulfate, while the bands at 1350 and 1040 cm⁻¹ were assigned to the S-O vibration of tri-coordinated sulfate species on Al₂O₃. Flushing in He and reduction in propylene resulted in negligible changes, which demonstrated the high stability of the formed sulfate species. Others have also seen the formation of these surface and bulk sulfur species on Ba and Al₂O₃ [22,35,194,196]. Furthermore, BaO was observed to form BaSO₄ even in the absence of gas phase oxygen [22,108]. Courson et al. [30] demonstrated that regeneration of sulfur poisoned NOₓ traps occurred more readily if the overall sulfur exposure during the poisoning process was lower. When the extent of poisoning was less than 30% of the BaO, the initial NOₓ storage capacity could be completely recovered using an extended rich environment. However if the extent of poisoning was high, it was impossible to recover the initial NOₓ storage capacity. Scheier et al. [197] determined that regeneration occurred more readily in rich environments (λ= 0.99-0.94), with λ= 0.94 showing the highest sulphate removal, and at higher temperatures (660-720°C). Increasingly rich environments at higher temperature also led to higher concentrations of effluent COS and H₂S. The authors suggested optimization of λ and the regeneration temperature to obtain selective desorption as SO₂. In summary, during lean conditions SO₂ can be oxidized over Pt to form surface and bulk barium sulfates[111], but SO₂ can also directly react with BaO to form BaSO₄ [22,71,108]. During rich periods, SO₂ was
reduced to form Pt-S and BaS [35,36,71,108], which can then be re-oxidized during subsequent lean conditions to form bulk like BaSO$_4$ [35,102,196]. Furthermore, cycling between lean and rich environments in the presence of sulfur seemed to preferentially poison sites near the Pt/BaO interface, which could explain the rapid deactivation of Ba containing NSR catalysts since the Pt/BaO interface is an important property of these materials, as discussed previously [36,71,102,111].

**Potassium Containing NSR Materials**

Potassium is the 2$^{nd}$ most commonly used storage material in NSR catalysts. In comparison to Ba, K has been reported to exhibit higher storage capacity at higher temperatures, but lower storage capacity at lower temperatures [198]. Choi et al. studied the low temperature storage region using spaci-MS techniques to try and elucidate why K performance was inferior to Ba at low temperatures [19]. They observed the WGS reaction to have little impact on Pt/K/Al$_2$O$_3$ samples and suggested that CO may poison Pt sites below 200 °C. Later, Choi et al. found Pt/K/Al$_2$O$_3$ to be active for the WGS reaction, but only after all gas phase O$_2$ had been consumed by oxidation of CO to CO$_2$ [199]. Additionally, CO oxidation caused a considerable exotherm which raised the storage-phase temperature. Primary NO$\_X$ release/reduction was vigorous and proceeded shortly after the rich period began with small NO or N$_2$O slip. Secondary NO$\_X$ release/reduction occurred at later times and produced mainly NH$_3$. Production of NH$_3$ could be explained by *in situ* generation of H$_2$ though the WGS reaction, which then reacted with NO$\_X$ over Pt to form NH$_3$. One possible reason for the differences at low temperatures over Pt/K/Al$_2$O NSR catalysts is the proposed increase in the thermal stability of nitrites/nitrates on K [198]. Park et al. compared BaO/Al$_2$O$_3$ and K$_2$O/Al$_2$O$_3$ using NO$_2$-TPD measurements and observed similar NO$_2$-TPD profiles, but co-impregnation of K and Ba did
induce a shift to higher temperatures for desorption of NO\(_X\), which indicated that co-loading K and Ba could increase the stability of stored nitrates. Unfortunately, the Ba loading was only 6.8 wt \% and the K loading was only 1.5 wt \%, which is much lower than typical NSR catalyst formulations. More recently Matarese et al. [200] reported that thermal release of NO\(_X\) from a Pt/K/Al\(_2\)O\(_3\) catalyst began around 350 °C, which is very similar to values reported for the Pt/Ba/Al\(_2\)O\(_3\) catalysts [34,201].

Numerous FTIR/DRIFTS studies have been conducted for Pt/K/Al\(_2\)O\(_3\) samples [146,165,198,202–208]. Above 200 °C, storage occurred as an ionic nitrate (1380 cm\(^{-1}\)) on K and bidentate nitrates (1535 and 1320 cm\(^{-1}\)) on Al\(_2\)O\(_3\). Below 200 °C, storage occurred as an ionic nitrite on K and a nitrite species on Al\(_2\)O\(_3\). These nitrite species were later oxidized to nitrates by gas phase NO\(_2\). Toops et al. [198], Prinetto et al. [165] and Liu et al. [206] all observed similar trends for NO\(_X\) adsorption as a function of temperature. At lower temperatures, storage occurred mainly as nitrites; but as the temperature was increased, storage occurred mainly as ionic nitrates on K. Thermal desorption of nitrates began at approximately 300 °C and all nitrites/nitrates were completely removed by 500 °C. These results are in agreement with the previously mentioned study by Park et al [164], as shown in Figs. 13 and 14. In this case, Liu et al. [206] used a TiO\(_2\)-ZrO\(_2\) supported samples, whereas Toops et al. [198] and Prinetto et al. [165] used Al\(_2\)O\(_3\) supported samples, but generally the trends were the same.
Figure 13. NO₂ evolution profiles for Ba and/or K supported on Al₂O₃ where (a) Pure Al₂O₃, (b) 6.7 wt % Ba/Al₂O₃, (c) 1.6 wt K/Al₂O₃, and (d) 6.7 wt % Ba and 2.7 wt % K/Al₂O₃, Park et al. [164].

Figure 14. In situ DRIFTS spectra of Pt/K/TiO₂-ZrO₂ after exposure to 400 ppm NO + 5% O₂ for 10 min at temperatures of 100, 200, 300, 350, 400 and 500 °C, Liu et al. [206].

Lesage et al. [205] and Castoldi et al. [202] proposed that NOₓ was stored according to a “nitrite” route, where NO₂ adsorbed as a nitrite and was then further oxidized to a nitrate by either gas phase NO₂ or O₂. Castoldi et al. [202] also proposed that NOₓ may be stored by a disproportionation route as previously observed in the case of Ba. Toops et al. [198] go into more detail regarding NOₓ storage mechanisms on K, but generally their mechanisms fit into the two listed above. Toops et al. [198] also proposed different types of K sites, as was the case for Ba [198,205,206]. Toops et al. [198] and Liu et al. [206] differentiated sites based on their proximity to Pt, whereas Lesage et al. [205] defined surface and bulk storage sites. Generally, sites in close proximity to Pt were thought to be responsible for rapid NOₓ storage since Pt can oxidize NO to NO₂. Sites far from Pt, while capable of storage, were only significant during later times once all of the “fast” sites were filled. The sites farther from Pt probably rely on disproportionation and dismutation mechanisms and are really not relevant to NSR catalysts unless NO₂ is used as the NOₓ source or very long storage times are employed. However,
disproportionation mechanisms are worth mentioning since they will always be operating simultaneously with the Pt-assisted NO$_X$ storage mechanism and will therefore constitute some fraction of the total storage observed. On the contrary, Lesage et al. [205] argued that site differentiation based on location of Pt particles was unclear and proposed that storage initially occurred rapidly on surface potassium sites, where storage was controlled by the rate of NO oxidation. At later times, NO$_2$ must diffuse into the bulk for storage to occur, which was a slow process and led to dramatic NO$_X$ slip.

The morphology of Pt/K/Al$_2$O$_3$ catalysts was investigated by Prinetto et al. [165] XRD patterns of a 1% Pt/5.4% K/Al$_2$O$_3$ (w/w) catalyst exhibited several low intensity peaks which inferred contributions from monoclinic K$_2$CO$_3$ and cubic K$_2$O. Subsequent FTIR experiments revealed strong peaks at 1570 and 1350 cm$^{-1}$, which were characteristic stretching frequencies for surface bidentate carbonates. A strong peak at 1420 cm$^{-1}$ was not observed. Bulk K$_2$CO$_3$ only exhibited one stretching frequency at 1420 cm$^{-1}$. Furthermore, outgassing at 823 K or heating in NO$_2$ at 623 K followed by outgassing at 823 K was sufficient for removal of the peaks at 1570 and 1350 cm$^{-1}$. This inferred that carbonate species stored on K/Al$_2$O$_3$ at room temperature have low stability and were removed easily. The FTIR is in agreement with XRD patterns, where small amounts of K$_2$CO$_3$ were present on the samples before reaction. K also stabilized Pt, where sintering of Pt particles after reaction was lower on Pt/K/Al$_2$O$_3$ than Pt/Al$_2$O$_3$.

Direct comparisons between Pt/Ba/Al$_2$O$_3$ and Pt/K/Al$_2$O$_3$ catalysts have been reported by several groups [136,200,202,208,209]. Pieta et al. [208] and Matarrese et al. [200,209,210] reported Pt/K/Al$_2$O$_3$ to be a better catalyst for simultaneous soot removal and NO$_X$ storage and reduction, but both catalysts were able to oxidize soot. Sakamoto et al. [211] compared K and
Ba supported catalysts on a millisecond time scale and revealed that NO\textsubscript{X} release from Pt/K/Al\textsubscript{2}O\textsubscript{3} samples was faster than Pt/Ba/Al\textsubscript{2}O\textsubscript{3}, which inferred Pt/K/Al\textsubscript{2}O\textsubscript{3} to be more active during reduction while both samples demonstrated similar activity during storage. Alternatively, Castoldi et al. [202] observed that Pt/K/Al\textsubscript{2}O\textsubscript{3} and Pt/Ba/Al\textsubscript{2}O\textsubscript{3} catalysts had different activity if H\textsubscript{2} or NH\textsubscript{3} were used as reductants. Pt/K/Al\textsubscript{2}O\textsubscript{3} was reported to be more active when NH\textsubscript{3} was used, while Pt/Ba/Al\textsubscript{2}O\textsubscript{3} was more active when H\textsubscript{2} was used. The relative activity of the stored NO\textsubscript{X} species and metal support interactions (i.e. Pt-K vs. Pt-Ba) were both suggested as a potential causes for this behavior. FTIR data supported the previous case, where the relative concentration of ionic nitrates to bidentate nitrates depended on the storage material, but higher activity at lower temperatures on Pt/K/Al\textsubscript{2}O\textsubscript{3} during reduction may infer the latter case to be important as well. On the other hand, Prikhodko et al. [136] observed no significant differences between commercial Pt/K/Al\textsubscript{2}O\textsubscript{3} and Pt/Ba/Al\textsubscript{2}O\textsubscript{3} (formulations also included Pd, Rh, Ce, Mg and Zr) catalysts if longer regeneration times were used. Therefore, differences in Pt/Ba/Al\textsubscript{2}O\textsubscript{3} and Pt/K/Al\textsubscript{2}O\textsubscript{3} may be irrelevant during actual operation.

Potassium, like barium, was also susceptible to sulfur poisoning. Toops et al. [212] reported that deactivation due to sulfur exposure was dependent on the temperature and the time of exposure. Exposure of the LNT catalyst at 200 °C showed mild deactivation even after only 15 hours of exposure. However, NO\textsubscript{X} storage capacity at this temperature was also low. At 400 °C, sulfur deactivation was rapid and the catalyst was completely deactivated after only 9 hours of exposure. Temperature programmed regeneration under rich conditions (5600 ppm CO, 3400 ppm H\textsubscript{2}, 5% CO\textsubscript{2} and 5% H\textsubscript{2}O) up to 800 °C mostly restored catalytic activity, which was not always true for Ba/Al\textsubscript{2}O\textsubscript{3} samples [30]. Others have also shown deactivation of K containing catalysts in the presence of SO\textsubscript{2}, where doping of Al\textsubscript{2}O\textsubscript{3} into TiO\textsubscript{2}-ZrO\textsubscript{2} to form a
nanocomposite-structure support seems to be especially promising for sulfur tolerance and removal. Nanocomposite-type supports are discussed in the follow section, where Fig. 16 represents the general idea [155,206,213–216]. Dissolution of K₂O in water could also be a problem since automotive catalysts can experience very high levels of water both from engine exhaust and ambient environmental conditions [164]. Lastly, Pt/K₂Ti₂O₅, Cu/K₂Ti₂O₅, Pt-K/MgAl₂O₄, [Ca₂₄Al₂₈O₆₄]⁴⁺ 4O/K, KₓGaₓSn₈₋ₓO₁₆, K/La₂O₃ and Pt/K-βAl₂O₃/Pt (electrocatalyst) have been investigated for NSR applications, but the results were omitted for brevity [130,131,217–223].

1.3.3.3 SUPPORTS

The support in an NSR catalyst primarily provides a surface to disperse precious metal and storage components, but it can also help with storage capacity, reduction activity, sulfur durability, thermal stability and may alter the catalytic activity of the metals or storage component. Alumina is by far the most commonly used support, but CeO₂, ZrO₂, TiO₂, MgO, varying mixtures of those elements, hydrotalcites and perovskites have all been tested for improved catalytic activity in NSR performance.

SINGLE OXIDE SUPPORTS

The first NSR catalysts were composed of Pt and Ba deposited on γ-Al₂O₃ [8]. Alumina was chosen because it offered a high surface area and methods for increasing the thermal stability and sulfur tolerance through incorporation of BaO, La₂O₃ and SiO₂ with and without heat treatments were previously established [7]. Shimizu et al. [224] demonstrated that NOₓ storage and reduction rates could be altered simply by changing the support. NOₓ storage capacity for Pt and Ba on various supports decreased as follows: MgO > Al₂O₃ > ZrO₂ > SiO₂. However, reduction activity for Pt and Ba on various supports decreased as follows: Al₂O₃ >
ZrO₂ > SiO₂ > MgO. The authors suggested that the inherent acid–base properties of the support either increased or decreased NOₓ storage and reduction activity. Therefore, alumina exhibited a good compromise between NOₓ storage and reduction. Corbos et al. [225] observed similar trends for mixed oxides. In addition to providing a surface to disperse Ba, alumina is also capable of storing some NOₓ, as Lindholm et al. observed significant amounts of NOₓ storage on Pt/Al₂O₃ samples with maximum storage occurring at 200 °C [182]. Westerberg et al. [33] assigned these species to monodentate, bidentate and bridged nitrites and nitrates on alumina and similarly found alumina to be an important storage component below 300 °C. Cant et al. [31,32] also observed storage on Al₂O₃, but the thermal stability of these species was much lower than those formed on Ba. Piacentini et al. [161,226–228] studied the thermal stability of carbonate and nitrate species on Pt–Ba samples supported on Al₂O₃, ZrO₂ and SiO₂ and found that the support significantly affected carbonate and nitrate stability on Ba. Decomposition of BaCO₃ supported on Al₂O₃ and SiO₂ began at around 250 – 300 °C, which was surprisingly low in comparison to the bulk decomposition temperature of approximately 800 °C. However, BaCO₃ supported on ZrO₂ decomposed primarily between 820 – 1000 °C, which was more similar to unsupported BaCO₃. In later works, Piacentini et al. [161,227,228] studied CeO₂ in comparison to SiO₂, ZrO₂, and Al₂O₃ and performed a detailed study on Pt-Ba/Al₂O₃ catalysts. They concluded that Ba(NO₃)₂ and BaCO₃ exhibit different thermal stabilities based on the support and loading of Ba. Formation of a low temperature BaCO₃ phase (LT-BaCO₃ – decomposition of BaCO₃ from 400 – 800 °C) was related to the storage activity for different samples. This phase was deemed the most relevant to NOₓ storage and reduction because Ba is able to form stable NOₓ species at temperatures of interest, but does not form bulk like BaCO₃. In summary, Pt and Ba supported on CeO₂ and ZrO₂ formed higher amounts of LT-BaCO₃ at
lower loadings, whereas Pt and Ba supported on Al₂O₃ and SiO₂ required higher loadings to form LT-BaCO₃. SiO₂ only formed BaCO₃ species at the highest loadings. The results from these studies are summarized in Fig. 15. Additionally, Cheng et al. [229] performed DFT calculations for NO₂ adsorption on unsupported BaO clusters and BaO clusters supported on γ-Al₂O₃. Their results indicated a synergistic effect between BaO and Al₂O₃ for NO₂ adsorption. They concluded that NO₂ preferentially binds to interfacial regions between BaO and Al₂O₃ for sub-monolayer coverages of BaO. While Pt-Ba/Al₂O₃ systems make good NSR catalysts, they are also susceptible to deactivation through formation of BaAl₂O₄ [162,192] or poisoning by sulfur [35,71,103,105,108,194,195]. Therefore, other single oxide and mixed-oxide supports have been investigated for increased thermal stability and sulfur tolerance.

Recently, CeO₂ has been suggested as a viable alternative to Al₂O₃. Maeda et al. [230] demonstrated that NOₓ storage capacity decreased as follows for 1Pt/20 Ba (wt%) supported on CeO₂ > Ce₀.₅Zr₀.₅O₂ > Al₂O₃ > ZrO₂ > TiO₂ > SiO₂. However, reduction activity proceeded in the reverse order, which is in general agreement with others in the literature [224,225]. In previous works, Piacentini et al. [161,226–228] studied the effect of Ba loading on different supports and concluded that optimum Ba loading changed based on the support used. Therefore, CeO₂ could be excellent support for maximum NOₓ storage efficiency. Unfortunately, Maeda et al. [230] found CeO₂ to be a poor support when reduction activity was studied. Poor reduction activity on CeO₂ was attributed to 1.) the basic nature of the support, which stabilized surface and bulk nitrates leading to longer regeneration times and 2.) high oxygen storage capacity, which provided facile oxygen during reduction and led excessive to consumption of reductants that could otherwise be used for the reduction of NOₓ.
Figure 15. CO$_2$ evolution profiles of BaCO$_3$ decomposition formed during calcination at 500 °C of the Ba(Ac)$_2$ precursor for varying loadings of Ba on different supports where (A) Pt-Ba/CeO$_2$, (B) Pt-Ba/ZrO$_2$ and (C) Pt-Ba/Al$_2$O$_3$. Pt-Ba/SiO$_2$ not shown, Piacentini et al. [161,228].

Previously, Martin and Duprez [231] investigated the acidity and basicity of many support materials. CeO$_2$ was characterized as a very basic support with little acidity, whereas alumina has both acidic and basic properties. This helps explain why alumina exhibits good characteristics for NSR operation. Interestingly, 12 wt % CeO$_2$ doped alumina still retained most of its acidic properties, but also increased in basicity. Therefore, CeO$_2$ may be more beneficial as a promoter than as a support (this aspect will be discussed in section 1.3.3.4 on Promoters). While CeO$_2$ suffers from reduction activity, it has gained support in the literature because it has
been suggested to increase sulfur tolerance, promote the WGS reaction and stabilize Pt particles against sintering during high temperature excursions [101,109,151,232–234]. Kim et al. [109] observed BaS formation in Pt-BaO/CeO$_2$ to be much lower than Pt-BaO/Al$_2$O$_3$ samples, which implied that CeO$_2$ suppressed the formation of these crystallite species. However, the formation of sulfur species with lower oxidation states was enhanced. H$_2$-TPRX evolution profiles showed negligible formation of H$_2$S, which inferred the H$_2$S produced from reduction of BaSO$_4$ was readily re-adsorbed by CeO$_2$ to form ceria-sulfur complexes. The proposed mechanism was in agreement with S XANES spectra, where the initial and final intensities of sulfur compounds remained fairly constant. Kwak et al. [101] also observed better sulfur tolerance for Pt-BaO/CeO$_2$ samples and excellent resistance to Pt sintering. Casapu et al. [232,233] observed that sintering of Pt was prevented due to formation of a temporary perovskite that anchors Pt to the support. At lower temperatures in oxidizing environments (600 – 700 °C), Pt reacted with Ba and CeO$_2$ to form BaPtO$_3$. At higher temperatures (> 800 °C), formation of the double perovskite Ba$_2$PtCeO$_6$ was observed. Reduction of these species occurred from 130 – 210 °C, which demonstrated the reversibility of the thermal aging. An additional advantage of CeO$_2$ is that BaCeO$_3$ formed at high temperature were easily decomposed by CO$_2$ unlike BaAl$_2$O$_4$ [180,234]. Unfortunately, Ba supported on CeO$_2$ samples in the presence of CO$_2$ may form very stable bulk-like BaCO$_3$ species. Lastly, CeO$_2$ has been suggested as a potential storage component. Svedberg et al. [235] found both Al$_2$O$_3$ and Pt/CeO$_2$/Al$_2$O$_3$ stored considerable amounts of NO$_X$ in the region of 100 – 200 °C, but still only half as much as Pt/BaO/Al$_2$O$_3$ systems. Philipp et al. [236] observed bands at 1162, 1277, 1067 and 823 cm$^{-1}$ (chelating nitrites), 1021 and 974 cm$^{-1}$ (cis-hyponitrites), 1097 cm$^{-1}$ (trans-hyponitrites), and 792, 1322 and 47
1607 cm\(^{-1}\) (nitrates). Philipp et al. [236] and others [235,237] proposed CeO\(_2\) to be a viable storage material at lower temperatures for lower Ba loadings.

SiO\(_2\) is generally regarded as a woefully inadequate support for NSR components. Piacentini et al. and others observed virtually no storage when Pt-Ba/SiO\(_2\) samples of varying Ba loading were exposed to NO\(_X\) [224–228]. Alternatively, ZrO\(_2\), TiO\(_2\) and MgO have potential for good NO\(_X\) storage-reduction properties. Yamato et al. [238] studied TiO\(_2\) as a support because TiO\(_2\) is well known to be resistant to sulfur poisoning. Li, Na, K, Cs, Sr, Ba and La were all tested as potential storage components for the Pt/TiO\(_2\) based system. Pt-Na/TiO\(_2\) and Pt-K/TiO\(_2\) performed best for both storage and reduction when SO\(_2\) was absent. In the presence of SO\(_2\), only the Pt-Li\(_2\)O/TiO\(_2\) samples activity remained unchanged. All other samples suffered from deterioration of NO storage activity. Although Pt-Li\(_2\)O/TiO\(_2\) was outperformed by Na or K based catalysts in the absence of sulfur, it offered excellent sulfur tolerance not observed for other NSR catalysts. ZrO\(_2\) is another promising support for NSR catalysts. As previously mentioned, Shimizu et al. [224] determined ZrO\(_2\) to be less active than Al\(_2\)O\(_3\) for NO\(_X\) storage, but more active for reduction of NO\(_X\) using H\(_2\). However, Piacentini et al. [228] found ZrO\(_2\) to be less active for reduction of NO\(_X\), which was attributed to much lower surface areas of ZrO\(_2\) supports. Lastly, the storage mechanism for NO\(_X\) on BaO/MgO systems was studied [239]. Storage proceeded through formation of barium-nitro species that later transformed to nitrite and/or nitrate species. This mechanism differs from the generally accepted mechanisms discussed in section 1.3.2.1 for Pt-BaO/Al\(_2\)O\(_3\) systems. The deviation may be explained by the high basicity of MgO supports. Storage above 400 °C was observed, but was suppressed in comparison to lower temperatures. Reduction with CO led to formation of thermally stable BaCO\(_3\), but transformation back to Ba(NO\(_3\))\(_2\) upon NO\(_2\) exposure was possible. Albeit the
transformation required 90 min to complete, which was drastically longer than usual NSR lean operation times. Therefore, accumulation of CO₂ and subsequent deactivation may occur with increasing cycle time.

**Mixed Oxides**

Many publications are devoted to investigation of various mixed oxides as supports. Generally, mixed oxides are of interest for several reasons including: 1.) they may promote higher NOₓ storage capacity or storage rate, 2.) increase reduction activity, 3.) stabilize catalytic components against thermal degradation processes and 4.) increase sulfur tolerance of the NSR catalyst.

The most common supports, other than Al₂O₃, are mixed oxides containing mixtures of two or more of the following materials: SiO₂, CeO₂, ZrO₂, TiO₂ and/or Al₂O₃. Takahashi et al. [240] studied the influence TiO₂, ZrO₂ and mixtures of TiO₂-ZrO₂ and found that TiO₂ suppressed sulfur formation on supported Pt-K samples, whereas ZrO₂ prevented solid phase reaction of potassium with the support. At higher temperatures, ZrO₂ rich supports performed better than TiO₂ rich supports, but the opposite was true at lower temperatures. Initially, Corbos et al. [241] determined storage capacity increased as follows: Pt/20Ba/Si < Pt/20Ba/Al5.5Si < Pt/10Ba/Al < Pt/5Ba/CeZr < Pt/30Ba/Al5.5Si < Pt/20Ba/Al < Pt/10BaCeZr. Again, trends in basicity were used to explain storage capacity. CO₂ inhibited NOₓ storage for all catalysts, but the effect was more pronounced on more basic supports and with increasing temperature. Water also had a detrimental effect, but the effect was observed more strongly for Al₂O₃ containing supports. While Ce-Zr systems offered the highest storage capacity, realistic experimental conditions favored the Pt/20Ba/Al5.5Si sample. In other works, Corbos et al. [225,241,242] studied the effect of sulfur and aging on similar sets of samples. They found all samples were
negatively affected by sulfur, but could be regenerated after treatment in H₂ at 550 °C. Interestingly, only the Pt/Ce₀.₇Zr₀.₃O₂ sample was regenerated completely. Additionally, Ce₀.₇Zr₀.₃O₂ samples exhibited BaSO₄ reduction temperatures around 100 °C lower in comparison to Al₂O₃ containing samples. This led the authors to conclude that mixtures of CeO₂ and ZrO₂ could provide better results when compared to conventional Al₂O₃ based systems when sulfur tolerance was considered. Continued work on CeₓZr₁₋ₓO₂ mixed oxides predicted Ce rich samples to be particularly interesting because they are especially resistant to sulfur poisoning and produced very little NH₃ during reduction, but the OSC of the materials did lead to higher consumption of reductants during reduction [243]. Other studies on CeO₂-ZrO₂/Al₂O₃[244], CeₓZr₁₋ₓO₂ [99], Al₂O₃ doped TiO₂-ZrO₂ [214] and TiO₂-Al₂O₃ [166,245] have been performed in an attempt to further elucidate the role of the support and/or how mixtures of support materials can provide improved results over Al₂O₃ supported samples. Preliminary results indicated positive effects for mixed oxide supports over single oxide options. One particularly interesting example of a novel support combined ZrO₂, TiO₂ and Al₂O₃ to form a thermally stable, sulfur resistant nanocomposite [155,213,215]. Imagawa et al. [155] prepared these nanocomposite samples using conventional co-precipitation techniques. Al(NO₃)₃·9 H₂O, Zr(NO₃)₂·2 H₂O and TiCl₄ were dissolved in ion exchanged water and then an ammonia containing solution was added for co-precipitation. The synthesized nanocomposite of Al₂O₃ and ZrO₂-TiO₂ (AZT) was then compared to physical mixtures of Al₂O₃ and ZrO₂-TiO₂ prepared in the same way. The nanocomposite samples were much more thermally resistant than samples prepared by physically mixing. Al₂O₃ was suggested to act as a diffusion barrier against aggregation of ZrO₂-TiO₂ particles at high temperatures. Fig. 16 depicts this concept and provides supporting TEM micrographs of the nanocomposite. Further work by Imagawa et al. focused on sulfur durability
of AZT and Ti-doped AZT [155,213]. They found catalysts consisting of Pt, Rh, Ba, and K supported on AZT were much more resistant to both sulfur poisoning and thermal aging than physical mixtures of Al₂O₃ and ZrO₂-TiO₂. Additionally, Ti-doped AZT samples offered increased sulfur tolerance in comparison to the AZT supported samples.

Figure 16. (A) Theoretical concept describing differences in aggregation phenomena for a physical mixture of Al₂O₃ and ZrO₂-TiO₂ vs. a nanocomposite of Al₂O₃ and ZrO₂-TiO₂, (B) FE-TEM micrograph for nanocomposite of Al₂O₃ and ZrO₂-TiO₂ after calcination at 1173 K and (C) FE-TEM micrograph for physical mixture of Al₂O₃ and ZrO₂-TiO₂ after calcination at 1173 K, Imagawa et al. [215].

Hydrotalcites and perovskites are another type of support material applied to NSR catalysts. Centi et al. [246] studied hydrotalcite (HT)-type compounds impregnated with Pt and/or Cu and found they generally outperformed Pt-Ba/Al₂O₃ catalysts prepared by incipient wetness impregnation. The HT catalysts were prepared using a commercially available precursor with an atomic ratio of 66:34 for Mg²⁺ and Al³⁺, respectively. The most active HT sample contained both 1 wt % Pt and 4% Cu. At low temperatures, the Pt-Cu/HT samples outperformed Pt-Ba/Al₂O₃; however, at intermediate and high temperatures the Pt-Ba/Al₂O₃ sample demonstrated higher NOₓ conversion. When sulfur tolerance was studied, Pt-Cu/HT
deactivated less than the Pt-Ba/Al₂O₃ sample, but deactivation was still observed. Hydrothermal treatments were also less detrimental to the performance of Pt-Cu/HT samples in comparison to both Pt-Ba/Al₂O₃ and Pt/HT. Formation of Pt-Cu alloys was suggested as one reason for higher thermal stability and sulfur resistance [246,247]. Formasari et al. [247,248] demonstrated that the Mg/Al ratio in HT derived samples plays a crucial role in their performance. Samples with lower Mg/Al ratios performed better at lower temperatures, but samples with higher Mg/Al ratios performed better at higher temperatures. This was explained by different susceptibilities for the Mg(Al)O mixed oxide to form the more inactive spinel MgAl₂O₄ phase. Later, Morandi et al. [249] proposed that storage on Pt-Mg(Al)O and Pt/Cu-Mg(Al)O occurred through two competing storage mechanisms. NO₂ proceeded through a “dismutation route”, while NO + O₂ proceeded through either the “dismutation route” or the “nitrite route”. Storage of NO in the absence of O₂ was not observed. Equations 11 – 13 display the “dismutation route”, where Equation 13 is the net result of Equations 11 and 12. Notice how similar these proposed storage mechanisms are to those presented for storage on BaO in Section 1.3.2.1.

\[
\begin{align*}
2NO_2 + O_2^{2-} & \rightarrow NOO^{-}_{(s)} + NO^{-}_3(s) \\
NO_2^{-}(s) + NO_2 & \rightarrow NO_3^{-}(s) + NO \\
3NO_2 + O_2^{2-} & \rightarrow 2NO_3^{-}(s) + NO
\end{align*}
\]

Yu et al. [250] and Li et al. [251] proposed slightly different storage mechanisms for hydrotalcite based NSR catalysts. Li et al. [251] proposed that storage of NO₂ occurred without evolution of gaseous NO. Yu et al. [250] also mentioned Equation 13 listed above as a storage mechanism, but additionally mentioned storage through formation of adsorbed N₂O₃ and hyponitrites (N₂O₂)²⁻. Generally, the use of hydrotalcite-like compounds in NSR catalysis can be
summarized by Fig. 17, where Pt-Mg(Al)O, Cu-Mg(Al)O, Pt/Cu-Mg(Al)O, CoMg/Al, Ca₂CoAl-oxide, Ca₂CoLaAl-oxide, Co-Mg, Pt/Co/Mg/Al, Pd/Co/Mg/Al, Ru/Co/Mg/Al, and V/Co/Mg/Al have all been considered [246–253].

Figure 17. Preparation of hydrotalcite-like catalysts for NOₓ storage/reduction/decomposition applications, Yu et al. [252].

Li et al. [254] studied Ba-Fe-O perovskite type NSR materials prepared by the sol-gel method. After calcination at 750 °C, the main diffraction peaks detected by XRD were perovskite BaFeO₃, defect perovskite BaFeO₃₋ₓ, and BaCO₃. Calcination at 900 °C led to significant decreases in all three of these phases and an increase in spinel BaFe₂O₄, which translated into a NOₓ storage capacity (NSC) decrease from 114.7 µmol/g to 15.4 µmol/g. Interestingly, the BaFeO₃ sample calcined at 750 °C retained 82% of its NSC during exposure to 100 ppm SO₂, while a reference Pt-Ba/Al₂O₃ samples only retained 15% of its storage capacity. So, perovskites may have lower NSC initially, but their long term sulfur durability may make them a viable alternative to conventional Pt-Ba/Al₂O₃ samples. Zhu et al. [255] observed high activity for direct decomposition of NO even in the presence of O₂ using La₂₋ₓBaₓNiO₄ (x ≤ 1.2) perovskite-type materials. The authors suggested that doping Ba into La₂NiO₄ increased the
oxygen vacancy content, which increased the mobility of lattice oxygen in the perovskite and improved the redox capability of Ni. Ba was used as a promoter because perovskite-type materials traditionally suffer from strongly adsorbed oxygen species on the active site that are hard to remove during regeneration, which subsequently leads to deactivation for these types of materials. Ueda et al. [256] used a (La, Ba)(Fe, Nb, Pd)O$_3$ perovskite catalyst and obtained 47% NO$_X$ conversion at 523 K, but only stored 3.1 – 11 µmol/g of NO$_X$, which was substantially lower than storage capacities for Pt-Ba/Al$_2$O$_3$ systems. In comparison, Xian et al. [257] measured NSC for a BaFeO$_3$-x perovskite and found storage ranged from 578 – 222.9 µmol/g for samples calcined at 850 and 950 °C, respectively; whereas, a Pt/BaO/Al$_2$O$_3$ reference sample only stored 290 µmol/g. Sulfur tolerance was also much greater for the perovskite materials. They retained 61% and 86% of their NSC after calcination at 850 and 950 °C, respectively. The reference Pt/BaO/Al$_2$O$_3$ sample only retained 30% of its initial NSC. Unfortunately, the authors did not measure the cycle averaged conversion for these samples. Recently, Kim et al. [172] demonstrated that a La$_{0.9}$Sr$_{0.1}$MnO$_3$ perovskite based LNT catalysts with precious metal loadings of 1.8 Pd/0.2 Rh (g liter$^{-1}$) outperformed a commercial Pt- based LNT with 1.6 Pt/0.3 Pd/ 0.2 Rh (g liter$^{-1}$) at 350 °C. Therefore, perovskite based samples could be viable alternative to Pt-Ba/Al$_2$O$_3$ because they may be more sulfur resistant and could reduce costs by up to 70% (incurred from incorporation of precious metals) in comparison to Pt based samples. Additionally, K$_2$Ti$_2$O$_5$ [130,131,223], Y$_2$O$_3$ doped MnO$_x$ metal oxides [258], MnO$_x$-SnO$_2$ [259], MgAl$_2$O$_4$ [217], NbMCM-41 [260], NaY + NbMCM-41[260], Ti$_x$Zr$_{1-x}$O$_4$ [261], MnO$_x$-CeO$_2$ [262], MnO$_2$/NaY composites [263], La$_{2-x}$Sr$_{1+x}$Cu$_2$O$_{6.5}$ (0 < x < 2) [173], MnO$_y$-ZrO$_2$ [264] and NaY [265] have all been investigated as NSR support materials and show some promise for future study.
1.3.3.4 Promoters

The most common promoters for NSR systems are Rh, Ce, Fe and Co. K, Ni, Cu, Mn, Nd, Si, Ca, Mg, Ti, La or La₂O₃, WO₃, MoO₃, V₂O₅, and Ga₂O₃ have also been investigated. Rabinowitz et al. [143] demonstrated that addition of ceria drastically improved NOₓ conversion on Pd/Rh TWCs, especially in combination with Rh, but could also increase the negative impact of sulfur due to its ability to store and release sulfur. Lin et al. [266] studied NOₓ storage and reduction on CeO₂ and La₂O promoted Pt/BaO/Al₂O₃ and Pt/SrO/Al₂O₃ catalysts. Pt₂.₅Ce₃₀.₅Ba₃₃.₄Al₁₀₀ and Pt₂.₅Ce₂₂.₅Ba₄₁.₇Al₁₀₀ offered the highest storage capacity (1020 and 911 µmol g⁻¹, respectively) and conversion. The Pt₂.₅Ce₃₀.₅Ba₃₃.₄Al₁₀₀ sample achieved 100% NOₓ conversion at 400 °C. The La₂O promoted Pt/BaO/Al₂O₃ and La₂O or CeO₂ promoted Pt/SrO/Al₂O₃ exhibited much lower storage capacity and conversion. Similarly, Ji et al. [267] found mixing Pt/BaO/Al₂O₃ with Pt/CeO₂ in a 76:26 ratio improved NOₓ storage capacity in the range of 200 – 400 °C. H₂-TPR and CO-TPR experiments suggested decreased stability of stored nitrite/nitrate species. Additionally, NOₓ conversion and N₂ selectivity were higher for the mixed catalysts. Schmeisser et al. [75] performed dynamic rich/lean reactor studies in the absence of sulfur on Pt, Rh, Ce, Ba and Al₂O₃ containing NOₓ storage and reduction materials and observed that ceria was a strong promoter for NO oxidation. Unfortunately, addition of Rh to a Pt/Ba/Ce/Al catalyst completely negated the beneficial role of ceria, which is counterintuitive since synergy of Rh/Ce systems has been demonstrated in TWCs [143]. However, the Pt-Rh/Ba/Ce/Al catalyst drastically outperformed Pt/Al, Pt/Ce/Al, Pt/Ba/Al, Pt/Ce/Ba/Al during steady-state reduction of NOₓ in rich environments. This could be explained by high reduction activity of Rh. Unfortunately the authors did not isolate the effect of Rh incorporation on reduction activity (e.g., through analysis of Rh/Al, Rh/Ce/Al and Rh/Ba/Ce/Al...
catalysts). Later, Ji et al. [151] studied the effect of adding physical mixtures of La$_2$O$_3$-stabilized ceria to Pt-Rh/BaO/Al$_2$O$_3$ NSR catalysts. The ceria mixtures exhibited increased storage efficiency, NO$_X$ conversion and decreased selectivity to NH$_3$ with increasing ceria content. Increased selectivity to N$_2$ was attributed to reaction of NH$_3$ with downstream oxygen stored by ceria. However, mixtures too high in ceria content caused decreased conversion of NO$_X$. Most likely because a significant portion of the reductant was consumed by oxygen stored in ceria, as evidenced by high reactor temperatures during reduction. Alternatively, the high catalyst temperature could increase the rate of NO$_X$ release that slips from the catalyst before reduction can occur. In later works, Ji et al. and Easterling et al. [139,267,268] studied the effects of sulfur and road aging on Pt/Ba/Al systems promoted by physical mixtures of Pt/CeO$_2$. In all cases, the addition of ceria or CeO$_2$-ZrO$_2$ positively influenced the NO$_X$ storage/reduction properties of the catalysts. Briefly, ceria or CeO$_2$-ZrO$_2$ addition can be summarized as follows: 1.) as a supplement to the main storage component – where deactivation of the Ba phase could be compensated by ceria, which could still participate in storage, 2.) ceria has shown to resist phase segregation – when Pt/BaO/Al$_2$O$_3$ samples were aged at high temperatures, sintering of Pt led to lower interfacial contact between Pt and BaO, which decreased spillover mechanisms and therefore lowered catalytic activity. Alternatively, sintering of Pt on CeO$_2$ is hindered due to a strong metal-support interaction, 3.) ceria containing samples exhibited superior sulfation/desulfation characteristics – The ability of ceria to trap and release sulfur could help protect Ba from high levels of sulfur accumulation. Similarly, Kaneeda et al. [174] found Mn and Ce played a beneficial role when incorporated into a RhPt–Na$_x$Al$_2$O$_3$ ($\alpha$= Ti, Si, Mg, Ca, Mn, Co, Ni, La, and Nd) NSR catalyst. The resulting RhPt–NaMn-Ce/Al$_2$O$_3$ sample was then tested in a lean-burn engine and achieved high NO$_X$ conversions even after being calcined at 700
°C, but higher calcination temperatures led to severe deactivation of the catalyst. Conversely, Zou et al. [216] observed a negative influence for both Ce and Co addition on a Pt/K/TiO$_2$-ZrO$_2$ catalyst. Initially, addition of Co or Ce (as a physical mixture or impregnated on the support) seemed positive because NSC increased from 194 µmol g$^{-1}$ to 280 and 380 µmol g$^{-1}$ for Co and Ce addition, respectively. However after sulfur exposure and subsequent regeneration, the promoted materials lost between 58% - 84% of the initial NSC; whereas the base Pt/K/TiO$_2$-ZrO$_2$ only lost 4% of the initial NSC.

Yamazaki et al. [269] studied transition metals as promoters for NSR catalysts. Pt/Ba/Fe/Al$_2$O$_3$, Pt/Ba/Co/Al$_2$O$_3$, Pt/Ba/Ni/Al$_2$O$_3$ and Pt/Ba/Cu/Al$_2$O$_3$ were compared with Pt/Ba/Al$_2$O$_3$, Pt/Fe/Al$_2$O$_3$, Pt/Co/Al$_2$O$_3$, Pt/Ni/Al$_2$O$_3$ and Pt/Cu/Al$_2$O$_3$. Prior to aging in 0.08% SO$_2$ for 5 hrs, addition of Fe, Co and Ni to Pt/Ba/Al$_2$O$_3$ or Pt/Al$_2$O$_3$ samples had no effect. After aging in SO$_2$, only addition of Fe had a positive effect on catalyst performance. Therefore, the authors concluded that addition of Fe could be beneficial, but addition of Ni and Co had no effect on NSR properties. Cu on the other hand, had a negative effect in all cases. However, Arena et al. [270] reported that Cu could be a promising promoter for addition to NSR catalysts because it was observed to increase NO$_X$ reduction. Hammache et al. [271] also reported that Cu addition increased sulfur tolerance, but diminished NSC in comparison to a reference Pt/Ba/Al$_2$O$_3$ sample. Formation of a Pt-Cu alloy was suggested to alter the SO$_2$ oxidation activity of the catalysts, which led to lower deactivation due to sulfur poising. However, SO$_2$ exposure during reducing environments led to stable sulfur species that were not oxidized in subsequent lean phases. Therefore, activity that was lost during rich sulfur exposures could not be recovered.

Generally, the addition of Co and Fe seem to be more promising than addition of Ni or Cu. However, promotion using Fe yielded contradictory results in the literature. Fanson et al.
[43] studied Fe promoted Pt/BaO/Al$_2$O$_3$ samples and suggested that formation of a stable bulk-like nitrate phase inhibited sulfur poisoning, where formation of a bulk-like nitrate phase was not observed in samples without Fe. In a later study, Hendershot et al. [129] determined using high-throughput experimentation, where Pt, Ba and Fe loading were all varied systematically, that the most important catalytic components were Pt and Ba and suggested an optimum wt. loading of 1.25-1.5% Pt and 15-25% Ba. However, earlier publications by Hendershot et al. indicated a positive influence when Fe was incorporated into Pt/Ba/Al$_2$O$_3$ NSR catalysts [128,272]. Similarly, Le et al. [273] observed modest promotion of NSC by Fe and increased sulfur tolerance, but a decrease in NO$_X$ conversion. Kayhan et al. [274] demonstrated that the morphology of the surface was dependent on the respective loading of Ba and Fe, which could help explain why contradictory results in the literature have been reported. Luo et al. [275] demonstrate that Fe encapsulates Pt, which decreases the Pt-Ba interaction and leads to decreased NO$_X$ storage capacity. Additionally, Fe selectively catalyzes the reduction of BaSO$_4$ to BaS, which makes sulfur removal more difficult. Therefore, the addition of Co as a promoter may be more promising Fe. For example, Vijay et al. [125] demonstrated that addition of Mn or Fe to a Pt/Ba/Al$_2$O$_3$ slightly improved NSC, but addition of Co nearly doubled the NSC. Additionally, a 5% Co/15% Ba/Al$_2$O$_3$ (w/w) sample stored equivalent amounts of NO$_X$ as the conventional 1% Pt/15% Ba/Al$_2$O$_3$ reference catalyst. While Co was capable of promoting high NSC, Vijay et al. [125] mentioned that incorporation of noble metals would still be necessary to catalyze reduction of stored NO$_X$ since Co exhibited poor reduction activity. Later, Vijay et al. [118] demonstrated that a 0.25% Pt/5% Co/15% Ba/Al$_2$O$_3$ catalyst showed superior performance over a 1% Pt/15% Ba/Al$_2$O$_3$ catalyst, with ¼ the Pt loading. More recently, Vijay et al. [126] studied the NO$_X$ storage and reduction mechanism for Co containing NSR catalysts. Co was
observed to exist in a highly oxidized state as Co$_3$O$_4$, but surface oxygen could be removed from the catalyst by 300 °C. In summary, the promotional role of Co was attributed to increased NO to NO$_2$ oxidation and increased interfacial contact between Co and Ba leading to increased NO$_2$ spillover onto Ba. Lastly, Kim et al. [153] examined the effect of Co and Rh promoters. Co was observed to catalyze NO oxidation; Rh catalyzed NO$_X$ reduction. Conversely, Co inhibited NO$_X$ reduction and Rh inhibited NO oxidation. Therefore, the loading of Co and Rh must be carefully balanced to negate the undesired properties of each promoter.

Dawody et al. [276] investigated WO$_3$, MoO$_3$, V$_2$O$_5$ and Ga$_2$O$_3$ as promoters in NSR catalysts for both NO oxidation and sulfur tolerance. In the absence of SO$_2$, WO$_3$ and MoO$_3$ exhibited the highest NO oxidation activity. NO oxidation on Pt/MoO$_3$/Al$_2$O$_3$ was least affected by SO$_2$. Therefore, the authors synthesized a Pt/MoO$_3$-BaO/Al$_2$O$_3$ sample to test for sulfur durability and found it deactivated more quickly than then reference Pt/Ba/Al$_2$O$_3$ sample. The deactivation method was not clear, but MoO$_3$ clearly did not increase sulfur tolerance. Lastly, physical mixtures of Mn/Ba/Al$_2$O$_3$ and Pt/Ba/Al$_2$O$_3$ have been reported to increase conversion of NO$_X$ and increase sulfur tolerance [277,278]. Ultimately, Ce, Co, Fe, Mn and Rh promoted systems, with particular emphasis on Mn, Ce, Co and Rh, may be interesting for further study because they could lower precious metal requirements and increase sulfur tolerance while maintaining the high activity of conventional Pt/Ba/Al$_2$O$_3$ systems.

1.3.4 Conclusions

Since their inception in the mid 1990s, many investigations have been performed and considerable progress has been made in understanding the NO$_X$ storage and reduction process. As evidence, the NO$_X$ storage mechanism has mostly been resolved. However, many aspects of this system remain unsolved and elucidation of results from existing literature is difficult because
very few investigations employ the same conditions. This is in part due to the large number of adjustable parameters including: choice of support, choice of the storage component, loading of the storage component, impregnation method of the storage component, choice of noble metal, loading of noble metal, impregnation method of the noble metal, impregnation order for the noble metal and storage component, precursors employed for impregnation, choice of promoters (Rh, CeO₂ etc.), loading of promoters, lean gas environment (NO, NO+O₂, NO₂), rich gas environment (H₂, CO, C₃H₆), inclusion of CO₂, H₂O or both, lean period duration, rich period duration, S.V. employed, pretreatment used, and lastly the inclusion of sulfur. All of these aspects were covered in this review and it emerges that a fundamental understanding of how each parameter affects the observed operation is still lacking. Furthermore, contradictory reports in the literature are really not too surprising given the large number of adjustable parameters, which ultimately leads to significantly different conditions and/or catalysts in many cases that are ultimately used during evaluation of NSR catalysts and comparison between one study to another can be difficult.

In closing, determination of the reduction mechanism will define target parameters for future development of novel NOₓ storage and reduction catalysts, where synergy between the support, storage component, precious metals and promoters in combination with high thermal and hydrothermal stability and increased sulfur tolerance are desirable attributes for the next generation of NOₓ storage and reduction catalysts.
1.4 **REAL SYSTEMS**

1.4.1 **EARLY CATALYTIC CONVERTER SYSTEMS**

Fig. 18 shows three different simplified schematics of early catalytic converter systems [14]. In this case, the mixture-formation system is a black box description of the fuel-injection system and the downstream reciprocating piston arrangement represents a simplified example of a single cylinder in an internal combustion engine, where additional details related to fuel-injection, mixing and combustion strategies is out of the scope of this work. Fig. 18A shows an engine exhaust system equipped with a two-way catalytic converter. The catalytic converter in this case is referred to as a two-way catalyst because it only oxidizes CO and HCs. The secondary oxygen added would result in a net lean environment, which favors oxidization of CO and HCs, but any NO\textsubscript{X} emitted from the engine would not be reduced under these conditions, as discussed at-length previously. The schematic shown in Fig. 18B, is a two-catalyst system, but would still not be considered a three-way catalyst since the upstream catalyst is only responsible for the reduction of NO\textsubscript{X} and the downstream catalyst is only responsible for the oxidation of CO and HCs. However, this system would be able to effectively remove all three pollutants simultaneously. In this case, the engine would likely be tuned slightly rich to effect NO\textsubscript{X} reduction over the upstream catalyst, which explains why it is necessary to introduce secondary air over the downstream catalyst to oxidize CO and HCs. The schematic shown in Fig. 18C represents a true three-way (TWC) system and has been the design of choice for automobiles from the late 70s to the present. Notice that a lambda/O\textsubscript{2} sensor has now been included and that it is connected to a feedback controller, which tunes the mixture-formation system to ensure that the exhaust gas is as close to the stoichiometric regime as possible. Kaspar et al. [279] and Shelef and McCabe [280] previously discussed the advantages of both on-board diagnostics
(OBD) and oxygen storage capacity (OSC) on TWC systems, as summarized in Fig. 19. Without OSC, the TWC spends a significant amount of time outside the optimum AFR, which results in lower conversion efficiencies for CO, HCs and NO$_x$. With OBD and OSC, the TWC spends the majority of the time very near the optimum AFR; as a result, conversion efficiencies higher than 95% are achieved [279].
Figure 18. Schematics showing early catalytic converter systems, Faiz et al. [14].
1.4.2 MODERN CATALYTIC CONVERTER SYSTEMS

In the 1990s, in California especially, a series of low-emission standards were implemented that started the progression towards a 10-fold reduction in HC emission and a 20-fold reduction in NO\textsubscript{X} emissions [281]. In the case of HCs, 50-80\% of the total HCs emissions are emitted during the cold-start period during FTP testing (i.e., the first 90-180 s of operation) before the TWC reaches the HC-light off temperature (≈300 °C) [15]. Practically, this means that a vehicle could fail an emissions test based on cold-start HCs alone after only 2 min. into a
23 min. test. As a result, close-coupled TWCs were implemented. These catalysts could achieve light-off within 10 s of operation and are composed of proprietary blends of metal oxides used to stabilize the Al$_2$O$_3$ and prevent Pd sintering [15]. Fig. 20 shows two possible examples of close-coupled catalysts. In one case, a small, close-coupled catalyst is used primarily to convert HCs, while the larger downstream, under-floor TWC is responsible for the majority of the CO oxidation and NO$_X$ reduction that takes place. The latter example shows a much larger close-coupled TWC that simultaneously converts all three pollutants, but at higher temperatures in comparison to the under-floor catalyst shown in the first example.

![Diagram](image)

**Figure 20.** Two examples comparing the location and size of close-coupled TWCs [15].

The combination of TWCs and close-coupled TWCs has allowed auto manufacturers to effectively meet emissions standards, but only for gasoline engines operating in the stoichiometric regime. Table 4 shows typical exhaust compositions for a diesel engine, four-stroke spark-ignited gasoline engine and a four-stroke spark-ignited lean burn gasoline engine.
The conditions were included for the two-stroke engine for comparison, but will not be discussed. Notice that in the case of diesel engines and lean-burn gasoline engines, the O\textsubscript{2} concentration is very high (e.g., 4-15\%). Comparison of these AFRs (26 and 17, respectively) with the results shown in Fig. 19 clearly demonstrates that poor performance in terms of NO\textsubscript{X} conversion is expected if a TWC-only system was used. So for diesel engines or lean-burn gasoline engines, different/new catalytic technologies are required. Figs. 21 - 25 summarize the most recent architectures suggested that are capable of removing lean-NO\textsubscript{X}, but still meeting the CO, HC and PM regulations.

The following chapters focus on the systems shown in Figs. 21 and 22 (Chapters 2 and 3) and in Fig. 23 (Chapter 4). Additional information regarding those systems is presented in the introductions of each corresponding chapter. The systems shown in Figs. 24 and 25 were included for comparison, since they provide corollary examples, but are not the specific focus of this dissertation since they were designed for diesel engines.
Table 4. Typical Exhaust composition for several common commuter vehicles, Kaspar et al. [279].

<table>
<thead>
<tr>
<th>Exhaust Components and conditions&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Diesel Engine</th>
<th>Four-stroke spark-ignited engine</th>
<th>Four-stroke lean-burn spark-ignited engine</th>
<th>Two-stroke spark-ignited engine</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO&lt;sub&gt;x&lt;/sub&gt;</td>
<td>350–1000 ppm</td>
<td>100–4000 ppm</td>
<td>≈1200 ppm</td>
<td>100–200 ppm</td>
</tr>
<tr>
<td>HC</td>
<td>50–330 ppm C</td>
<td>500–5000 ppm C</td>
<td>≈1300 ppm C</td>
<td>20,000–30,000 ppm C</td>
</tr>
<tr>
<td>CO</td>
<td>300–1200 ppm</td>
<td>0.1–6 %</td>
<td>≈1300 ppm</td>
<td>1-3 %</td>
</tr>
<tr>
<td>O&lt;sub&gt;2&lt;/sub&gt;</td>
<td>10–15 %</td>
<td>0.2–2 %</td>
<td>4–12 %</td>
<td>0.2–2 %</td>
</tr>
<tr>
<td>H&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>1.4–7 %</td>
<td>10–12 %</td>
<td>12 %</td>
<td>10–12 %</td>
</tr>
<tr>
<td>CO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>7 %</td>
<td>10–13.5 %</td>
<td>11 %</td>
<td>10–13 %</td>
</tr>
<tr>
<td>SO&lt;sub&gt;x&lt;/sub&gt;</td>
<td>10–100&lt;sup&gt;b&lt;/sup&gt; ppm</td>
<td>15–60 ppm</td>
<td>20 ppm</td>
<td>≈20 ppm</td>
</tr>
<tr>
<td>PM</td>
<td>65 mg/m&lt;sup&gt;3&lt;/sup&gt;</td>
<td>r.t. - 650 °C</td>
<td>r.t. – 1100&lt;sup&gt;c&lt;/sup&gt; °C</td>
<td>r.t. - 850 °C</td>
</tr>
<tr>
<td>Temperatures (test cycle)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>GHSV (hr&lt;sup&gt;-1&lt;/sup&gt;)</td>
<td>30,000-100,000</td>
<td>30,000-100,000</td>
<td>30,000-100,000</td>
<td>30,000-100,000</td>
</tr>
<tr>
<td>λ (A/F)&lt;sup&gt;d&lt;/sup&gt;</td>
<td>≈1.8 (26)</td>
<td>≈1 (14.7)</td>
<td>≈1.16 (17)</td>
<td>≈1 (14.7)&lt;sup&gt;e&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

<sup>a</sup>N<sub>2</sub> is remainder
<sup>b</sup>For comparison: diesel fuels with 500 ppm of sulfur produce of about 20 ppm of SO<sub>2</sub>
<sup>c</sup>Close-coupled TWC
<sup>d</sup>λ defined as ratio of actual A/F to stoichiometric A/F, λ=1 at stoichiometry (AFR<sub>STOICH</sub> = 14.7)
<sup>e</sup>Part of the fuel is employed for scavenging of the exhaust, which does not allow for a precise definition of the A/F ratio.
**Figure 21.** Close-coupled TWC, under-floor LNT configuration, as present on the BMW 120i (Model Year, 2009).

**Figure 22.** Close-coupled TWC, under-floor LNT + SCR configuration. *(Further discussed in Chapter 3.)*
Figure 23. Layout of the passive-NH$_3$, urea-less TWC + SCR approach, Li et al [282]. *(Further discussed in Chapter 4.)*

Figure 24. Layout of the emissions system for a light-duty diesel vehicle containing a diesel oxidation catalyst (DOC) and LNT + SCR configuration and a diesel particulate filter (DPF), McCabe et al. [283].
Figure 25. Layout of the modern medium- or heavy-duty DPF-SCR system (based on urea), Johnson et al. [284].
CHAPTER 2. *In situ* FTIR Investigation of the Role of Surface Isocyanates in the Reduction of NO\textsubscript{X} by CO and C\textsubscript{3}H\textsubscript{6} over Model Pt/Ba/Al\textsubscript{2}O\textsubscript{3} and Rh/Ba/Al\textsubscript{2}O\textsubscript{3} NO\textsubscript{X} Storage and Reduction (NSR) Catalysts

2.1 Preface

Monometallic Pt- and Rh-containing model NO\textsubscript{X} storage and reduction (NSR) catalysts were investigated by *in situ* FTIR spectroscopy in order to determine the type of species present on the surface under simulated lean exhaust conditions and to identify potential reaction intermediates during reduction by CO and propylene. The effect of precious metal selection, temperature, and water presence on NO\textsubscript{X} storage and reduction chemistry was considered. The formation of surface isocyanate (NCO) species was observed during all cycling experiments, even in the presence of H\textsubscript{2}O, which prompted additional investigation on the role of these species in the NO\textsubscript{X} reduction mechanism. Stability and reactivity experiments with Ba/Al\textsubscript{2}O\textsubscript{3}, Pt/Ba/Al\textsubscript{2}O\textsubscript{3} and Rh/Ba/Al\textsubscript{2}O\textsubscript{3} confirmed that the reactions of NCO with NO and O\textsubscript{2} - producing N\textsubscript{2} - are metal catalyzed pathways, while reaction of NCO with H\textsubscript{2}O - producing NH\textsubscript{3} - is not. The contribution of NCO-related pathways to the overall N\textsubscript{2} production mechanism could be significant, since quantification of the FTIR results suggests that up 30% of the total N\textsubscript{2} produced could be directly related to the reaction of NCO with O\textsubscript{2}. 

71
2.2 INTRODUCTION

Lean-burn engines have attracted the attention of automobile manufactures due to the higher engine efficiencies achieved under these conditions, translating into better fuel economy and lower CO$_2$ emissions. For example, Heck and Farrauto [1] reported that lean-burn engines can achieve efficiencies 20 - 30% higher than conventional engines. However, three-way catalysts (TWCs) employed for the oxidation of carbon monoxide (CO) and hydrocarbons (HCs) and the reduction of nitrogen oxides (NO$_X$) in conventional engine exhausts are not effective in reducing NO$_X$ in the presence of excess O$_2$. Since their introduction in the mid 1990s [8,285], NO$_X$ storage and reduction (NSR) catalysts have been shown to represent a viable solution for the removal of NO$_X$ from lean exhausts. To date, numerous investigations have been performed on NSR catalysts and the results are summarized in several recent reviews [3,4,6]. Briefly, common NSR formulations consist of noble metals (mainly Pt, Pd or Rh) and an alkaline/alkaline earth component (mainly Ba or K) supported on $\gamma$-Al$_2$O$_3$. During the lean phase (60 - 120 s in length), NO is oxidized to NO$_2$ on the precious metal, with the NO$_2$ spilling over onto the storage component where it is initially stored in the form of a nitrite and can be further oxidized to a nitrate with increasing time [22,34,40,74,86,117]. During the rich phase (1 - 2 s in length), the storage component is regenerated and the accumulated nitrites and/or nitrates are reduced to N$_2$, NH$_3$ or N$_2$O, with N$_2$ being the desirable product [16,62].

While the NO$_X$ storage mechanism is fairly well understood by now and widely accepted, the NO$_X$ reduction mechanism strongly depends on the reductant used with many critical details still to be resolved [42]. For example, Nova et al. [23,60,63,64] have proposed that the reduction of stored NO$_X$ by H$_2$ is a Pt-catalyzed pathway that proceeds through an NH$_3$ intermediate, where subsequent reaction of NH$_3$ with adsorbed nitrates is responsible for the production of N$_2$. In fact
several groups agree that NH$_3$ is a critical reaction intermediate when H$_2$ is used as the reducing agent [66,67,286].

Similar agreement regarding the nature of the reaction intermediates has not been reached for the cases when CO and hydrocarbons (HC) are used as reductants, in part because significantly fewer investigations have been performed using such reductants [24–28,43,59,107,287–290]. The mechanism of the reduction of NO$_X$ by CO is currently thought to proceed through an isocyanate (NCO) intermediate, which can react with NO, O$_2$, stored nitrites/nitrates and H$_2$O to form N$_2$ or NH$_3$ [24,27,43,287–290]. The NH$_3$ formed by the hydrolysis of NCO can further react with stored NO$_X$, thus contributing to overall N$_2$ formation [64]. However, Lesage et al. suggested that formation of NCO species was undesirable and attempted to avoid it through rational catalyst design [145,146]. The presence of high concentrations of CO$_2$ and H$_2$O vapor in automotive exhausts, further affects the formation and reaction of surface NCO indirectly through the water gas shift (WGS) and steam reforming reactions. These reactions competitively consume the CO and HCs needed for the formation of NCO species, while at the same time they generate H$_2$ that can readily react with such species [20,64].

Historically, the role of NCO species in other types of NO$_X$ reduction schemes has been examined and debated at length. Lorimer and Bell [291] for example, reported that an NCO related NO reduction pathway on three way catalysts (TWCs) accounts for less than 5% of the total NO reduction and is therefore of limited significance. Others also observed NCO formation under the stoichiometric TWC conditions, but similarly concluded that the NCO species were spectators in this environment [292–295]. Under lean exhaust conditions however, and over hydrocarbon-SCR type of catalysts many groups have postulated that NCO species contribute
significantly as intermediates to the overall reduction of NO [5,296–305]. However, as Burch et al. [5] have pointed out, the lack of kinetic data comparing the rate of removal of surface NCO species to the rate of formation of N\textsubscript{2} still represents a major problem in validation of NCO-related mechanisms.

The goal of this work is to investigate the formation and reaction of surface NCO on model NSR catalysts under conditions approaching those of realistic exhausts. In situ Fourier transform infrared (FTIR) spectroscopy was used in these efforts. The effects of the type of precious metal used (i.e., Pt vs. Rh), the presence of water, the reductant selection (i.e., CO vs. C\textsubscript{3}H\textsubscript{6}) and the temperature (250 and 350 °C) were considered. Since NCO formation was observed under all conditions studied, the stability and reactivity of these species in different gas environments was investigated in detail in an effort to determine the extent to which an NCO related reaction pathway contributes to the overall NO\textsubscript{X} reduction mechanism.

2.3 EXPERIMENTAL

2.3.1 CATALYST PREPARATION

A set of 17 wt % Ba/Al\textsubscript{2}O\textsubscript{3}, 1 wt % Pt/17 wt % Ba/Al\textsubscript{2}O\textsubscript{3} and 0.5 wt % Rh/17 wt % Ba/Al\textsubscript{2}O\textsubscript{3} catalysts were prepared by a step-wise incipient wetness impregnation process. For simplicity, the catalyst samples will subsequently be referred to as Ba/Al\textsubscript{2}O\textsubscript{3}, Pt/Ba/Al\textsubscript{2}O\textsubscript{3} and Rh/Ba/Al\textsubscript{2}O\textsubscript{3}, respectively. Prior to impregnation, the Catalox SBa-200 γ-Al\textsubscript{2}O\textsubscript{3} (Sasol; 192 m\textsuperscript{2}/g) support was calcined in air for 24 h at 600 °C. Ba was deposited first on the support by adding an aqueous solution of barium acetate (Alfa Aesar) to the calcined Al\textsubscript{2}O\textsubscript{3}. Samples thus prepared were first dried, and then calcined in air for 12 h at 600 °C. Aqueous solutions of rhodium (III) nitrate hydrate (Sigma-Aldrich) or tetraammineplatinum (II) nitrate (Sigma-
Aldrich) were then impregnated onto the Ba/Al₂O₃ material to prepare the Pt/Ba/Al₂O₃ and Rh/Ba/Al₂O₃ catalysts, where the nominal weight loadings of the noble metals were chosen to yield equal molar loadings. The catalysts were then dried and subsequently calcined in air for 5 h at 500 °C. The loadings of Pt and Rh were then verified by Atomic Absorption Spectroscopy (AAS) measurements performed using a Perkin Elmer AAnalyst 400 spectrometer. The Ba loading was verified by further elemental analysis (Galbraith Laboratories). Table 5 provides a list of the catalysts used in this investigation and includes some of basic characterization results for these materials.

Table 5. Characterization of the catalysts used in this investigation.

<table>
<thead>
<tr>
<th>Catalyst Name</th>
<th>Pt Loading (wt %)</th>
<th>Pt Loading (µmol g⁻¹)</th>
<th>Rh Loading (wt %)</th>
<th>Rh Loading (µmol g⁻¹)</th>
<th>Ba Loading (wt %)</th>
<th>Metal Dispersion (%)</th>
<th>SSA (m² g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ba/Al₂O₃</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>13.4</td>
<td>-</td>
<td>153</td>
</tr>
<tr>
<td>Pt/Ba/Al₂O₃</td>
<td>1.01</td>
<td>52</td>
<td>-</td>
<td>-</td>
<td>13.4</td>
<td>25</td>
<td>178</td>
</tr>
<tr>
<td>Rh/Ba/Al₂O₃</td>
<td>-</td>
<td>-</td>
<td>0.49</td>
<td>48</td>
<td>13.4</td>
<td>30</td>
<td>169</td>
</tr>
</tbody>
</table>

2.3.2 BET Surface Area and H₂-Chemisorption

BET surface area measurements and H₂-chemisorption of O₂-precovered metals was performed using a ChemBET-3000 analyzer (Quantachrome Instruments). Prior to the BET measurements, the catalysts were outgassed in He for 12 h at 200 °C. The surface area was then
determined using the multipoint BET method for adsorption of N\textsubscript{2} at -196 °C. The SSA values determined for the catalysts used in this investigation are shown in Table 5.

Prior to chemisorption measurements, the catalysts were outgassed in He for 12 h at 200 °C, heated in He to 300 °C, reduced in H\textsubscript{2} for 2 h at 300 °C, flushed with He for 2 h at 300 °C to remove all H\textsubscript{2} and finally, cooled back to room temperature in He. Following this pretreatment, O\textsubscript{2} titration of the exposed metal atoms was performed using 100 µL pulses of pure O\textsubscript{2}. Consecutive O\textsubscript{2} pulses were introduced until no further uptake of O\textsubscript{2} was observed. Subsequent flushing with He for 15 min ensured removal of any excess oxygen before 100 µL pulses of pure H\textsubscript{2} were introduced over the O\textsubscript{2}-precovered metals. Similarly, H\textsubscript{2} was pulsed until no further uptake of H\textsubscript{2} was observed. The stoichiometry for the adsorption of H\textsubscript{2} on an O\textsubscript{2}-precovered metal was assumed to be 3:1 (i.e. 3[H] + O-M → H-M + H\textsubscript{2}O) [306,307]. Both O\textsubscript{2}- and H\textsubscript{2}-chemisorption measurements with the O\textsubscript{2}-pretreated Ba/Al\textsubscript{2}O\textsubscript{3} catalyst indicated negligible uptake of O\textsubscript{2} and H\textsubscript{2}, respectively, suggesting that the Ba phase is inert under these conditions. The % dispersions of the precious metals calculated from the chemisorption measurements are shown in Table 5.

2.3.3 Scanning Transmission Electron Microscopy

Scanning transmission electron microscopy (STEM) images were collected using a JEOL 2100F 200 kV FEG-STEM/TEM microscope equipped with a CEOS Cs corrector on the illumination system. The geometrical aberrations were measured and controlled to provide less than a \(\pi/4\) phase shift of the incoming electron wave over the probe-defining aperture of 15.5 mrad. High-angle annular darkfield (HAADF) STEM images were obtained with a Fischione Model 3000 HAADF detector with a camera length such that the inner cut-off angle of the
detector was 50 mrad. The scanning acquisition was synchronized to the 60 Hz AC electrical power to minimize 60 Hz noise in the images and a pixel dwell time of 16µs was chosen.

2.3.4 FOURIER TRANSFORM INFRARED SPECTROSCOPY (FTIR)

FTIR spectra were collected with a Nexus 470 FTIR spectrometer (Thermo-Fischer Scientific) operated in transmission mode with a resolution of 2 cm\(^{-1}\). Catalyst samples were used as self supported wafers (≈ 15-22 mg cm\(^{-2}\)). Immediately following analysis, the wafers were weighed and all spectral intensities were adjusted to an average sample size of 18.8 mg cm\(^{-2}\). A homemade cell was used for the in situ collection of spectra, consisting of a stainless steel tube (≈35mm x 12 cm) with cooling water flanges welded to each end. The flanges were machined to accommodate polished NaCl windows (32mm x 3mm – Alfa Aesar) held in place by Viton O-rings. Cooling water was passed through the flanges to keep the O-ring temperature below 100 °C. The cell was wrapped in a 400 W, 4 ft heating cord (Glas-Col), which allowed heating up to 400 °C. A thermocouple was placed in close proximity to the sample for temperature measurement. A gas manifold with five mass flow controllers and two needle valves was used to prepare and deliver gas mixtures to the cell. Certified gas mixtures (National Welders) of 1.00% NO/He, 1.00% H\(_2\)/He, 0.965% NO\(_2\)/He, 0.975% C\(_3\)H\(_6\)/He, 2.985% CO/He, 9.990% O\(_2\)/He, and UHP He were used as sources for the different gas components. The total gas flow through the cell was maintained at 100 cm\(^3\) min\(^{-1}\) throughout all experiments.

Background spectra were collected following treatment of the samples in a NO/O\(_2\) environment for 10 h at 400 °C in order to exchange residual carbonates with nitrites/nitrates, followed by reduction in H\(_2\) for 1 h at 400 °C in order to completely remove any stored nitrites/nitrates. The background spectra collected after such pretreatment did not exhibit any significant bands in the 1000 - 1650 cm\(^{-1}\) region, confirming the complete removal of any
residual carbonate and nitrate components on the surface. Similar behavior has also been observed and reported in the literature by other groups [34,290]. Samples were then oxidized in 10% O₂/He for 5 h at 400 °C, flushed with He for 1 h at 400 °C and then cooled in He to either 250 °C or 350 °C to initiate *in situ* spectra collection.

Storage experiments were conducted at 350 °C in either 1000 ppm NO/He, 1000 ppm NO/5% O₂/He, 1000 ppm NO₂/He or 1000 ppm CO/He. Cycling experiments employed three discrete phases each lasting 2 min: a lean phase during which samples were exposed to a 1000 ppm NO/5% O₂/He mixture; a He flushing phase used to remove any residual NO and O₂ and to minimize thermal effects due to the introduction of the reductant into an O₂ rich environment [61]; and a rich phase during which samples were exposed to either 9000 ppm CO/He or 1000 ppm C₃H₆/He mixture. The effect of H₂O during cycling was also investigated. During these experiments water was introduced by bubbling an additional He stream through a VLE saturator held at 20.9 °C in order to achieve a 1% (mol.) H₂O concentration in the final gas flow.

In a separate set of experiments, NCO species were formed on the catalyst surface at 350 °C by first a 1000 ppm NO/5% O₂/He mixture to the samples for 2 min in order to increase the concentration of nitrite and nitrate species on the surface. Next, He was flowed over the samples for 2 min to flush all O₂ from the cell, followed by 9000 ppm CO/He for 2 min to reduce the stored NOₓ species and generate surface NCO species. Finally, He, 9000 ppm CO/He, 1000 ppm NO/He, 1000 ppm O₂/He or 1000 ppm H₂O/He were used to investigate the stability and reactivity of the surface NCO species in these gas mixtures.

### 2.3.5 Product Analysis

A flow reactor system equipped with a quadruple mass spectrometer (Leybold Inficon, Model type – TSPTT300) was employed for the analysis of the gaseous products formed during
the reaction of NCO and other surface species with He, 1000 ppm NO/He or 1000 ppm O₂/He at the end of the rich phase. These measurements were conducted in parallel and under the same conditions with the stability and reactivity measurements performed and monitored by \textit{in situ} FTIR, as described in the previous section. In order to differentiate between CO and N₂ formed, isotopically labeled $^{13}$CO (Sigma Aldrich – 99 atom % $^{13}$C, <5 atom % $^{18}$O) was used as the reductant and the following m/z signals were followed for identification of the products: N₂ (28), $^{13}$CO (29), NO (30), N₂O (44), $^{13}$CO₂ (45) and NO₂ (46). Prior to catalyst evaluation, cycling was performed in an empty quartz reactor and the resulting m/z signals were used as a baseline. Additionally, the m/z signals were normalized to a constant leak rate, which was necessary in order to correct for changes in the baseline caused by large differences in the average molecular weight of the gas mixtures (lean vs. rich) entering the mass spectrometer.

2.4 RESULTS AND DISCUSSION

2.4.1 CATALYST CHARACTERIZATION

The results of Table 5 indicate that the Pt and Rh catalysts compared in this study are very similar in terms of their compositions and structural characteristics (i.e. molar metal loading, metal dispersion and surface area). As a result, a direct comparison of the concentration of surface species formed – including NCO – and rates of consumption can directly demonstrate differences in the behavior of the two metals as compared to differences in surface area and/or particle size and dispersion.

STEM images collected from different regions of the Pt/Ba/Al₂O₃ catalyst indicates that Ba was present both as an amorphously distributed phase and in large crystalline regions on the Al₂O₃ support. Fig. 26A depicts one such Ba crystallite region, where corollary elemental
analysis (Fig. 26C) confirmed only the presence of Ba. Additional bright regions in Fig 26A lacking crystalline structure were assigned to amorphously distributed BaO and/or BaCO$_3$. The significant difference in the morphology of the two regions of the same material shown in Figs. 26A and 26B demonstrates the heterogeneous nature of the Pt/Ba/Al$_2$O$_3$ material. Interestingly, the formation of large, crystalline Ba regions was suppressed for the Ba/Al$_2$O$_3$ catalyst. While crystalline regions were also observed, in that case, they were generally much smaller, less frequent and exhibited duller edges than those observed for the noble metal containing catalysts, where Pt and Rh may be assisting in the formation of these large, crystalline Ba phases during calcination. Similar SEM results for a Pt/Ba/Al$_2$O$_3$ sample were previously reported by Vijay et al. [126].

The small (≈2-3 nm) bright spots observed in Fig. 26B most likely represent Pt particles. EDX measurements (Fig. 26D) confirmed the presence of both Pt and Ba in the region of Fig. 26B, although definitive assignment of individual particles is difficult because the molecular weights of Pt and Ba are similar and the loading of Ba is high. It should be pointed out that no 2-3 nm particles were observed in the STEM images of the non-metal containing Ba/Al$_2$O$_3$ sample, further supporting assignment of such particles to the noble metal component. Confirmation of the Pt particles located on top or immediately next to a Ba phase, as commonly portrayed in the literature [3,6,66,308] is exceedingly difficult. However, our STEM images suggest that Pt and Ba appear to be in close contact. HRTEM micrographs collected by Frola et al. [179] exhibited similar findings, where crystalline BaCO$_3$ regions observed on “as prepared” catalysts partially masked the presence of Pt. Subsequent conditioning resulted in clear identification of Pt particles on the support, but the location of the Ba containing phase became less clear.
Interestingly, Ji et al. [139] did not observe any large, BaCO$_3$ crystallite regions and Pt was clearly visible in their STEM images of an “as prepared” Pt-Rh/Ba/La-Al$_2$O$_3$ washcoat catalyst.

**Figure 26.** STEM images and corresponding EDX analyses of two different regions of the Pt/Ba/Al$_2$O$_3$ catalyst used in this investigation.

### 2.4.2 Storage of NO$_x$ and CO at 350 °C

In order to identify and assign the different FTIR bands observed during cycling, separate nitrate and carbonate storage experiments were performed with the Pt- and Rh-containing
samples. Band assignments were made according to previously published results, as summarized in Table 6.

### Table 6. FTIR band assignments.

<table>
<thead>
<tr>
<th>Species</th>
<th>Wavenumbers (cm(^{-1}))</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>NO(_x) Species on Ba</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bidentate nitrate</td>
<td>970-1050, 1200-1320, 1540-1650</td>
<td>[34,40]</td>
</tr>
<tr>
<td>Monodentate nitrate</td>
<td>1290-1330, 1425-1540</td>
<td>[31,33]</td>
</tr>
<tr>
<td>Ionic nitrate</td>
<td>1038, 1300-1360, 1400-1460</td>
<td>[34,37,40,188]</td>
</tr>
<tr>
<td>Monodentate nitrite</td>
<td>970-1340, 1410-1500</td>
<td>[31,33,34]</td>
</tr>
<tr>
<td>Bidentate nitrite</td>
<td>1230, 1300</td>
<td>[31,34]</td>
</tr>
<tr>
<td><strong>CO(_x) Species on Ba</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bridged bidentate carbonate</td>
<td>1020-1060, 1320-1340, 1610-1650</td>
<td>[37,179]</td>
</tr>
<tr>
<td>Chelating bidentate carbonate</td>
<td>1060, 1350-1380, 1550-1600</td>
<td>[37,179]</td>
</tr>
<tr>
<td>Monodentate carbonate</td>
<td>1440, 1740</td>
<td>[37,179]</td>
</tr>
<tr>
<td>Ionic carbonate</td>
<td>1430-1450</td>
<td>[37,179]</td>
</tr>
<tr>
<td><strong>NCO Species on Al(_2)O(_3) and Ba</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Octahedral Al(^{3+}) isocyanate</td>
<td>2260</td>
<td>[24,27,145]</td>
</tr>
<tr>
<td>Tetrahedral Al(^{3+}) isocyanate</td>
<td>2222</td>
<td>[24,27,145]</td>
</tr>
<tr>
<td>Ba(^{2+}) isocyanate</td>
<td>2162</td>
<td>[24,27,145]</td>
</tr>
</tbody>
</table>

Introduction of a NO/O\(_2\) mixture to Pt/Ba/Al\(_2\)O\(_3\) at 350 °C initially resulted in the appearance of three bands centered at 1467, 1300 and 1210 cm\(^{-1}\) in the corresponding spectrum (Fig. 27A). These bands were rapidly converted (<1 min) to bands centered at 1547, 1465, 1418, 1306 and 1024 cm\(^{-1}\). Since many of the vibrations of nitrate species overlap (see Table 6), it is difficult, if not impossible, to definitively differentiate between these species on the surface [287]. However, nitrites can be distinguished from nitrates and the bands at 1300 and 1210 cm\(^{-1}\) have been previously assigned to bidentate nitrite species on Ba [40]. Bands at 1547, 1465, 1418, 1306 and 1024 cm\(^{-1}\) are most likely associated with monodentate, bidentate or ionic nitrates on
Ba, where the bands at 1418, 1306 and 1024 cm\(^{-1}\) have been widely assigned in the literature to ionic (“bulk-like”) nitrates [74,179,188]. The results shown in Fig. 27A indicate that the storage of NO\(_X\) in the presence of O\(_2\) on Pt/Ba/Al\(_2\)O\(_3\) proceeds via a nitrite to nitrate route, where this mechanistic pathway has already been established by our group and others in the literature [22,34,40,117]. Finally, in agreement with previous literature reports, our results show that at 350 °C surface nitrates are the dominant storage species at times relevant to NO\(_X\) storage (60 - 120 s). Identical results were also obtained with the Rh/Ba/Al\(_2\)O\(_3\) sample (not shown for brevity).

The NO\(_X\) storage capacity of the Pt/Ba/Al\(_2\)O\(_3\) and Rh/Ba/Al\(_2\)O\(_3\) samples was estimated by integration of the bands in the 1050 -1650 cm\(^{-1}\) region. A similar approach has been also followed by Saito et al. [309]. The resulting area can then be plotted as a function of storage time. The Pt/Ba/Al\(_2\)O\(_3\) and Rh/Ba/Al\(_2\)O\(_3\) samples exhibited similar storage capacity, as shown in Fig. 28. Corollary experiments performed in a fixed bed reactor yielded similar results. These results may at first appear surprising since Rh is, in general, assumed to be less active than Pt in NO oxidation [16] and Abdulhamid et al. [25] previously reported a lower NO\(_X\) storage capacity for Rh/Ba/Al\(_2\)O\(_3\) than Pt/Ba/Al\(_2\)O\(_3\). In another publication however, Abdulhamid et al. [27] reported that Rh/Ba/Al\(_2\)O\(_3\) outperformed Pt/Ba/Al\(_2\)O\(_3\) in NO\(_X\) storage. Large differences in precious metal dispersion were listed as the most likely reason for this behavior, since Pt and Rh dispersions were 5% and 31%, respectively. In contrast, Vijay et al. [118] observed similar storage capacities for Pt/Ba/Al\(_2\)O\(_3\) and Rh/Ba/Al\(_2\)O\(_3\) if long cycle times were used, which is similar to our experimental protocol. Overall it appears in our case that with the same metal loading and particle size (i.e., dispersion) both metals exhibit similar behavior.
Introduction of CO to Pt/Ba/Al₂O₃ at 350 °C resulted in the appearance and subsequent growth of bands centered at 1569, 1336 and 1057 cm⁻¹ in the spectrum of this material (Fig. 27B). These bands can be assigned to carbonate species on Ba [37, 179]. An additional weak band was observed at 2020 cm⁻¹ and can be assigned to a Pt carbonyl species [24]. Identical results were also obtained with the Rh/Ba/Al₂O₃ sample with the carbonyl band in this case appearing at 2006 cm⁻¹.

![Figure 27](image)

**Figure 27.** *In situ* FTIR spectra of a Pt/Ba/Al₂O₃ catalyst during exposure to (A) 1000 ppm NO/5% O₂ in He and (B) 1000 ppm CO in He mixtures at 350 °C (Spectra shown at 0, 0.5, 1, 2, 3, 5, 10 and 20 min of exposure).
Figure 28. NO\textsubscript{X} storage capacity of (▲) Pt/Ba/Al\textsubscript{2}O\textsubscript{3} and (■) Rh/Ba/Al\textsubscript{2}O\textsubscript{3} in a 1000 ppm NO/5\% O\textsubscript{2} in He mixture at 350 °C (obtained by integration of FTIR bands in the 1050 - 1650 cm\textsuperscript{-1} region).

2.4.3 NO\textsubscript{X} Storage-Reduction Cycling Studies

\textit{In situ} cycling studies between NO\textsubscript{X} storage and reduction conditions were conducted at two different temperatures in order to investigate potential differences in the NO\textsubscript{X} storage and reduction mechanisms. Fig. 29 shows one such example of NSR cycling monitored with FTIR spectroscopy using CO as the reducing agent at 350 °C over Pt/Ba/Al\textsubscript{2}O\textsubscript{3}. In this case, the spectra collected were plotted in a 3D representation in order to more clearly show the NSR cycling behavior. The bands in the 1200 - 1650 cm\textsuperscript{-1} region of the spectrum are characteristic of nitrite/nitrate and carbonate species adsorbed on the surface and the bands at 2030, 2162 and 2221 cm\textsuperscript{-1} appear when CO is introduced as the reductant molecule. The first several lean and rich phases are denoted in Fig. 29 and help show the distinct changes observed in the spectra.
under different NSR cycling conditions. Fig. 29 also clearly shows the reproducibility of both the cycling protocol used in our experiments and the behavior observed on the surface from cycle to cycle. In the following sections, closer examination of the lean and rich phases will be conducted using 2D figures because the band assignments are more clearly resolved in this representation of the data.

![Figure 29](image)

**Figure 29.** A 3D plot showing the *in situ* spectra collected during three lean-rich phases of NO\textsubscript{X} storage-reduction cycling on Pt/Ba/Al\textsubscript{2}O\textsubscript{3} using CO as the reducing agent at 350 °C.
**CO CYCLING AT 250 °C**

*In situ* FTIR spectra collected during such cycling over Pt/Ba/Al\(_2\)O\(_3\) at 250 °C are shown in Fig. 30. CO was used as the reducing agent in this case. For clarity, the first lean cycle is shown in this figure because spectra collected during subsequent lean cycles contain both carbonate and nitrite/nitrate features, which makes elucidation of the different bands more complex. The spectra of Fig. 30 indicate that during NO\(_X\) storage at 250 °C, both in the absence (Fig. 30A) and presence (Fig. 30C) of 1% H\(_2\)O, bands centered at approximately 1360 and 1200 cm\(^{-1}\) are formed in the corresponding spectra. The band at 1200 cm\(^{-1}\) was previously assigned to bidentate nitrite species on Ba [40]. Assignment of the band at 1360 cm\(^{-1}\) is more ambiguous since monodentate nitrite, monodentate nitrate and ionic nitrate species on Ba have features in this area [31,33,34,40,179,188]. It has been reported that Al\(_2\)O\(_3\) could also contribute to NO\(_X\) storage at this temperature [33], although in our case such a contribution is unlikely because no bands attributed to nitrates on Al\(_2\)O\(_3\) were observed in the vicinity of 1600 cm\(^{-1}\). Overall, it is apparent from Figs. 30A and 30C that the Ba nitrite species represents the dominant NO\(_X\) storage form at 250 °C, for storage times corresponding to realistic NSR operations (i.e., 60-120 s). The presence of water does not have a significant effect during storage, since Figs. 30A and 30C are qualitatively very similar. Epling et al. [29] previously reported that the presence of water was detrimental to NO\(_X\) storage, especially at lower temperatures. This effect may not have been observed in our case due to the lower concentration of H\(_2\)O used (1% vs. 8%).
Figure 30. *In situ* spectra collected during NO\textsubscript{x} storage-reduction cycling on Pt/Ba/Al\textsubscript{2}O\textsubscript{3} at 250 °C. Panes (A) and (C) display spectra collected during the first lean periods (conditions: 1000 ppm NO/5%O\textsubscript{2}/He); panes (B) and (D) display spectra collected during the rich periods (conditions: 9000 ppm CO/He). Spectra in panes (A) and (B) were collected during dry cycling; spectra in panes (C) and (D) were collected in the presence of 1% H\textsubscript{2}O.

Figs. 30B and 30D show spectra collected during the rich phase of cycling in the absence and presence of 1% H\textsubscript{2}O, respectively. In the absence of H\textsubscript{2}O, bands at 2228, 2166, 2061, 2043, 1950, 1557, 1356 and 1062 cm\textsuperscript{-1} are present in the spectra collected during rich phases (Fig. 30B). The bands at 1557, 1356 and 1062 cm\textsuperscript{-1} can be assigned to Ba carbonate features, in agreement with the results of the storage measurements described in Section 2.4.2. It is worth noting that significant contributions from carbonate features carry over from cycle to cycle since these species are stable under both lean and rich conditions at this temperature. Furthermore, spectra collected during the subsequent lean phase indicated slow growth of the band centered at approximately 1200 cm\textsuperscript{-1}, characteristic of stored nitrites on BaO, which indicates that a
significant portion of the Ba storage sites are saturated with relatively stable carbonate species that are not removed during lean phases at 250 °C.

The bands at 2061 and 2043 cm$^{-1}$, as well as the broad band centered at approximately 1950 cm$^{-1}$, can be assigned to linear and bridged CO carboxyls on Pt sites [27,310,311]. Finally, the bands at 2228 and 2166 can be assigned to NCO species adsorbed on Al$^{3+}$ and Ba$^{2+}$ sites, respectively [24]. The NCO bands are fairly intense in comparison to the other surface species observed, leading some groups to postulate that these species may be intermediates in the reduction process [24,27,43].

Spectra collected at 250 °C during the rich phase in the presence of 1% H$_2$O (Fig. 30D) showed significant differences in the NCO region when compared to the corresponding spectra collected under dry conditions. More specifically no Al NCO band (2228 cm$^{-1}$) was observed in this case, while the band associated with the Ba NCO species (2166 cm$^{-1}$) had significantly lower intensity. Additionally, the Ba NCO band also increases, reaches a maximum and then decreases as the rich phase progresses. Similar behavior has previously been reported by Lesage et al. [145]. Several factors may be contributing to this effect. First, it is possible that H$_2$O could inhibit the formation of NCO species through the formation of hydroxyl groups that block active Pt sites and thus decrease the surface concentration of the NCO precursors [312,313]. However in this case, one would expect the surface concentration of Pt carboxyls to decrease as well. Given that the intensities of the carboxyl peaks in the 1900- 2100 cm$^{-1}$ region are essentially the same in the spectra of Figs. 30B and 30D, this explanation appears to be less plausible.

Alternatively, it is also possible that the presence of H$_2$O initiates the WGS reaction, which in turn decreases the concentration of CO available for adsorption and reaction with N adatoms on the surface [64]. Once again however, a decreased CO concentration should have
resulted in a decrease in the intensity of the carbonyl bands that was not observed. Thus, the most likely explanation is that the surface NCO species are formed at the same rate and to the same extent as under dry case, but weaker band intensities are observed because in the presence of H₂O, they are rapidly hydrolyzed to NH₃ [24,64].

Cycling in the presence of H₂O also affects, to a lesser extent, the carbonate and nitrite/nitrate bands. For example, the carbonate band at 1356 cm⁻¹ appears to shift to 1366 cm⁻¹, while a shoulder at 1440 cm⁻¹ is also formed, along with a new band at 1577 cm⁻¹, which overlaps with the band at 1557 cm⁻¹ and significantly contributes to the overall spectral intensity in that region of the spectrum. The appearance of the new bands at 1577 and 1366 cm⁻¹ can be attributed to the formation of surface formate species in addition to the surface carbonates [298]. Furthermore, the presence of the band at 1440 cm⁻¹, which was previously assigned to bulk Ba carbonate [34,179], indicates that bulk-type carbonates are formed in the presence of water. This result is not surprising since Szanyi et al. [187,191] noticed similar behavior for transition of surface Ba nitrates to bulk Ba nitrates in the presence of water. Further comparison between Figs. 30B and 30D indicates that lower concentrations of carbonates and higher concentrations of nitrites are present on the surface during cycling in the presence of H₂O. This in turn, may suggest that water facilitates storage and release of NOₓ at 250 °C. These results are in agreement with the results of a recent study on the effect of H₂O conducted by Nova et al. [64].

**CO and C₃H₆ Cycling at 350 °C**

*In situ* cycling experiments were also performed at 350 °C, where the effects of precious metals and reductant selection were also considered. Fig. 31 shows spectra collected during cycling at 350 °C over the Pt/Ba/Al₂O₃ catalyst, in the presence and absence of H₂O and with 9000 ppm CO used for the reduction phase.
Figure 31. *In situ* spectra collected during NO<sub>x</sub> storage-reduction cycling on Pt/Ba/Al<sub>2</sub>O<sub>3</sub> at 350 °C. Panes (A) and (C) display spectra collected during the first lean periods (conditions: 1000 ppm NO/5%O<sub>2</sub>/He); panes (B) and (D) display spectra collected during the rich periods (conditions: 9000 ppm CO/He). Spectra in panes (A) and (B) were collected during dry cycling; the spectra in panes (C) and (D) were collected in the presence of 1% H<sub>2</sub>O.

During the 1<sup>st</sup> lean phase, bands appeared immediately in the spectra at 1300 and 1210 cm<sup>-1</sup>, while additional bands also appeared at 1541, 1465, 1410 and 1315 cm<sup>-1</sup> with increased exposure time (Figs. 31A and 31C). As discussed in the previous sections and with the aid of Table 6, the initial bands at 1300 and 1210 cm<sup>-1</sup> can be assigned to Ba nitrites, while the bands at 1541, 1465, 1410 and 1315 cm<sup>-1</sup> can be assigned to Ba nitrates. The most significant difference observed between the cycling experiments at 250 and 350 °C was that storage of NO<sub>x</sub> at 250 °C occurred mainly in the form of surface nitrites, while as storage at 350 °C occurred mainly in the form of surface nitrates. It is also clear that the dominant NO<sub>x</sub> storage form on the surface is a function of storage temperature and contact time, in agreement with previous literature reports.
Differentiation between the types of NO\textsubscript{X} species stored on the surface is important because nitrites have lower thermal stability and are therefore expected to be more reactive than nitrates [31,112]. Therefore, storage of NO\textsubscript{X} as Ba nitrites instead of nitrates may be favorable for NSR cycling, but NO\textsubscript{X} slip due to thermal release of nitrites during exotherms created by introduction of reductants to lean environments also represents a problem [61]. The presence of H\textsubscript{2}O does not appear to affect storage significantly, consistent with the storage results obtained at 250 °C.

Spectra collected under dry conditions during the rich phase of cycling over the same Pt/Ba/Al\textsubscript{2}O\textsubscript{3} catalyst are shown in Fig. 31B. In contrast to the results obtained at 250 °C, prior to the introduction of CO (Fig. 31B, 0 s), the surface is mostly free of carbonate species and the nitrate bands at 1541, 1410 and 1315 cm\textsuperscript{-1} are the dominant features in the spectrum. Hence, it appears that most of the carbonate species formed during the previous rich phase were removed during the subsequent lean phase, indicating a faster exchange between barium carbonates and nitrates at 350 °C. Following the introduction of CO, the intensity of the nitrate bands decreases, while new carbonate bands appear at 1567 and 1344 cm\textsuperscript{-1}. Furthermore, significant amounts of NCO species are formed both on Al and Ba as indicated by the appearance of strong corresponding bands at 2221 and 2162 cm\textsuperscript{-1}, respectively.

The presence of H\textsubscript{2}O significantly affects the concentration of surface NCO at 350 °C. Spectra collected under these conditions (Fig. 31D) indicate that the Al NCO species are no longer present, while the intensity of the band at 2162 cm\textsuperscript{-1} corresponding to the Ba NCO species is dramatically reduced in intensity. In agreement with the results from 250 °C, the Ba NCO band also grows intensity, reaches a maximum and then decreases as the rich phase progresses, where the dramatic decrease in intensity due to the presence of water makes this behavior much
harder to distinguish in Fig. 31D. The effect of temperature and the presence of H$_2$O on the concentration of NCO species formed during cycling using CO as the reducing agent is more clearly demonstrated in Fig. 31, where the integrated intensities of the bands in the NCO region (i.e. 2100-2350 cm$^{-1}$) is plotted as a function of time. The results of Fig. 31 clearly show that higher concentrations of surface NCO species were formed under dry conditions at 350 °C than at 250 °C. Szailer et al. [24] previously reported that the highest concentrations of NCO were formed at 250 °C, but in their experimental protocol, NO$_2$ was first adsorbed on BaO at room temperature and the temperature was then ramped in the presence of CO up to 300 °C. The thermal stability of NCO was also investigated in the same study and it was concluded that their decomposition does not start until approximately 350 °C. In contrast, Abdulhamid et al. [27] have also reported that higher concentrations of surface NCO are formed during in situ DRIFTS measurements at 350 °C rather than at 250 °C, in agreement with our observations. Additionally, Fanson et al. [43] concluded that the concentration of surface NCO species formed is strongly related to the amount of NO$_X$ stored on Ba. Therefore, the higher concentration of NCO species observed at 350 °C can be attributed to the increased NO$_X$ storage at this temperature. Furthermore, the subtlety between amount of NO$_X$ stored at different temperatures and the reaction leading to the formation of surface NCO species demonstrates that attempts to decouple the reduction process from the NO$_X$ storage process may result in misleading conclusions, since storage under different conditions most likely results in differences in both the amounts and type of NO$_X$ species stored on Ba.
The results of Fig. 32 also demonstrate the effect of water on the concentrations of surface NCO at 250 and 350 °C. While the effect is strong at both temperatures, the observed decrease is less at 250 °C presumably because of a lower rate of hydrolysis in this case. At 350 °C changes were also observed in the carbonate and nitrate bands (Fig. 32D). More specifically, new bands appear to form at 1365 and 1557 cm\(^{-1}\) and a shoulder at 1440 cm\(^{-1}\) was also observed. Again, the formation of bands at 1365 and 1557 cm\(^{-1}\) can be assigned to surface formate species in addition to surface carbonates [298]. The shoulder at 1440 cm\(^{-1}\) can be assigned to a bulk BaCO\(_3\) species [34,179]. The formation of this band in the presence of water was in agreement with our results from 250 °C. A promotional effect of the presence of H\(_2\)O addition during CO cycling at 350 °C has been described by other groups [28,64], however such an effect could not be discerned through examination of the FTIR spectra alone since the rate and extent of
reduction of stored NO\textsubscript{X} species cannot be determined due to the overlapping of carbonate and nitrate bands.

Similar experiments were also performed using C\textsubscript{3}H\textsubscript{6} as the reducing agent and the spectra collected are shown in Fig. 33. For brevity, only spectra collected during the rich phase are shown since the storage phase is unaffected by the choice of reducing agent. The concentration of C\textsubscript{3}H\textsubscript{6} (i.e., 1000 ppm) was selected in order to keep the reductant potential of CO and C\textsubscript{3}H\textsubscript{6} the same and therefore obtain results that are directly comparable. Spectra collected under rich conditions indicate the presence of several types of carbon-containing surface species, with characteristic bands in the 1250-1600 cm\textsuperscript{-1} region. In addition to carbonates, the formation of formates and carboxylates is also expected when a hydrocarbon reductant is used [298]. Due to the overlapping of the respective bands, band assignments in this region should be regarded as tentative. Nevertheless, comparison of the spectra collected in the presence of CO and C\textsubscript{3}H\textsubscript{6} (Fig. 31 and Fig. 33) indicates that in both cases the nitrate bands are no longer present in the spectra, thus providing evidence that both reducing agents can effectively reduce the stored nitrates. Abdulhamid et al. [26] previously investigated the effect of the reductant used during NSR and concluded that the reducing activity follows the order: H\textsubscript{2}>CO>C\textsubscript{3}H\textsubscript{6}>>C\textsubscript{3}H\textsubscript{8}. While H\textsubscript{2} and CO were reported to be significantly more active than C\textsubscript{3}H\textsubscript{6}, C\textsubscript{3}H\textsubscript{6} was also shown to reduce stored NO\textsubscript{X} to an appreciable extent. These previous results appear to be consistent with our FTIR data, although detailed information regarding the rate and extent of reduction cannot be discerned through examination of the FTIR spectra alone.
Figure 33. *In situ* spectra collected during NO\textsubscript{X} storage-reduction cycling on 1Pt/17Ba/Al\textsubscript{2}O\textsubscript{3} at 350 °C. Panes (A) and (B) display spectra collected during rich periods (conditions: 1000 ppm C\textsubscript{3}H\textsubscript{6}/He). Spectra in pane (A) were collected during dry cycling; the spectra in pane (B) were collected in the presence of 1% H\textsubscript{2}O.

Once again, the formation of a barium NCO band (2162 cm\textsuperscript{-1}) was observed under rich conditions even in the presence of 1% H\textsubscript{2}O, although their surface concentration was dramatically reduced in this case. However, no aluminum NCO species are formed even in the absence of H\textsubscript{2}O since the corresponding band at 2221 cm\textsuperscript{-1} is not present in the spectra. Furthermore, the concentration of Ba NCO species is significantly lower than the corresponding case during the use of CO. This observation can be attributed to either the *in situ* generation of H\textsubscript{2}O (from oxidation of C\textsubscript{3}H\textsubscript{6}) and/or to the lower reducing activity of C\textsubscript{3}H\textsubscript{6}. Water formed *in situ* can decrease the concentration of NCO species through one of the possible mechanisms already described, with the hydrolysis of the NCO species being the most likely explanation. An
additional factor to consider is that by having the reductant potential of CO and C_3H_6 the same, we have effectively lowered the amount of carbon present during reduction to 1/3 of the corresponding carbon in the presence of CO. The formation of surface NCO species during the reduction of stored nitrates by C_3H_6 was previously interpreted to suggest that the reduction by CO and C_3H_6 proceed through the same pathway [26]. It is possible however, that in situ generation of CO from C_3H_6 may be the pathway leading to NCO formation in the presence of C_3H_6.

The presence of surface NCO during reduction in the presence of H_2O even in small concentrations is particularly interesting, because it is generally believed that such species are rapidly hydrolyzed to NH_3 in the presence of H_2O [24,145]. The results from Figs. 30D, 31D and 33B suggest that the rate of their formation is faster than the rate of their hydrolysis, which is supported by the maximum in NCO concentration on the surface as the rich phase progresses in the presence of H_2O. However, at this point, and prior to the analysis of the rates of reactivity that follows, it is not possible to assess their involvement in the overall NO_X reduction mechanism.

Comparisons of the amounts of NCO formed over Pt- and Rh-containing catalysts is attempted in Fig. 34. The data shown were generated by integrating the NCO bands formed under rich conditions and plotting the integrated area as a function of time. As mentioned previously, the amount of stored NO_X was approximately the same on the Pt/Ba/Al_2O_3 and Rh/Ba/Al_2O_3 catalysts, which is important since the concentration of NCO species formed is known to be dependent on the amount of stored NO_X [43]. Therefore, the effect of the nature of the noble metal can only be observed when the amount of stored NO_X during the lean phase is constant, as was the case here. Indeed, the type of noble metal used appears to affect the
concentration of NCO species formed. When CO is used as the reducing agent higher concentrations of NCO species are formed on the Pt/Ba/Al₂O₃ catalysts (Fig. 34A), where the opposite is true when C₃H₆ is used as the reducing agent (Fig. 34B).

**Figure 34.** Comparison between the amounts of NCO species formed on (▲) Pt/Ba/Al₂O₃ and (■) Rh/Ba/Al₂O₃ at 350 °C in the absence of H₂O (Lean: 1000 ppm NO/5% O₂/He; Rich: pane (A) 9000 ppm CO/He; pane (B) 1000 ppm C₃H₆/He).
2.4.4 The Stability/Reactivity of NCO Species at 350 °C

In order to understand better the role of surface NCO in the NSR mechanism, their stability and reactivity was investigated in different gas mixtures.

Spectra collected during exposure of a Pt/Ba/Al₂O₃ catalyst at the end of the rich phase to He or a 1000 ppm O₂/He mixture at 350 °C are shown in Fig. 35. The NCO bands at 2221 and 2162 are present in the initial spectra since the NCO species were generated during and are present at the end of the rich phase. The results indicate that the NCO species are relatively stable under He, since both bands were still clearly visible after 5 min. The intensity of the band at 2221 cm⁻¹ (Al-NCO species) decreased faster than that of the band at 2162 cm⁻¹ (Ba-NCO species), indicating the higher stability of the Ba-NCO at this temperature. The intensity of the carbonyl band at 2030 cm⁻¹ also decreased with time, indicating that adsorbed CO is removed from Pt at this temperature, and thus CO poisoning due to strong adsorption on Pt appears unlikely at 350 °C, as previously suggested by Abdulhamid et al [26,27]. When a 1000 ppm O₂/He mixture was used instead (Fig. 35B), the NCO species were rapidly removed from the surface, and no indication of any of the corresponding bands could be found in the spectra after 2 min on stream. This significant difference between the stability of NCO species in He and O₂/He strongly indicates that a reaction is taking place between the surface NCO species and O₂.

Additional reactions were also considered with NO and H₂O and the results of the corresponding experiments are summarized in Fig. 36, which shows the normalized integrated intensities of the NCO bands observed on Pt/Ba/Al₂O₃ and Rh/Ba/Al₂O₃ during exposure at the end of the rich phase to He, O₂/He, NO/He and H₂O/He mixtures at 350 °C. Results obtained with the Ba/Al₂O₃ are also included in Fig. 36. The concentration of NCO on this material is approximately 20% of that on Pt/Ba/Al₂O₃ or Rh/Ba/Al₂O₃. Since the presence of noble metals
is known to catalyze the formation of these species [314,315], it is not surprising that their concentration is dramatically lower. Actually, as previously outlined by Alexeev et al. [176], it is more surprising that these species are formed at all, especially in high enough concentrations to be observable, since the reaction was previously believed to occur only on the surfaces of metals. Clearly, this is not the case and Forzatti et al. [290] recently described this phenomenon for Ba/Al$_2$O$_3$ in more detail.

Some differences were observed between the NCO stability/reactivity in He, shown in Fig. 36A. The reaction of NCO species with residual surface nitrites/nitrates cannot be excluded in this case, since Nova et al. [64] reported that CO treatment at 350 °C only removes approximately 80% of the NO$_X$ stored on Pt/Ba/Al$_2$O$_3$. Similarly, Forzatti et al. [290] reported removal of only 22% of the NO$_X$ stored on Ba/Al$_2$O$_3$ and 43% of the NO$_X$ stored on Pt/Ba/Al$_2$O$_3$ following CO TPSR treatment up to 400 °C. While some of the stored NO$_X$ was converted and remained as NCO on the surface, residual nitrites/nitrates could be present as well. The notion that a reaction with another surface species is responsible for the decreased intensities observed in Fig. 36A is also supported by previous reports by Forzatti et al. [290] who observed that NCO species were stable at 350 °C, even under vacuum, and Szailer et al. [24] who reported that thermal decomposition of surface NCO begins at temperatures slightly above 350 °C and is not completed even at 450 °C. The results of Fig. 36A further show that the reaction of NCO with residual nitrites/nitrates is significantly slower than the corresponding reactions shown in the other gas mixtures investigated. Surface distribution and diffusion of the NCO and the residual nitrites/nitrates could account for this effect, as well as for differences observed between the different metals.
Figure 35. Spectra collected during exposure of a Pt/Ba/Al₂O₃ catalysts at the end of the rich phase to (A) He or (B) 1000 ppm O₂/He at 350 °C.

The results obtained during the reaction of surface NCO species with O₂, NO and H₂O are shown in Figs. 36B, 36C and 36D, respectively. The reactivity of NCO with these molecules has been well documented in the literature [24,28,145,176,288,290,299,302,316,317]. In contrast, exposure of surface NCO species to CO did not result in a decrease in their concentration, even after prolonged, in agreement with previously published results on the stability of NCO in CO [318]. An initial increase was observed in the NCO concentration during
the reaction with NO (Fig. 36C). These additional NCO species formed can be attributed to the reaction of NO with CO adsorbed on the surface or residual gas phase CO in the FTIR cell.

![Figure 36](image)

**Figure 36.** Normalized integrated intensity of NCO bands observed on (●) Ba/Al₂O₃, (▲) Pt/Ba/Al₂O₃ and (■) Rh/Ba/Al₂O₃ during exposure at the end of the rich phase to (A) He, (B) 1000 ppm O₂/He, (C) 1000 ppm NO/He and (D) 1000 ppm H₂O in He at 350 °C.

The results of Fig. 36 further indicate that the reaction of surface NCO species with NO and O₂ is a metal catalyzed reaction, since a significant difference in the rate of removal of NCO is observed between the Ba/Al₂O₃ and the Pt/Ba/Al₂O₃ and Rh/Ba/Al₂O₃ materials. Very little difference however, is observed in both cases over the noble metal containing catalysts. In contrasts, the rapid removal of NCO in the presence of H₂O over the Ba/Al₂O₃ material, and the
similar rates observed in this case with all three materials demonstrate that a precious metal is not necessary for this reaction to occur. Finally, the reactions of surface NCO with NO, O₂ and H₂O on Pt/Ba/Al₂O₃ and Rh/Ba/Al₂O₃ all exhibited similar activity, with the majority of the NCO species being removed from the surface after approximately 2 min.

Fig. 37 shows the evolution of N₂ from the Rh/Ba/Al₂O₃ catalyst during the rich phase and subsequent exposure to He, O₂ and NO. As shown in Fig. 37A, N₂ is generated during the rich phase, but not during subsequent exposure to He after the rich phase ends, although the results of Fig. 36A indicate a gradual decrease in surface NCO concentrations in this case. This indicates that the NCO species present on the Rh/Ba/Al₂O₃ surface at the end of rich period did not significantly decompose to gas phase N₂ or react quickly enough with residual nitrites/nitrates to produce N₂. It is possible that the decomposition products of the surface NCO were re-adsorbed as nitrites/nitrates, but an increase in surface nitrite/nitrate concentrations could not be observed in our results due to strong overlapping of the nitrite/nitrate and carbonate bands. Forzatti et al. [290] however, were able to observe formation of nitrites during similar experiments. In our case, the concentration of NCO species on the surface may simply not have been high enough to allow us to observe such formation.

Exposure of the surface NCO species to 1000 ppm O₂/He resulted in the formation of significant amounts of N₂, as shown in Fig. 37B. Evolution of N₂ during two discrete periods – i.e. during the rich phase and during the subsequent lean phase – has previously been observed by Breen et al. [16] and Scholtz et al. [28,319,320] during NSR operation. At the end of rich phases, nitrites/nitrates, carbonates and NCO species were the only species observed on the surface. Exposure of nitrites/nitrates or carbonates to O₂ increases the stability of these species and does not result in evolution of N₂. Some authors [16] have also suggested the NH₃ may be
Figure 37. N$_2$ profiles (m/z = 28) obtained during the reaction of stored NO$_X$ with $^{13}$CO and the subsequent reaction of residual NCO species with (A) He, (B) 1000 ppm O$_2$/He or (C) 1000 ppm NO/He on Rh/Ba/Al$_2$O$_3$ at 350 °C.
stored on the catalyst during the rich phase, but the formation of significant amounts NH₃ in the absence of H₂O and H₂, as well as subsequent storage and oxidation to N₂ is unlikely under our conditions [175]. It is therefore reasonable to assume that the N₂ produced during the exposure to O₂ is the product of the reaction between surface NCO and O₂. Integration of the two N₂ peaks observed in our case (Fig. 37B) indicated that approximately 30% of the total N₂ production resulted from the reaction of NCO species with O₂.

Exposure of the surface NCO species to 1000 ppm NO/He also resulted in the formation of a second N₂ peak, which in this case was even larger than the first N₂ peak (Fig. 37C), constituting approximately 70% of the total N₂ produced. Comparison between the N₂ peaks shown in Figs. 37B and 37C confirmed while the first peaks were approximately the same in both cases, the N₂ peak observed during NO exposure was approximately 5 times larger than the one observed during O₂ exposure. Stoichiometric calculations indicate that reaction of NCO species with NO theoretically results in twice as much N₂ produced. Since in both cases similar amounts of NCO species were completely removed from the catalyst surface (see Figs. 36B and 27C) the remaining N₂ formed is in all likelihood the result of reactions between the gaseous NO and other surface reducing agents. Evidence to this direction is provided in Fig. 36C, which shows additional surface NCO formation upon introduction of NO, indicating that an NCO species may act as an intermediate even for this addition N₂ formation. The small increase observed in Fig. 36C is misleading since it represents the net difference during the first 30-60 s between NCO formation and consumption. NCO consumption during this initial period is at its highest point, as indicated by the very steep slope of the N₂ production curve in Fig. 37C.

Overall, the results of Fig. 36 and 37 indicate that surface NCO contribute to a significant percentage of the overall amount of N₂ formed, when CO is used as the reducing agent. While it
is difficult to quantify the exact amount, it could exceed in some cases 30% of the total. Furthermore, such species could be responsible for N$_2$ retention on the NSR catalyst surface during the rich phase and contribute to a second N$_2$ release observed during NSR operation at the onset of the lean phase.

2.5 CONCLUSIONS

The results of in situ FTIR measurements conducted with Pt/Ba/Al$_2$O$_3$ and Rh/Ba/Al$_2$O$_3$ catalysts of very similar molar loading and dispersion of precious metals indicate that surface nitrites are the predominant NO$_X$ storage form at 250 °C, while surface nitrates become the predominant storage form at 350 °C. The presence of water did not have a significant effect during storage. Surface isocyanates (NCO) were formed under a variety of conditions investigated and their concentration was dependent on the temperature, the reductant selected, the presence of H$_2$O and the type of precious metal used. The highest concentrations of surface NCO species were observed during dry conditions with CO used as the reductant at 350 °C. The NCO stability measurements demonstrate that these species are stable in CO and moderately stable in He. In contrast, the reaction of surface NCO species with NO and O$_2$ is fast and catalyzed by precious metals, with no difference observed between Pt and Rh. A similarly fast reaction is also observed with H$_2$O, even in the absence of the noble metal component. Comparison of N$_2$ evolution amounts during the rich phase and subsequent reaction of residual NCO species with O$_2$ and NO confirmed that reaction of NCO species could contribute significantly to the total amount of N$_2$ formed, when CO is used as the reducing agent. These
species represent a reduced form of stored N$_2$ that could be responsible for N$_2$ release observed at the onset of the lean phase.

2.6 ACKNOWLEDGEMENTS

The authors gratefully acknowledge financial support from the National Science Foundation (Division of Chemical, Bioengineering, Environmental and Transport Systems (CBET); Award ID 0730937). The authors further acknowledge Dr. Douglas Blom and the University of South Carolina Electron Microscopy Center for instrument use, scientific and technical assistance.
CHAPTER 3. NH₃ FORMATION OVER A LEAN NOₓ TRAP (LNT) SYSTEM: EFFECTS OF LEAN/RICH CYCLE TIMING AND TEMPERATURE

3.1 PREFACE

A commercial lean NOₓ trap (LNT) catalyst containing Pt, Pd, Rh, BaO, and CeO₂ was evaluated in this investigation. The effects of lean/rich cycle timing on the NOₓ, CO and C₃H₆ conversions and on the NH₃ and N₂O selectivities were considered. Two distinct lean/rich cycling regimes were identified. At low temperatures, NOₓ release and reduction were kinetically limited. As a result, a longer, lower-concentration rich dose favored increased cycle averaged NOₓ conversions. For example, extending the rich period from 5 to 15 s at 250 °C, while holding the overall reductant dose constant, resulted in an increase in cycle averaged NOₓ conversion from 59 to 87%. At high temperatures, the opposite was found to be true. Above 450 °C, NOₓ release and reduction occurred very rapidly and shorter, higher concentration rich doses yielded significantly higher NOₓ conversions. For example, extending the rich period from 5 to 15 s at 500 °C, while holding the overall rich dose constant, resulted in a decrease in the cycle averaged NOₓ conversion from 76 to 54%. The selectivities to NH₃ and N₂O were found to be primarily a function of temperature, with both being higher at lower temperatures. The effect of cycle timing and reductant concentration were of secondary importance. In contrast, NH₃ and N₂O yields were significantly affected by the cycle timing since they depend on the NOₓ conversion. Therefore, any combination of changes in the lean/rich timing protocol or reductant concentrations that resulted in increased NOₓ conversion also resulted in increased NH₃ and N₂O yields for a given temperature. As a result, concerted control of NH₃ generation
by varying the lean/rich cycle timing was demonstrated, although the effect was relatively small near the optimum temperature (i.e., 350 – 400 °C) of the LNT catalyst. In contrast, both at lower and higher temperatures, variations in the rich cycle duration resulted in NH₃/NOₓ ratios that could extend the region of operation for a close-coupled LNT-SCR system. However, N₂O yield also increased with NH₃ yield under the same conditions.

3.2 INTRODUCTION

Lean-burn engines are more fuel efficient and produce less overall CO₂ per mile when compared to traditional stoichiometric-burn ones. However, meeting NOₓ emission regulations for lean-burn engines through the use of advanced catalytic converter technologies still represents a significant technical challenge. Over the past 15 years, lean NOₓ trap (LNT) [4] and selective catalytic reduction (SCR) [321] catalysts have been identified as two promising systems for the removal of NOₓ from the exhausts on lean-burn engines. In several recent publications and patents, there has been considerable discussion regarding the advantages of combining these two technologies into a coupled LNT-SCR system [154,156,283,322–338]. As a brief review, LNTs are designed to function under periodic lean/rich environments, where NOₓ is stored in the form of nitrites or nitrates on a storage component (e.g., Ba) during lean periods typically lasting 60 - 120 s [4,339]. As time elapses, the storage component becomes saturated with NOₓ and a subsequent rich step, typically lasting 1 - 5 s, must be employed to reduce the stored NOₓ and in the process regenerate the storage component. Catalytic formulations used commercially generally include platinum group metals (PGM; e.g., Pt, Pd and Rh) supported on a BaO and CeO₂-modified γ-Al₂O₃ [4]. While N₂ is obviously the most desirable product during NOₓ reduction, NH₃ and N₂O can also be formed and under certain conditions, the selectivity to these
undesirable by-products can be significant. For example, Ren and Harold [340] reported selectivities to NH$_3$ of 40\%, or greater, for a series of model LNT catalysts operating below 200 °C. At similar temperatures, Bonzi et al. [330] attributed the high selectivity to NH$_3$ to a combination of significant NH$_3$ formation and slow subsequent reaction of the NH$_3$ formed with the remaining stored nitrites/nitrates. This reaction becomes significantly faster at higher temperatures, thus contributing to reduced NH$_3$ selectivities. While NH$_3$ formation over the LNT catalyst is undesirable in a single catalyst system, it also clearly demonstrates the potential for a coupled LNT-SCR configuration.

In contrast to LNT catalysts, NH$_3$-SCR catalysts are operated under steady-state conditions and were originally designed for use in stationary applications [2,341]. Current commercial SCR catalytic formulations include V$_2$O$_5$-WO$_3$/TiO$_2$ or Cu/Fe exchanged zeolites [2,341], with the zeolite-based materials favored for automotive applications due to their lower temperature activity, as well as their ability to store significant amounts of NH$_3$ under transient conditions [342,343]. Initially, commercialization of zeolite-based SCR catalysts was limited due to hydrothermal stability issues, but recent advances in this area have led to the development of hydrothermally stable Cu-zeolite catalysts that are active over a broad temperature range [342,344]. Zeolites are particularly attractive for a coupled LNT-SCR configuration because of their ability to store NH$_3$ generated over the LNT catalysts during short rich cycles, which is stable under lean conditions. NH$_3$ thus stored can be used in the subsequent lean cycle to reduce NO$_X$ that is not trapped by the LNT catalyst. As outlined by Bonzi et al [330], the LNT-SCR configuration has the advantage of both increasing the selectivity to N$_2$ and the overall NO$_X$ conversion when compared to a single LNT system. For example, Lindholm et al. [338] reported a cycled averaged NO$_X$ conversion of 99.5\% for an LNT-SCR system operating at 300 °C, but
also observed increases in the NOX conversion and N2 selectivity over the entire temperature range (200 – 400 °C) investigated when compared to a single LNT system. Similarly, Xu et al. [283] recently reported that LNT-SCR systems have the additional benefit of requiring a lower PGM content for the LNT, increasing the temperature window for high NOX conversion and mitigating catalyst deactivation due to aging. In summary, a consensus has emerged that addition of an SCR catalyst, either in series, as a physical mixture or in a layered geometry, to an LNT exhaust system can result in significant improvements in overall catalytic performance. However, the majority of these investigations have either been performed under typical LNT cycling conditions (e.g., 60 s lean, 5 s rich) or under extended isothermal step conditions and the role of cycle timing has not been investigated in detail.

In this manuscript, the role of both lean and rich LNT cycle timing is addressed with specific emphasis placed on the amount of NH3 generated in relation to the amounts NOX and CO slip from the LNT catalyst. In addition, N2O formation was closely monitored under these conditions. Finally, the concept of concerted control over the NH3 generation by the control of cycle timing and conditions is introduced with the goal optimizing the LNT-SCR system as a function of the under-floor catalyst temperature.

3.3 EXPERIMENTAL

3.3.1 CATALYTIC MATERIAL

A fully-formulated LNT monolith (wash-coated honeycomb cordierite monolith removed from a Lean-GDI, BMW 120i, Model Year 2009) was utilized in the present investigation. On the vehicle, the LNT catalyst brick of 413 cell per square inch (cpsi) is used in an under-floor configuration. The catalyst has now been adopted as the new representative commercial LNT
catalyst in the Crosscut Lean Exhaust Emissions Reduction Simulations (CLEERS) research community [345].

3.3.2 CATALYST CHARACTERIZATION

Semi-quantitative metals screening of the LNT catalyst using Inductively Coupled Plasma - Mass Spectrometry (ICP-MS) was conducted by Galbraith Laboratories, Inc. (Knoxville, Tennessee). Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES), which afforded quantitative results, was also conducted by Galbraith Laboratories, Inc.

A JEOL JXA-8200 SuperProbe Electron Probe Micro Analyzer (EPMA) was used to map the elemental composition of the catalyst washcoat. Samples were prepared for imaging by mounting them in epoxy and polishing. The spot size was approximately one cubic micron, which is smaller than the typical grain size of the constituent phases. A Hitachi 4800 field emission gun scanning electron microscope (FEG-SEM) with an EDAX energy dispersive spectroscopy (EDS) x-ray detector was also used to measure the element composition of individual grains. Since the sample was heterogeneous and porous, no attempt was made to calibrate the x-ray intensities with standard samples. Therefore the compositional data is likely accurate to no less than one percent and should be viewed more as a relative comparison between different grains in the washcoat.

3.3.3 CATALYTIC EVALUATION

Lean/rich cycling was performed using a laboratory bench-flow reactor, as described in more detail elsewhere [135,346]. Briefly, the LNT monolithic core (2.1 cm wide X 5.5 cm long; SV=30,000 hr^{-1}; \approx 9150 standard cm^3/min) was tightly wrapped in Zetex insulation tape and inserted into a horizontal quartz tube reactor. The reactor was heated using a horizontal bench-
top furnace (Lindberg/Blue M). Lean/rich gas mixtures were prepared using pressurized gas cylinders (UHP, Air Liquide) and a system of mass flow controllers (Unit Instruments Series 7300, Kinetics Electronics). A rapid switching 4-way valve system was used to alternate between the lean and rich gas mixtures. Water was introduced using a peristaltic pump (Cole-Parmer) that fed into a heated, flash-vaporization zone held at 350 °C. All gas lines downstream of the water introduction zone were heated and quartz chips were placed upstream of the monolithic core to ensure that the feed gas temperature reached the set point temperature prior to contacting the catalyst. Three thermocouples were used to measure the temperature. The first was placed 1 cm upstream of the core and was used to record the inlet/set-point temperature. The second thermocouple was placed in the middle of the monolithic core and was used to record the actual monolith temperature. The third was placed 1 cm downstream of the core and was used to record the temperature exiting the core. After exiting the reactor, the gas was fed to an MKS MultiGas™ 2030 HS FT-IR analyzer, which allowed for continuous tracking (5 Hz) of NO, NO₂, N₂O, NH₃, CO, C₃H₆, CO₂ and H₂O concentrations. Prior to the reactor measurements, the as-received catalyst was “de-greened” at 700 °C in a 10% H₂O/air mixture for 16 h to establish reproducible performance. Unless otherwise denoted, all calculations were performed using the last 4 cycles obtained during lean/rich cycling, where Eqns. 14-16 were used to calculate the cycle averaged NOₓ, CO and C₃H₆ conversion, respectively.

\[
X_{NOX} = \frac{\int NO_{X,Fed} - \int NO_{X,Slipped}}{\int NO_{X,Fed}} \times 100
\]  
(14)

\[
X_{CO} = \frac{\int CO_{Fed} - \int CO_{Slipped}}{\int CO_{Fed}} \times 100
\]  
(15)

\[
X_{C3H6} = \frac{\int C3H6_{Fed} - \int C3H6_{Slipped}}{\int C3H6_{Fed}} \times 100
\]  
(16)
Eqns. 17-20 were used to calculate the NH$_3$ and N$_2$O yields and selectivities, respectively. The total amount of products formed was calculated based on the total amount of NO$_x$ consumed. Since N$_2$ formation could not be quantified by the FTIR analyzer, the N$_2$ yield and selectivity was calculated using a nitrogen mass balance by assuming that NH$_3$, N$_2$O, and NO$_x$ were the only nitrogen containing by-products formed.

\[ Y_{NH_3} = \frac{\int NH_3^{Produced}}{\int NO_x^{Fed}} \times 100 \]  
\[ S_{NH_3} = \frac{\int NH_3^{Produced}}{\int NO_x^{Fed} \times X_{NO_x}} \times 100 \]  
\[ Y_{N_2O} = \frac{\int N_2O^{Produced}}{\int NO_x^{Fed}} \times 100 \]  
\[ S_{N_2O} = \frac{2 \times \int N_2O^{Produced}}{\int NO_x^{Fed} \times X_{NO_x}} \times 100 \]

A total of 81 sets of conditions were considered in this investigation, consisting of combinations of nine temperatures (150 – 550 °C, in 50 °C increments) and nine different cycle timing protocols. The lean period gas concentration was held constant at 500 ppm NO, 8% O$_2$, 5% H$_2$O and 5% CO$_2$ in N$_2$. The rich period included a variable amount of reductants with a balance of 5% H$_2$O and 5% CO$_2$ in N$_2$. The required amount of reductants (i.e., H$_2$, CO and C$_3$H$_6$) in the rich dose was calculated by adding the stoichiometric amount of reductant required to completely reduce all of the NO$_x$ fed plus the required amount of reductants required to consume all of the O$_2$ storage capacity of the LNT catalyst. The calculated rich dose (i.e., the total number of moles of reductant required) was then held constant and the rich cycle duration was varied. Therefore, shorter rich cycle times (e.g., 5 s) contained higher concentrations of reductants, while longer rich cycle times (e.g., 10 and 15 s) contained lower concentrations of
reductants. Once the total amount of reductants needed was determined, their relative concentrations were calculated based on a 18:6:1 ratio for CO:H₂:C₃H₆, respectively. This ratio is considered to be representative of rich engine exhaust [347].

The oxygen storage capacity (OSC) on the LNT catalyst was measured by cycling (60 s lean / 5 s rich) in a lean gas mixture comprised of 10% O₂, 5% H₂O and 5% CO₂ in N₂ and a rich gas mixture comprised of X% CO, 5% H₂O and 5% CO₂ in N₂. The CO concentration was adjusted during this cycling (0.1% increments) until consistent breakthrough of CO was observed by both the FT-IR analyzer and lambda sensor (ECM AFRecorder 1200A air-fuel ratio meter). Fig. 38 demonstrates the OSC protocol for cycling at 550 °C. The results demonstrate that a CO concentration of 1.6% resulted in minimal CO breakthrough during rich periods. The lambda sensor reading, which was used as a secondary metric for CO breakthrough (λ<1.00=rich), never dipped below 1.00, which implied incomplete consumption of the OSC. Alternatively, when the CO concentration was increased to 1.7%, breakthrough of CO was consistently measured by the FT-IR analyzer. In this case, the CO breakthrough also coincided with a lambda sensor reading of approximately 0.96 at the end of the rich period. Therefore, an OSC of 1.7% CO was used in the calculations to determine the reductant concentration necessary during the rich periods at 550 °C. Table 7 displays the OSC values measured for the LNT catalyst as a function of temperature. For temperatures below 300 °C, a value of 1.6% was assumed because the kinetics of O₂ consumption required longer times than provided in the 5 s rich period and accurate measurements could no longer be obtained.

Table 8 shows the calculated reductant concentrations for different cycling times for an OSC corresponding to 1.6% CO. As shown in the Table, these concentrations varied both with the lean cycle timing (since the total amount of NOₓ fed varies in this case) and rich cycling
timing (since the total amount of reductants fed has to remain constant regardless of the length of the rich period). Slightly higher concentrations were used at temperatures above 450 °C due to the increase in the OSC to 1.7% CO (not shown for brevity).

Figure 38. OSC measurement performed at 550 °C over the LNT catalyst (See experimental section for conditions).
Table 7. OSC values measured for the LNT catalyst at different temperatures.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>OSC (CO %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>350</td>
<td>1.6</td>
</tr>
<tr>
<td>400</td>
<td>1.6</td>
</tr>
<tr>
<td>450</td>
<td>1.7</td>
</tr>
<tr>
<td>500</td>
<td>1.7</td>
</tr>
<tr>
<td>550</td>
<td>1.7</td>
</tr>
</tbody>
</table>

Table 8. Calculated reductant concentrations for the cycle timing protocols used in this investigation in the 150 – 400 °C range (OSC = 1.6% CO).

<table>
<thead>
<tr>
<th>Lean/Rich Timing (s)</th>
<th>CO (%)</th>
<th>H₂ (%)</th>
<th>C₃H₆ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>60/5</td>
<td>2.01</td>
<td>0.67</td>
<td>0.112</td>
</tr>
<tr>
<td>60/10</td>
<td>1.01</td>
<td>0.34</td>
<td>0.056</td>
</tr>
<tr>
<td>60/15</td>
<td>0.67</td>
<td>0.22</td>
<td>0.037</td>
</tr>
<tr>
<td>120/5</td>
<td>2.83</td>
<td>0.94</td>
<td>0.157</td>
</tr>
<tr>
<td>120/10</td>
<td>1.42</td>
<td>0.47</td>
<td>0.079</td>
</tr>
<tr>
<td>120/15</td>
<td>0.94</td>
<td>0.31</td>
<td>0.052</td>
</tr>
<tr>
<td>180/5</td>
<td>3.65</td>
<td>1.22</td>
<td>0.203</td>
</tr>
<tr>
<td>180/10</td>
<td>1.82</td>
<td>0.61</td>
<td>0.101</td>
</tr>
<tr>
<td>180/15</td>
<td>1.22</td>
<td>0.41</td>
<td>0.068</td>
</tr>
</tbody>
</table>

3.4 RESULTS AND DISCUSSION

3.4.1 CATALYST CHARACTERIZATION

Semi-quantitative inductively Coupled Plasma-Mass Spectrometry (ICP-MS) analysis of the LNT catalyst indicated the presence of Mg, Al, Ce, and Ba as major components. Other elements of significance included Zr, La, Pt, Pd, and Rh. The results of inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES) also indicated the presence of Pt, Pd, Rh, Ba,
Ce, Zr, and La on the LNT catalyst used. The loadings of these elements are summarized in Table 9.

**Table 9.** Elemental composition of the LNT catalyst used in this investigation.

<table>
<thead>
<tr>
<th>Element</th>
<th>Lean GDI, BMW 120i (2009) loading (g/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt</td>
<td>2.2</td>
</tr>
<tr>
<td>Pd</td>
<td>0.8</td>
</tr>
<tr>
<td>Rh</td>
<td>0.3</td>
</tr>
<tr>
<td>Total PGM (g/L)</td>
<td>3.3</td>
</tr>
<tr>
<td>PGM Ratio (Pt/Pd/Rh)</td>
<td>7/3/1</td>
</tr>
<tr>
<td>Ba</td>
<td>19.9</td>
</tr>
<tr>
<td>Ce</td>
<td>55.5</td>
</tr>
<tr>
<td>Zr</td>
<td>4.3</td>
</tr>
<tr>
<td>La</td>
<td>2.5</td>
</tr>
</tbody>
</table>

The wash coat was composed of three separate layers of roughly equal thickness, which suggests that three separate dip coats were conducted during processing. Of the elements measured, the Ba elemental map obtained by EPMA revealed these three layers the best, as shown in Fig. 38. Mud-cracks normal to the substrate surface, which stop at the layer interfaces, also indicate that three separate drying steps were performed during processing of the wash coat. The elemental composition of these three layers appears to be identical.

Three compositionally distinct domains (or grains) were observed in the washcoat using EPMA: a CeO$_2$ phase with low amounts of La, Zr, Pt and Pd (Ce/Zr mixed oxide domain); a Mg/Al oxide spinel phase with some Ce and Pd also present (Mg/Al mixed oxide domain); and in a few spots, an Al$_2$O$_3$ phase with Rh, as well as some Pd present (Al oxide domain). In addition to these three domains, there was another type of grain rich in Ba (results not shown), as in the case of the old CLEERS reference LNT [135,346]. As discussed in the experimental section however, no attempt was made to calibrate the x-ray intensities with standard samples and the results shown in Fig. 41 were included as a qualitative comparison between different
grains in the wash coat. Generally, the number of Ba-rich grains appeared to be rather limited, which may indicate a more uniform Ba dispersion in this LNT catalyst in comparison to a different LNT catalyst formulation considered in previous investigations [135,346]. The Mg/Al mixed oxide domain exhibits a bimodal grain size distribution with large 5 – 10 µm grains interspersed with submicron-sized grains. Fig. 40 shows a cross-section of the washcoat with the bright particles corresponding to the Ce/Zr mixed oxide domain and the darker matrix representing the Mg/Al mixed oxide domain. The compositions of the Ce/Zr and coarse-grained Mg/Al mixed oxide domains measured with EDS are shown in Fig. 41.

![EPMA map for Ba in a washcoat corner of the front section of the LNT catalyst brick. White dashed lines separate the three apparent layers of the washcoat.](image)

**Figure 39.** EPMA map for Ba in a washcoat corner of the front section of the LNT catalyst brick. White dashed lines separate the three apparent layers of the washcoat.
Figure 40. SEM image of the washcoat cross-section.

Figure 41. Approximate elemental compositions in weight percentage of the two primary phases in the washcoat as measured by EDS (carbon signal originating from the mounting epoxy).
3.4.2 Representative Lean/Rich Cycling over the LNT Catalyst

Reactor effluent concentrations observed at 300 °C during 60 s lean/5 s rich cycling over the LNT catalyst used in this investigation are shown in Fig. 42 as a representative example for the performance of this catalyst. As expected, low concentrations of NO\textsubscript{X} were observed during the lean period indicating that the majority of NO\textsubscript{X} was stored on the LNT catalyst. As the reactor feed was switched to the rich mixture (after 60 s) and the regeneration of the LNT catalyst was initiated, a significant un-reacted NO\textsubscript{X} release was observed simultaneously with the formation of N\textsubscript{2}O. Previous literature reports have addressed both of these observations [140,151,346,348–351], with the NO\textsubscript{X} release attributed to the slower NO\textsubscript{X} reduction kinetics at this temperature in comparison to the surface nitrite/nitrate decomposition [140,151] and the N\textsubscript{2}O formation linked to the relative concentrations of surface NO and N intermediates present [140,151,346,348–351]. Subsequent formation and breakthrough of NH\textsubscript{3} and CO were also observed during the rich cycle, with an approximately 2.5 s delay between the onset of the rich cycle and the appearance of these products in the reactor outlet. The delay for NH\textsubscript{3} has previously been attributed to the reaction of NH\textsubscript{3} formed upstream on the LNT catalyst with downstream surface nitrites/nitrates and oxygen stored on the catalyst [23,60,286,351,352]. Likewise, the delay in CO breakthrough is most likely a combination of several contributing factors including the amount of CO reacting with stored NO\textsubscript{X} and oxygen, as well as its participation in the water gas shift reaction (WGS). The near-simultaneous appearance of CO and NH\textsubscript{3} in the reactor outlet during reduction is an important feature of the LNT catalyst behavior in light of its potential use in an LNT-SCR configuration. While NH\textsubscript{3} could be stored in the SCR material, CO storage and/or oxidation over the downstream SCR catalyst under rich conditions is highly unlikely. Therefore, for practical implementation of the LNT-SCR
technology, the amount of CO slip from the LNT catalyst needs to be closely monitored as a function of operating conditions and or catalytic formulation and eventually converted to CO$_2$.

Table 10 summarizes the performance of the LNT catalyst at 300 °C (60 s lean/5 s rich) and provides corollary results calculated from the results shown in Fig. 42. The majority of NO$_X$ fed to the reactor during the lean cycle is stored and reduced during the subsequent rich step, resulting in a cycle averaged NO$_X$ conversion of 99.2%. Interestingly, the selectivity to N$_2$ for this cycle timing protocol and temperature is fairly low (59.2%), in agreement with other investigations conducted under similar conditions [151,340]. A significant percentage of the stored NO$_X$ (29.0%) reacted to form NH$_3$, where the NH$_3$ production is approximately 62 µmol/cycle, while the total amount of NO$_X$ slip is only 1.6 µmol/cycle. The difference between the amount of NH$_3$ produced and NO$_X$ slip as well as the difference in time evolution of the two species demonstrate the need for NH$_3$ storage on the SCR, since equimolar NH$_3$ and NO$_X$ amounts are needed for optimum LNT-SCR operation. The selectivity to N$_2$O was also high (11.8%) under these conditions, while CO and C$_3$H$_6$ conversions were relatively low (87.1 and 77.5%, respectively). Once again, we should point out that the data from this cycling condition were included only as a representative example because they demonstrate both the potential advantages and drawbacks of LNT operation under conditions favorable for NH$_3$ production. In subsequent sections, the NH$_3$ and N$_2$O trends will be discussed in more detail.
Figure 42. A 60 s lean/5 s rich cycling experiment performed at 300 °C, where the NO\textsubscript{X}, (■) NO\textsubscript{2}, (▲) N\textsubscript{2}O, (●) NH\textsubscript{3} and (x) CO concentrations are plotted as a function of cycle time.

Table 10. Summary of the cycling performance of the LNT catalyst at 300 °C (60 s lean/5 s rich).

<table>
<thead>
<tr>
<th></th>
<th>60/5</th>
</tr>
</thead>
<tbody>
<tr>
<td>X\textsubscript{NO\textsubscript{X}}</td>
<td>99.2 %</td>
</tr>
<tr>
<td>X\textsubscript{CO}</td>
<td>87.1 %</td>
</tr>
<tr>
<td>X\textsubscript{C\textsubscript{3}H\textsubscript{6}}</td>
<td>77.5 %</td>
</tr>
<tr>
<td>NO\textsubscript{X} Fed (lean)</td>
<td>214.8 μmol/cycle</td>
</tr>
<tr>
<td>NO\textsubscript{X} Stored</td>
<td>214.2 μmol/cycle</td>
</tr>
<tr>
<td>NO\textsubscript{X} Slip (total)</td>
<td>1.6 μmol/cycle</td>
</tr>
<tr>
<td>NO\textsubscript{X} Slip (rich)</td>
<td>1.1 μmol/cycle</td>
</tr>
<tr>
<td>NH\textsubscript{3} Produced</td>
<td>61.9 μmol/cycle</td>
</tr>
<tr>
<td>N\textsubscript{2}O Produced</td>
<td>12.5 μmol/cycle</td>
</tr>
<tr>
<td>Y\textsubscript{NH\textsubscript{3}}</td>
<td>28.8 %</td>
</tr>
<tr>
<td>Y\textsubscript{N\textsubscript{2}O}</td>
<td>5.8 %</td>
</tr>
<tr>
<td>S\textsubscript{NH\textsubscript{3}}</td>
<td>29.0 %</td>
</tr>
<tr>
<td>S\textsubscript{N\textsubscript{2}O}</td>
<td>11.8 %</td>
</tr>
<tr>
<td>S\textsubscript{N\textsubscript{2}}</td>
<td>59.2 %</td>
</tr>
</tbody>
</table>
3.4.3 CYCLE AVERAGED NO\textsubscript{X}, CO AND C\textsubscript{3}H\textsubscript{6} CONVERSIONS

The results shown in Fig. 43 summarize the cycle averaged NO\textsubscript{X} conversions measured in this investigation at different temperatures and under different lean/rich cycle timing protocols. These results indicate that with respect to NO\textsubscript{X} conversion the optimum operating temperature for this LNT catalyst is between 350 and 400 °C. Cycling conducted using a 60 s lean period resulted in cycle averaged NO\textsubscript{X} conversions over 80% from 300 – 450 °C temperature range. However as the extent of the lean period duration was increased, the temperature window for high NO\textsubscript{X} conversion was decreased. As a result, longer lean periods (e.g., 120 and 180 s, respectively) can only be used if the LNT catalyst is operated at, or very near, an optimum temperature of 350 – 400 °C. For all timing protocols investigated, dramatic decreases in the cycle averaged NO\textsubscript{X} conversion were observed at temperatures below 300 °C and above 450 °C. Under such conditions, higher cycle averaged NO\textsubscript{X} conversions were observed for longer rich periods in the low temperature regime (i.e., below 300 °C). By contrast at temperatures above 450 °C, the highest cycle averaged NO\textsubscript{X} conversions were observed for shorter (5 s) rich periods. The results for the two extreme cases (i.e., 250 and 500 °C) are further displayed in the two limiting cases displayed in Fig. 44.
**Figure 43.** Cycle averaged NO\textsubscript{X} conversions obtained for the LNT catalyst as functions of temperature for different lean/rich cycle timing protocols.
Figure 44. Cycle averaged NO\textsubscript{X} conversions obtained for the LNT catalyst for different lean/rich cycle timing protocols at 250 and 500 °C.

The results shown in Fig. 44 can be rationalized considering differences in the relative rates of NO\textsubscript{X} release and reduction as a function of temperature. For example, at 250 °C both the NO\textsubscript{X} release and its subsequent reduction take place at lower rates, which explains why longer, lower concentration rich doses are more effective. In this case, extending the rich period led to a significant increase in the cycle averaged NO\textsubscript{X} conversion from 59 to 87\% for a 60 s lean period with 5 and 15 s rich periods, respectively. While the rich period duration was increased, the total
number of moles of reductant was held constant, as discussed in the experimental section. Thus it becomes apparent that because of the slow NO\textsubscript{X} release and reduction kinetics a more extended temporal distribution of the reductants can optimize the NO\textsubscript{X} conversion characteristics of the LNT catalyst. At 500 °C, NO\textsubscript{X} release and reduction are no longer kinetically limited and as a result, shorter, high concentration rich doses are needed to effectively reduce the NO\textsubscript{X} that is rapidly released from the LNT catalyst. This behavior is not surprising since thermal release of NO\textsubscript{X} is favored even in the absence of a reducing agent at temperatures exceeding 470 °C for ceria containing LNTs [150]. In summary, longer, lower concentration rich doses result in higher NO\textsubscript{X} conversions at below 300 °C, while shorter, higher concentration rich doses achieve the same result at temperatures above 450 °C. Breen et al. [353] similarly observed increased NO\textsubscript{X} conversions for longer, lower concentration rich doses, but concluded that such timing protocols were always more effective regardless of the operating temperature. Al-Harbi et al. [354] also observed increased NO\textsubscript{X} conversions at 500 °C for shorter rich periods, but the effects in their case was more modest than what was observed over the LNT catalyst used in our study. Ultimately, Al-Harbi et al. [354] concluded that the simultaneous increase in NH\textsubscript{3} generation for the shorter, higher concentration, rich doses at high temperatures negated the benefits of increased NO\textsubscript{X} conversion. However in an LNT-SCR configuration, NH\textsubscript{3} generation can be mitigated by the downstream SCR catalysts and might even be desirable.

The cycle averaged CO and C\textsubscript{3}H\textsubscript{6} conversions are shown in Fig. 45. Since both the CO and C\textsubscript{3}H\textsubscript{6} conversions were largely insensitive to the cycle timing, only data for the 60 s lean period are shown. In all cases, the LNT catalyst exhibited low CO and C\textsubscript{3}H\textsubscript{6} conversions below 200 °C, indicating a low reactivity between these two reductants and NO\textsubscript{X} at these temperatures. This is consistent with previous results reported by Abdulhamid et al. [26], which indicate that
CO is not as effective as H\textsubscript{2} in reducing NO\textsubscript{X} at temperatures below 200 °C. Furthermore, more recent investigations by different groups [28,64,288,289,339] indicate that hydrolysis of isocyanates and hydrogen production via the WGS reaction exhibit significant activity above 250 °C, which may explain the higher consumption of CO observed in Fig. 45 at these temperatures. However, the most important factor for the higher CO conversions observed in the 300 – 500 °C temperature range may be the relative amounts of NO\textsubscript{X} stored and CO fed, as shown in Fig. 46, since it becomes apparent that at these temperatures, the CO conversion tracks very closely the amount of NO\textsubscript{X} stored on the LNT catalyst. Above 500 °C, where the thermal desorption of NO\textsubscript{X} becomes thermodynamically favored, the CO conversion is no longer strongly related to the amount of NO\textsubscript{X} stored, but it also appears to be affected by the WGS reaction equilibrium conversion, as implied by a comparison of the slopes of the two lines. The results in Fig. 46 suggest that CO may be involved in two parallel reactions; the direct reduction of stored NO\textsubscript{X} and the WGS reaction, which yields H\textsubscript{2} that can subsequently reduce stored NO\textsubscript{X}. The relative contribution appears to be dependent reduction temperature.

The C\textsubscript{3}H\textsubscript{6} cycle-averaged conversion curves shown in Fig. 45B resemble typical, steady-state light-off curves although the data were collected under cycling conditions. Once again, the differences due to the length of the rich cycle are minimal. In the absence of H\textsubscript{2}O, Abdulhamid et al. [26] reported that propylene shows limited activity towards the reduction of NO\textsubscript{X} when compared to CO and H\textsubscript{2} at 250 °C, but similar activity with the other two reductants at 350 °C. Furthermore, Resini et al. [355] reported that the steam reforming of propene over a Pd-Cu/Al\textsubscript{2}O\textsubscript{3} catalyst yielding CO and H\textsubscript{2}, which could reduce stored NO\textsubscript{X} as discussed previously, becomes significant at temperatures above 275 °C. Both reports appear to be consistent with the data of Fig. 45, which suggests increased activity above 200 °C, reaching complete conversion of
C₃H₆ at 350 °C. However, it is not possible to differentiate from this data between the amounts of C₃H₆ consumed during the direct reduction of NOₓ and the amount converted to CO and H₂ via steam reforming. Finally, the results of Fig. 45B indicate that hydrocarbon slip may represent a problem for LNT catalyst operation lower temperatures, where NH₃ formation is favored, as will be discussed below.

**Figure 45.** Cycle averaged CO (A) and C₃H₆ (B) conversions obtained for the LNT catalyst as functions of temperature for different lean/rich cycle timing protocols.
Figure 46. Cycle averaged CO conversion obtained for the LNT catalyst in comparison to the amount of NO\(_X\) stored and the WGS equilibrium conversion as a function of temperature (60 s lean / 5 s rich).

3.4.4 NH\(_3\) AND N\(_2\)O YIELD AND SELECTIVITY

The results shown in Fig. 47 summarize the cycle-averaged NH\(_3\) yield and NO\(_X\) slipped for the set of conditions considered in this investigation. This side by side comparison of NH\(_3\) yield and NO\(_X\) slipped can be used as an indicator of the feasibility of an LNT-SCR configuration, since in this setup NH\(_3\) stored downstream is used to reduce NO\(_X\) that “slips” from the LNT catalyst. Along these lines, the results shown in Fig. 47 demonstrate that it may be possible to select the appropriate temperature and cycling conditions to achieve the desired NO\(_X\) and NH\(_3\) amount reaching the SCR catalyst. For example, if the length of the lean period is set at 60 s and the catalyst temperature is 250 °C, the length of the rich period pulse can be used to control the amount of NH\(_3\) formed. When 10 or 15 s rich pulses are used, an NH\(_3\) yield of 46%
is observed, while the corresponding NOX slip is 21% and 13% of the total NOX fed, respectively. Since the SCR reaction requires a 1:1 NH3:NOX ratio, as shown Eqn. 18,

\[
4NH_3 + 4NO + O_2 \rightarrow 4N_2 + 6H_2O
\] (18)

under these conditions the amount of NH3 generated is approximately twice the amount needed to operated a downstream SCR catalyst.

Consequently, the SCR catalyst would quickly become saturated with adsorbed NH3 and significant concentrations of NH3 instead of NOX could appear in the final exhaust stream. This indicates that in this case the overall LNT-SCR configuration operates with excess reducing agent due to the longer than needed rich cycles. Not surprisingly then, when a 5 s rich cycle is used, the NOX slip is approximately 41%, while the NH3 yield is only 29%. In this case, more NOX would be slipped from the catalyst system than NH3. The downstream SCR catalyst would improve the cycled averaged NOX conversion, as previously observed by Lindholm et al. [338], but not all of the NOX slipped from the LNT could be converted to N2. In summary, the results shown in Fig. 47 can be used to determine the theoretical “best-case” scenario for an LNT-SCR configuration for a specific set of conditions, assuming that all of the NH3 produced over the LNT catalyst can be stored on the SCR and subsequently used to reduce NOX. However in practice, complete storage and reaction of the NH3 formed may not be possible. Further analysis of the results in Fig. 47 indicates the presence of two temperature ranges for potential application of concerted control of the cycling timing protocol in an LNT-SCR configuration: one between 250 and 300 °C, and the second between 400 and 450 °C. Significant NOX slip was observed below 250 °C and above 450 °C without sufficient NH3 formation observed to allow for
operation of a downstream SCR catalyst. On the other end of the spectrum, almost complete 
NO\textsubscript{X} conversion is observed between 300 and 400 °C; in this case, the NH\textsubscript{3} formed over the LNT catalyst represents a problem because very little NO\textsubscript{X} remains to react with NH\textsubscript{3} over the SCR catalyst.

Regardless of the length of the lean/rich cycle used, the NH\textsubscript{3} yield peaked at either 250 or 300 °C (Fig. 47), but NH\textsubscript{3} selectivity always reached a maximum at 250 °C, as shown in Fig. 48. The NH\textsubscript{3} selectivities measured at 250 °C are in excellent agreement with previously reported results by Ren and Harold [340] over a similar series of catalysts even though in their case H\textsubscript{2} was used as the reducing agent and CO\textsubscript{2} and H\textsubscript{2}O were not simultaneously present in the feed. In contrast, below 250 °C, Ren and Harold [340] reported significantly higher NH\textsubscript{3} selectivities than in our case most likely due to the use of H\textsubscript{2} and its higher reduction potential over CO for temperatures below 250 °C [26,356]. Furthermore, the narrow NH\textsubscript{3} selectivity maximum at 250 °C, for a variety of cycle timing and reductant concentration conditions, clearly illustrates that the selectivity to NH\textsubscript{3} is primarily controlled by the reaction temperature over the LNT catalyst used. At temperatures below 250 °C, the slow formation of surface isocyanates and the low rate of the WGS reaction, which represent the two most likely pathways to NH\textsubscript{3} formation [24,60,64,286,339], can account for the low NH\textsubscript{3} yields.
Figure 47. Cycle averaged NH$_3$ yield and NO$_X$ slip from the LNT catalyst as functions of temperature and lean/rich cycle timing.
Figure 48. Cycle averaged NH$_3$ selectivity obtained for the LNT catalyst as a function of temperature and lean/rich cycle timing.

Cycle-averaged N$_2$O yield and selectivity are shown as functions of temperature and cycle timing in Fig. 49. The results indicate that the N$_2$O yield shows a maximum at approximately the same temperature range as the NH$_3$ yield (i.e., 250 – 300 °C). As a result, N$_2$O production will be an issue if the LNT catalyst operates under the most favorable conditions for NH$_3$ production. In a recent publication however, Wang and Crocker [335] demonstrated that N$_2$O reduction over a downstream Cu-chabazite SCR catalyst can significantly reduce the amount of N$_2$O ultimately present in the exhaust of the overall after-treatment system; in their case, complete reduction of N$_2$O was reported at 315, 350 and 450 °C when H$_2$, NH$_3$ and CO, respectively, were used as the reducing agents. Furthermore, Wang and Crocker [335] reported significant decreases N$_2$O formation by 225 °C in an LNT-SCR configuration and complete removal by 275 °C. Consequently, one can conclude that the presence of a downstream SCR
catalyst will significantly reduce the amount of N$_2$O slipped from the LNT catalyst at temperatures above 250 °C, but N$_2$O slip will still be a problem at temperatures below 250 °C.

**Figure 49.** Cycle averaged N$_2$O yield (A) and selectivity (B) obtained for the LNT catalyst as functions of temperature and lean/rich cycle timing.
In comparison to NH$_3$ selectivity, the selectivity to N$_2$O did not exhibit a maximum but instead it decreased monotonically as the temperature was increased (Fig. 49B). Once again, changes in the lean/rich cycle timing had a relatively small impact on the N$_2$O selectivity, in agreement with the results discussed above for the NH$_3$ selectivity, further supporting the conclusion that the predominant factor controlling NH$_3$ and N$_2$O selectivity over the LNT catalyst is the operating temperature.

Finally, the NH$_3$ and N$_2$O yields can be affected by the NO$_X$ storage–reduction regime under which cycling is conducted. For example, the results shown in Fig. 50 depict two limiting cases for the NH$_3$ and N$_2$O yields. The cycle averaged NO$_X$ conversions observed under these conditions are shown in Fig. 44. As previously discussed, the NO$_X$ release and reduction kinetics were slower at 250 °C; therefore, longer, lower reductant concentration rich doses resulted in increased overall NO$_X$ conversions. The amount of NO$_X$ stored by the LNT catalyst at 250 °C also increased with the length of the rich cycle, with the 60 s lean/5 s rich and 60 s lean/15 s rich combinations resulting in 185 and 202 µmol of stored NO$_X$, respectively. As seen in Fig. 50, extending the length of the rich cycle also resulted in higher NH$_3$ and N$_2$O yields even though the reductant concentrations were lower in this case. Initially this result appears to contradict previous observations by Pihl et al. [351], where higher reductant concentrations resulted in increased NH$_3$ and N$_2$O yields. However, one has to consider that at lower temperatures the product distribution is significantly affected by the NO$_X$ release and reduction kinetics in addition to the reductant concentration. At 250 °C for example, the increased NH$_3$ and N$_2$O yields can be attributed to a combination of increased NO$_X$ conversion, which is affected by the length of the rich cycle, and constant selectivities to NH$_3$ and N$_2$O, which are almost independent of the length of the rich cycling duration (Figs. 48 and 49B). As a result, if
the NO\textsubscript{X} conversion and the amount of NO\textsubscript{X} stored increase without a significant change in the product selectivities, the yield to those products increases as well. Alternatively at 500 °C, the higher reductant concentrations used during shorter rich cycles results in both higher NO\textsubscript{X} conversions and higher NH\textsubscript{3} and N\textsubscript{2}O yields, consistent with the results reported by Pihl et al. [351]. In this case, the NO\textsubscript{X} stored on the LNT catalyst is released very quickly and high concentrations of reductant are needed to reduce all of the NO\textsubscript{X} released. The amount of NO\textsubscript{X} stored is also not affected by the length of the rich cycle, since the catalyst regeneration is very fast.

![Graphs showing NH\textsubscript{3} and N\textsubscript{2}O yields for different lean/rich cycle timing protocols at 250 and 500 °C.]

**Figure 50.** Cycle averaged NH\textsubscript{3} and N\textsubscript{2}O yields obtained for the LNT catalyst for different lean/rich cycle timing protocols at 250 and 500 °C.
At this point, it is important to differentiate between regeneration limited conditions (e.g., \( \leq 250 \text{ – } 300 \, ^\circ C \)) and storage limited conditions (e.g., \( \geq 450 \, ^\circ C \)), as previously discussed by Breen and Burch [16,353], because the kinetics of storage and regeneration have major implications on the observed catalytic performance for the production of \( \text{NH}_3 \), as indicated by our results. At low temperatures when \( \text{NO}_x \) release and regeneration are kinetically limiting, a longer, lower concentration rich cycle results in higher \( \text{NO}_x \) conversion than a shorter, higher concentration rich cycle because extending the length of rich cycle is critical for achieving complete regeneration. In this case, despite the lower selectivity to \( \text{NH}_3 \), more \( \text{NH}_3 \) is actually produced because of higher \( \text{NO}_x \) conversions. At higher temperatures, this is no longer the case and higher concentration, albeit short rich cycles, results in both higher \( \text{NH}_3 \) yield and selectivity, as previously reported by others [351,356].

### 3.4.5 Reactor Effluent Profiles

Concentration profiles for \( \text{NO}, \text{NO}_2, \text{NH}_3, \text{CO}, \text{N}_2\text{O} \) and \( \text{C}_3\text{H}_6 \) observed downstream of the LNT catalyst during a 5 s rich cycle following a 60 s lean cycle are shown for different temperatures in Fig. 51. As it becomes apparent from the results, these profiles vary significantly with temperature. For both \( \text{NO} \) and \( \text{NO}_2 \), for example, at temperatures above 450 \( ^\circ C \) maxima in the effluent concentrations are observed within the first 1-2 s following the switch to rich conditions. As previously reported [140,151], the reason for this behavior is that \( \text{NO}_x \) is released much faster than it is reduced. At 550 \( ^\circ C \), the maximum in the total \( \text{NO}_x \) concentration approached 4500 ppm, which is actually 9 times higher than the total \( \text{NO}_x \) concentration present in the feed. The \( \text{NO} \) and \( \text{NO}_2 \) profiles just prior to the switch to rich conditions at 60 s also demonstrate the poor storage capacity of the LNT at this temperature, since the \( \text{NO}_x \) concentration has already reached the feed concentration. At all other temperatures, with the
exception of 200 °C, where storage is significantly limited, very low breakthrough of NOX is observed prior to the onset of the rich period. Significant concentrations of NOX are also observed during the rich cycle downstream of the LNT catalyst in the lower temperature range (i.e., 200 – 300 °C). In this case however, the maxima are lower and are more evenly distributed during the entire rich cycle and even extend in to the first 1 – 2 s of the subsequent lean cycle. This behavior can be attributed to the lower reduction activity of the LNT catalyst at these temperatures.

The appearance of NH3 downstream of the LNT catalyst did not coincide with the onset of the rich cycle. Instead, a delay was observed at all temperatures examined; in fact, for temperatures above 350 °C, no NH3 was observed until approximately 4 sec into the 5 s rich cycle. This delay in NH3 breakthrough has previously been attributed to NH3 decomposition and oxidation and/or reaction with stored nitrites/nitrates as the NH3 propagates through the catalyst bed [23,286,351,352,356]. Since higher temperatures favor these NH3 reactions, especially for catalysts containing significant amount of OSC as in this case, the delay increases with reaction temperature. The CO concentration profiles closely matched the behavior observed for NH3, with the exception of the lower temperature studied (200 °C), where apparently no significant CO-NOX reaction takes place. The overall amount of CO in the LNT effluent stream reaches a minimum between 350 and 400 °C and then begins to increase as the temperature is further raised. The 350 – 400 °C temperature range represents the optimum operating temperature for this catalyst, where the amount of reductants fed most closely matches the amount of NOX stored. At higher temperatures (>450 °C), the NOX storage capacity of the LNT catalyst is reduced and as a result the reduction process becomes unbalanced during the rich cycle.
The C$_3$H$_6$ concentration profiles closely match those of CO at temperatures below 350 °C, which is consistent with results previously reported by Abdulhamid et al. [26] for H$_2$, CO and C$_3$H$_6$ at these temperatures. Above 350 °C, no C$_3$H$_6$ was observed in the effluent from the LNT catalyst. In contrast, CH$_4$ formation was observed starting at 350 °C, although the amount of CH$_4$ produced was relatively low. For example, the maximum CH$_4$ concentration did not exceed 150 ppm for any condition, yielding a cycled averaged concentration below 6 ppm. Hydrocarbon yields and selectivities can be rationalized via a complex network of parallel reactions incorporating oxidation, reforming and hydrogenolysis steps. The final concentration observed depends on the relative rates of these reactions, which change significantly with temperature and a detailed analysis of this network is beyond the scope of the current manuscript.

Finally, the N$_2$O profiles (Fig. 51) indicate the presence of N$_2$O in the effluent immediately after the transition from lean to rich conditions. At lower temperatures (i.e., ≤ 300 °C) an additional period of increased N$_2$O production was also observed during the transition from rich back to lean conditions. Results previously reported by Breen et al. [16] also showed two periods of N$_2$O production at 250 °C, but not 350 °C, in agreement with our results. In general, N$_2$O formation is believed to occur over LNT catalysts when low H$_2$/NO$_X$ ratios are present on the catalyst surface, frequently associated with transition from lean to rich environments [16,26,140,335,348,349]. At lower temperatures, where the N$_2$O generation is especially pronounced, NO dissociation occurs slowly and N$_2$O formation is favored through coupling of an adsorbed N and NO adatom, especially in the absence of high H$_2$ concentrations [16]. Conversely, NH$_3$ formation is favored at high H/NO$_X$ ratios, which are more likely to be present as regeneration proceeds in later stages of the rich cycle [140]. The NH$_3$ and N$_2$O
profiles shown in Fig. 51 are consistent with these previous postulations, with the production of N₂O and NH₃ generally being mutually exclusive. An alternative pathway for the production of N₂O during the rich to lean transition could be the reaction of residual surface isocyanates (NCO) with NO or O₂. We have previously reported the presence of surface NCO species during cycling studies over a model LNT catalyst even in the presence of H₂O at 250 °C [339] and have shown along with others [288] that these species can react with NO or O₂, yielding N₂O. The surface concentration of isocyanates is significantly reduced at temperatures above 300 °C, which coincides with the disappearance of N₂O during the rich to lean transition in the profiles of Fig. 51, providing further support to the hypothesis that an isocyanate-based reaction mechanism may be responsible for this second period of N₂O production.
Figure 51. LNT reactor effluent profiles for NO, NO$_2$, NH$_3$, CO, N$_2$O and C$_3$H$_6$ observed during a 5 s rich cycle following a 60 s lean cycle at different temperatures.
3.5 CONCLUSIONS

The results of the activity measurements performed in this study over a commercial catalyst and realistic lean/rich cycling conditions indicate the presence of two distinctly different kinetic regimes. At temperatures below 300 °C, NO\textsubscript{X} release and subsequent reduction were kinetically limiting. Therefore, longer, lower concentration rich pulses result in increased cycle averaged NO\textsubscript{X} conversions. For example, extending the rich cycle from 5 to 15 s at 250 °C, while holding the overall reductant amount constant, resulted in an increase in cycle averaged NO\textsubscript{X} conversion from approximately 59 to 87%, respectively. At temperatures above 450 °C, the opposite is true. Under these conditions, NO\textsubscript{X} release and reduction occurs rapidly and shorter, higher concentration rich pulses are needed to achieve high NO\textsubscript{X} conversions. For example, rich cycles of 5 to 15 s at 500 °C – once again, with a constant overall reductant amount – resulted in cycle averaged NO\textsubscript{X} conversions of approximately 76 and 54%, respectively. The selectivities to NH\textsubscript{3} and N\textsubscript{2}O are primarily functions of temperature and are higher at lower temperatures. The effect of cycle timing and reductant concentrations were of secondary importance on these selectivities. NH\textsubscript{3} and N\textsubscript{2}O yields however, are significantly affected by the cycling timing parameters, since these strongly affect NO\textsubscript{X} conversion as indicated above. The effects of cycling parameters are much less pronounced around the optimum operating temperature (i.e., 350 – 400 °C) of the LNT catalyst indicating that the maximum in NO\textsubscript{X} conversion observed under these conditions is fairly robust. Finally, concerted control of NH\textsubscript{3} generation by varying the lean/rich cycle timing was demonstrated. The most significant effects, in terms of both NO\textsubscript{X} conversion and NH\textsubscript{3} yield, were observed either by extending the rich cycle at lower temperatures (i.e., kinetically limiting regime) or by shortening the rich cycle at higher temperatures (i.e., storage limiting regime). In both cases, NH\textsubscript{3}/NO\textsubscript{X} ratios close to
stoichiometry could be obtained at the effluent of the LNT, demonstrating the potential for extending the region of operation with the utilization of a coupled LNT-SCR system. N₂O yields however, also increased with NH₃ yields, especially at low temperatures, indicating that an efficient LNT-SCR configuration will also need to covert N₂O downstream of the LNT catalyst.

3.6 ACKNOWLEDGEMENTS

A portion of this research was sponsored by the U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy, Vehicle Technologies Program. The authors thank program managers Ken Howden and Gurpreet Singh for their support. This manuscript has been co-authored by UT-Battelle, LLC, under Contract No. DE-AC05-00OR22725 with the U.S. Department of Energy. The United States Government retains and the publisher, by accepting the article for publication, acknowledges that the United States Government retains a non-exclusive, paid-up, irrevocable, world-wide license to publish or reproduce the published form of this manuscript, or allow others to do so, for United States Government purposes. Additionally, the authors would like to acknowledge the contributions of Wei Li, Chang Kim and Kushal Narayanaswamy of General Motors in addition to Davion Clark and Christopher Owens of Umicore for discussions and guidance in this portion of our research.
CHAPTER 4. PASSIVE-AMMONIA SELECTIVE CATALYTIC REDUCTION (SCR): UNDERSTANDING NH₃ FORMATION OVER CLOSE-COUPLED THREE WAY CATALYSTS (TWC)

4.1 PREFACE

In the passive-NH₃, TWC-SCR system, NH₃ is formed over a close-coupled three-way (TWC) during rich periods and then stored on a downstream selective catalytic reduction (SCR) catalyst for use in a subsequent lean period. NH₃ formation over TWCs during steady-state operation is well known, but NH₃ formation during cycling is poorly understood. In this investigation, NH₃ formation under steady-state and lean/rich cycling conditions was investigated using four commercial catalysts including: 1.) a Pd-only, high precious metal loading (HPGM) catalyst, 2.) a Pd/Rh + CeO₂, low (LPGM) catalyst, 3.) a combination of the HPGM and LPGM (Dual-Zone) catalysts and 4.) a lean NOₓ trap (LNT) operated as a TWC. NH₃ formation during steady-state operation was shown to be dependent on the AFR (air-to-fuel ratio), temperature and catalytic formulation. Generally, the NH₃ yield decreased as follows: HPGM ≥ Dual-Zone >> LPGM ≈ LNT. Catalysts containing Rh and/or CeO₂ generally produced less NH₃, but all of the formulations could produce significant amounts of NH₃ if operated under sufficiently rich conditions. The AFR was determined to be a sensitive parameter that could be used to tune NH₃ generation. At higher temperatures, progressively richer AFRs were necessary to achieve high NH₃ yields. During cycling, richer AFRs were required to generate NH₃ in comparison to the steady-state results. The HPGM catalyst demonstrated the most robust NH₃ formation in comparison to the amount of NOₓ slipped for all of the
temperatures considered, with an optimum operating region from approximately 400 to 450 °C. At moderate temperatures (275 – 500 °C), inclusion of NO\textsubscript{X} storage capacity (i.e., results collected for the LNT) dramatically increased the amount of NH\textsubscript{3} produced in relation to the amount of NO\textsubscript{X} slipped, even though the LNT catalyst generally exhibited the lowest NH\textsubscript{3} yield for steady-state operation. This implied that inclusion of an “optimum” amount of NO\textsubscript{X} storage capacity could significantly improve the performance of the TWC-SCR system. CO slip was observed under all conditions favorable for NH\textsubscript{3} generation, and with therefore need to be addressed. N\textsubscript{2}O formation, on the other hand, was generally insignificant for temperatures above 400 °C, which is a unique advantage of TWC-SCR system.

4.2 INTRODUCTION

Lean-burn engines are more fuel efficient and produce less CO\textsubscript{2} than traditional, stoichiometric-burn ones [1,282,357,358]. Unfortunately, a fleet-wide implementation of lean-burn engines has not occurred because the development of cost effective catalysts capable of meeting current emissions regulations under lean-burn exhaust conditions still represents a major technical challenge. Since the late 1970s, three-way catalysts (TWC) have been employed for the simultaneous reduction of nitrogen oxides (NO\textsubscript{X}) and oxidation of unburned hydrocarbons and carbon monoxide (CO) present in engine exhaust. However, TWCs only sufficiently remediate pollutants if operated in a very narrow region near the stoichiometric combustion regime and exhibit very low NO\textsubscript{X} conversion if operated under the high O\textsubscript{2} conditions encountered in lean-burn engine exhausts [279]. Two existing solutions for the reduction of lean exhaust NO\textsubscript{X} include lean NO\textsubscript{X} trap (LNT) and NH\textsubscript{3}-selective catalytic reduction (NH\textsubscript{3}-SCR) catalysts. Operation of these systems has been summarized in several recent reviews [2,4,6,279,359,360].
Briefly, LNTs are designed for operation in periodic lean (≈60 s) and rich (≈5 s) environments. During lean periods, NO is oxidized to NO₂ over precious metal sites (e.g., Pt, Pd, Rh) and then subsequently stored on an alkali or alkali-earth storage component (e.g., Ba) in the form of nitrites or nitrates [22,339]. As storage elapses, the storage component becomes saturated with NOₓ and a brief rich period must be employed to regenerate the catalyst and convert stored NOₓ to N₂. Commercial formulations include relatively high weight loadings of Pt (≈2 – 3 wt%), with smaller amounts of Pd and/or Rh, supported on a Ba containing high surface area γ-Al₂O₃ [4,135]. Conversely, NH₃-SCR catalysts do not rely on cycling strategies and instead operate through the selective reaction of NH₃ with NOₓ in the presence of large amounts of excess oxygen, where NH₃ is typically provided via on-board storage of urea – which is rapidly hydrolyzed to NH₃ under automotive exhaust conditions [2]. Commercial SCR catalytic formulations typically include V₂O₅-WO₃/TiO₂ or Cu/Fe exchanged zeolites [2,279,359,360]. In Europe, V₂O₅-WO₃/TiO₂ based formulations were introduced in 2005 for heavy-duty diesel applications, but high activity for SO₂ oxidation, toxicity of volatile vandia species (>650 °C) and poor activity and selectivity above 550 °C generally make the zeolite based formulations more attractive for lean-gasoline applications [360]. Zeolite-based catalysts also store significantly more NH₃ than their V₂O₅ based counterparts [341,343]. Initially, commercialization of zeolite based SCR catalysts was limited because of substantial problems related to hydrothermal stability, but recent advances in zeolite technology have led to the discovery of hydrothermally stable, small pore, metal-exchanged zeolites that are active over a broad temperature range [342,344]. Stabilization of the zeolite structure using a metal oxide coating has also been demonstrated [361].
Both LNT and SCR technologies suffer from different, but significant drawbacks. For example, LNT catalysts require high platinum group metal (PGM) loadings, which results in a significant cost per catalyst, and they are also particularly susceptible to sulfur poisoning; therefore, periodic, high-temperature regenerations schemes are required that can partially degrade LNT performance [4,359]. NH₃-SCR catalysts are comparatively inexpensive, but the dosing system required to deliver urea to the exhaust stream is expensive and does not seem practical for smaller gasoline engines. The urea dosing system also requires on-board storage of urea to function (e.g., a 30-litre tank) and customer resistance to the additional “fuel” tank, the lack of existing infrastructure, a relatively high freezing point (approx. -12 °C) and long-term stability issues (>32 °C) are all topics of considerable concern. With these considerations, NH₃-SCR is emerging as the key technology for large vehicle applications, while LNT catalysts are favored for smaller engines [359].

Recently however, researchers at GM have demonstrated a new technology referred to as the “passive-ammonia” or “urealess” SCR approach [282,357,358,362–364]. As in the case of LNT systems, the passive-NH₃ approach is based on periodic lean-rich cycling mode of operation, but does not include an LNT catalyst. Instead, a close-coupled TWC is used to generate NH₃ during periods of rich operation. The NH₃ is then stored on a downstream, under-floor SCR catalyst. After a sufficient amount of NH₃ has been stored, the engine switches back to lean operation and the stored NH₃ is used to reduce NOₓ that slips un-reacted from the upstream TWC. This is particularly attractive in gasoline applications because it allows the vehicle resort back to stoichiometric operation if necessary. Ultimately, the successful operation of the passive approach relies on the following factors: 1.) robust and selective NH₃ generation over the TWC, 2.) significant storage of NH₃ on the downstream SCR catalyst, 3.) efficient
utilization of stored NH\textsubscript{3} for NO\textsubscript{X} reduction and 4.) optimization of the required lean/rich engine timing, where a higher ratio of lean to rich time increases efficiency gains.

Of these, the selective generation of NH\textsubscript{3} over the TWC is arguably the most important aspect of the passive-NH\textsubscript{3} approach. While the potential for NH\textsubscript{3} formation over TWCs is well known [120], early research efforts were focused on avoiding NH\textsubscript{3} formation. Even so, subsequent reactor screening experiments [365–367], engine chassis dynamometer studies [368–372] and tunnel investigations [373–375] confirmed NH\textsubscript{3} slip from vehicles equipped with TWCs, where NH\textsubscript{3} generation was not necessarily expected under typical operating conditions. Heeb et al. [371,372] clearly demonstrated that NH\textsubscript{3} was produced as a secondary pollutant over the TWC and was not generated by the engine. They further argued that NH\textsubscript{3} standards should be included in future regulations. While NH\textsubscript{3} slip from TWCs may be unfavorable in the traditional sense, in this case the main goal is to produce NH\textsubscript{3} over the TWC for use in a downstream SCR catalyst.

In this manuscript, we focus on NH\textsubscript{3} generation over a series of TWCs including: a high PGM, low PGM, dual-zone TWC and a TWC with NO\textsubscript{X} storage capacity. The catalysts were evaluated under both steady-state and lean-rich cycling conditions using commercial monolithic cores loaded into a bench-core reactor. The effects of catalytic formulation, temperature and steady-state vs. cycling conditions on NH\textsubscript{3} generation will be discussed.

4.2 EXPERIMENTAL

4.2.1 CATALYSTS

Four fully formulated cores (wash-coated honeycomb cordierite monoliths) were used in the present investigation and have been summarized in Table 11. Three of the cores were
obtained from a commercial 1.3 L TWC that is employed in a 6-speed, Chevy Malibu (Model Year: 2009). The catalyst design was constructed using a dual-zone approach, where the front and rear sections were intentionally synthesized using different formulations. The first 62 mm (0.6 L) section of the monolith is a Pd-only, high platinum group metal (HPGM), Pd-only TWC (0/4/0 g of Pt/Pd/Rh, respectively) and the rear 73 mm (0.7 L) section is a low platinum group metal (LPGM), Pd/Rh TWC (0/0.8/0.21 g Pt/Pd/Rh, respectively – which also contained CeO₂).

In this case, the HPGM catalyst, the LPGM catalyst and the combination of the two were independently evaluated, where the HPGM catalyst was placed upstream of the LPGM catalyst in the Dual-Zone designation – as is the case on the vehicle.

**Table 11.** Elemental compositions of the four catalysts used in this investigation.

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Cat. Volume (on vehicle) (L)</th>
<th>PGM loading (g/L of Pt/Pd/Rh)</th>
<th>Oxygen Storage Capacity (OSC)</th>
<th>NOₓ Storage Capacity (NSC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.) High PGM TWC</td>
<td>0.6</td>
<td>0/6.7/0</td>
<td>No</td>
<td>No</td>
</tr>
<tr>
<td>2.) Low PGM TWC</td>
<td>0.7</td>
<td>0/1.14/0.3</td>
<td>Yes (CeO₂-based)</td>
<td>No</td>
</tr>
<tr>
<td>3.) Dual-Zone (1+2)</td>
<td>1.3</td>
<td>0/3.7/0.16</td>
<td>Yes (CeO₂-based)</td>
<td>No</td>
</tr>
<tr>
<td>4.) LNT as TWC</td>
<td>2.6</td>
<td>2.2/0.8/0.3</td>
<td>Yes (CeO₂-based)</td>
<td>Yes (Ba-based)</td>
</tr>
</tbody>
</table>

In addition to the TWCs, a lean NOₓ trap catalyst (LNT) was evaluated under identical conditions as the TWCs. Obviously, the LNT also included a significant amount of NOₓ storage capacity (NSC) – leading to the designation: TWC with NSC. The LNT catalyst is employed in a lean-GDI, BMW 120i (Model year: 2009). More detailed information regarding the characterization of this catalyst can be found in a recent manuscript [376]. Briefly, semi-quantitative metals screening conducted using ICP-MS (inductively coupled plasma mass spectroscopy) conducted at Galbraith Laboratories confirmed Mg, Al, Ce and Ba as major
components, with other elements of interest including: Zr, La, Pt, Pd, and Rh. Subsequent electron microscopy with complementary elemental analysis exposed three compositionally distinct grains including: a Ce/Zr mixed oxide domain, a Mg/Al mixed oxide domain and an Al oxide domain. In this case, Pt, Pd and Ba all seemed to be preferentially deposited on the Ce/Zr domain.

4.2.2 Evaluation

Catalytic evaluation was performed using a laboratory bench-flow reactor, as described in more detail elsewhere [135,376]. Briefly, the monolithic cores were tightly wrapped in Zetex insulation tape and inserted into a horizontal quartz tube reactor. The quartz tube was heated using a horizontal bench-top furnace (Lindberg/Blue M). Gas mixtures were prepared using pressurized gas cylinders (UHP, Air Liquide) and a bank of mass flow controllers (Unit Instruments Series 7300, Kinetics Electronics). A rapid switching 4-way valve system was used to alternate between the lean and rich gas mixtures, when necessary. Water was introduced using a peristaltic pump (Cole-Parmer) that fed into a heated, flash-vaporization zone held at 350 °C. All gas lines downstream of the water introduction zone were heated and quartz chips were placed upstream of the monolithic core to ensure that the feed gas temperature reached the set point temperature prior to contacting the catalyst. Three thermocouples were used to measure the temperature. The first was placed 1 cm upstream of the core and was used to record the inlet/set-point temperature. The second thermocouple was placed in the middle of the monolithic core and was used to record the actual monolith temperature. The third was placed 1 cm downstream of the core and was used to record the temperature exiting the core. After exiting the reactor, the gas was fed to an MKS MultiGas™ 2030 HS FT-IR analyzer, which allowed for continuous tracking (5 Hz) of NO, NO₂, N₂O, NH₃, CO, C₃H₆, CO₂ and H₂O. Prior to the
reactor measurements, the as-received catalyst was “de-greened” at 700 °C in a humidified air (2.7% H₂O) mixture for 16 h to establish reproducible performance.

STEADY-STATE EXPERIMENTS

Steady-state experiments were conducted in order to measure NH₃ formation over TWCs as a function of catalytic formulations and temperature and compare the results to those obtained during cycling. A realistic gas mixture containing: 0.15% NO, 1.8% CO, 0.60% H₂, 0.10% C₃H₆, 5% CO₂, 5% H₂O and variable amount of oxygen was used, where the oxygen content was systematically changed in order to vary the air to fuel ratio (AFR). The inlet gas temperature was varied from 150 to 550 °C, in 50 °C increments, at a space velocity (S.V.) of 75,000 hr⁻¹, where the monolithic core volume (≈0.8” x 0.45”, W x L) was used to calculate the required flow rate necessary to achieve the desired S.V. The reductant ratio was set to 18:6:1 for CO:H₂:C₃H₆, respectively, which is representative of rich-tune engine exhaust. In this case, an AFR of 14.59 was calculated to represent stoichiometric operation for the previously described gas mixture containing 1.59% O₂. Table 12 summarizes the conditions for steady-state operation, where the corresponding AFR varies with the O₂ content as previously described. The NOₓ conversion, CO conversion and C₃H₆ conversion were calculated using equations 19 – 21.

\[
X_{NO_X} = \frac{\int NO_{Fed} - \int NO_{Slipped}}{\int NO_{Fed}} \times 100
\]  (19)

\[
X_{CO} = \frac{\int CO_{Fed} - \int CO_{Slipped}}{\int CO_{Fed}} \times 100
\]  (20)

\[
X_{C_3H_6} = \frac{\int C_3H_6_{Fed} - \int C_3H_6_{Slipped}}{\int C_3H_6_{Fed}} \times 100
\]  (21)
In the case of steady state operation, the integral can be simplified as shown in Eqn. 22, where the average NO\textsubscript{X} concentration at steady state is divided by the feed concentration.

\[
x_{NO_{X}} = \left(1 - \frac{NO_{X,SS}}{NO_{X,Fed}}\right) \times 100
\]  

(22)

Similarly, Eqns. 23-26 were used to calculate the NH\textsubscript{3} and N\textsubscript{2}O yield and selectivity, respectively.

\[
Y_{NH_{3}} = \frac{\int NH_{3,Produced}}{\int NO_{X,Fed}} \times 100
\]  

(23)

\[
S_{NH_{3}} = \frac{\int NH_{3,Produced}}{\int NO_{X,Fed} \times X_{NO_{X}}} \times 100
\]  

(24)

\[
Y_{N_{2}O} = \frac{\int N_{2}O_{Produced}}{\int NO_{X,Fed}} \times 100
\]  

(25)

\[
S_{N_{2}O} = \frac{2 \times \int N_{2}O_{Produced}}{\int NO_{X,Fed} \times X_{NO_{X}}} \times 100
\]  

(26)

In the case of selectivity, NO\textsubscript{X} was excluded as a product and the total number of moles of N\textsubscript{2}, NH\textsubscript{3} and N\textsubscript{2}O formed was determined by multiplying the total NO\textsubscript{X} fed by the cycle averaged NO\textsubscript{X} conversion, which was calculated using Eqn. 19. The calculations were performed in this manner because N\textsubscript{2}, and other diatomic molecules (e.g., O\textsubscript{2} and H\textsubscript{2}), cannot be measured using the FT-IR gas analyzer.
Table 12. Reaction conditions for the steady-state catalytic evaluation of TWCs, with calculated AFRs and \( \lambda \) values.

<table>
<thead>
<tr>
<th>AFR ((AFR = \frac{mass_{air}}{mass_{fuel}}))</th>
<th>( \lambda ) (= \frac{AFR_{act}}{AFR_{stoich}} )</th>
<th>( O_2 ) (%)</th>
<th>( NO ) (%)</th>
<th>( CO ) (%)</th>
<th>( H_2 ) (%)</th>
<th>( C_3H_6 ) (%)</th>
<th>( CO_2 ) (%)</th>
<th>( H_2O ) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>14.59</td>
<td>1.000</td>
<td>1.590</td>
<td>0.15</td>
<td>1.8</td>
<td>0.60</td>
<td>0.10</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>14.54</td>
<td>0.996</td>
<td>1.525</td>
<td>0.15</td>
<td>1.8</td>
<td>0.60</td>
<td>0.10</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>14.52</td>
<td>0.995</td>
<td>1.510</td>
<td>0.15</td>
<td>1.8</td>
<td>0.60</td>
<td>0.10</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>14.40</td>
<td>0.987</td>
<td>1.340</td>
<td>0.15</td>
<td>1.8</td>
<td>0.60</td>
<td>0.10</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>14.20</td>
<td>0.973</td>
<td>1.060</td>
<td>0.15</td>
<td>1.8</td>
<td>0.60</td>
<td>0.10</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>14.00</td>
<td>0.960</td>
<td>0.790</td>
<td>0.15</td>
<td>1.8</td>
<td>0.60</td>
<td>0.10</td>
<td>5</td>
<td>5</td>
</tr>
</tbody>
</table>

**CYCLING EXPERIMENTS**

The TWCs were also analyzed under lean/rich cycling conditions, where cycle timing was fixed according to the NO\(_X\) concentration. The rich and lean-NO\(_X\) concentrations exiting a lean-burn engine under these conditions were estimated to be 1500 ppm and 750 ppm, respectively using a recent publication by Parks et al. [377]. As a point of reference, this rich:lean NO\(_X\) ratio of 2:1 is fairly conservative if compared to recent data published by Kašpar et al. [279]. The cycle timing was then fixed so that equivalent amounts of NO\(_X\) were delivered in the lean and rich periods. The rich period duration was set to 20 s, which corresponded to a 40 s lean period for equivalent NO\(_X\) delivery at a S.V. of 75,000 hr\(^{-1}\), as in the case of the steady-state experiments. Similarly, the inlet gas temperature was varied from 150 – 550 °C, in 50 °C increments. Two rich phase concentrations were selected for investigation. The first corresponded to an AFR ratio of 14.4, which is slightly rich. The second corresponded to an AFR of 14.2, which was richer than the first case, but not so rich that a significant fuel penalty would result [357]. The gas concentrations for the lean and rich cycling experiments are shown in Table 13. The cycle averaged NO\(_X\), CO, C\(_3\)H\(_6\) conversions and NH\(_3\) and N\(_2\)O yield and selectivity, respectively, were calculated using Eqns. 19 – 21 and 23 – 26 using the last 4 cycles after the periodic steady state had been achieved, as demonstrated previously [376].
Table 13. Reaction conditions for lean/rich cycling evaluation of TWCs, with calculated AFRs and $\lambda$ values.

<table>
<thead>
<tr>
<th>AFR</th>
<th>$\lambda$</th>
<th>Duration (s)</th>
<th>$O_2$ (%)</th>
<th>NO (%)</th>
<th>CO (%)</th>
<th>$H_2$ (%)</th>
<th>$C_3H_6$ (%)</th>
<th>$CO_2$ (%)</th>
<th>$H_2O$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lean</td>
<td>24.00</td>
<td>1.65</td>
<td>40</td>
<td>8.0</td>
<td>0.075</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>5</td>
</tr>
<tr>
<td>Rich 1</td>
<td>14.40</td>
<td>0.987</td>
<td>20</td>
<td>1.34</td>
<td>0.15</td>
<td>1.8</td>
<td>0.60</td>
<td>0.10</td>
<td>5</td>
</tr>
<tr>
<td>Rich 2</td>
<td>14.20</td>
<td>0.973</td>
<td>20</td>
<td>1.06</td>
<td>0.15</td>
<td>1.8</td>
<td>0.60</td>
<td>0.10</td>
<td>5</td>
</tr>
</tbody>
</table>

4.4 RESULTS AND DISCUSSION

4.4.1 Steady-state NH$_3$ formation

**Effluent Gas Profiles at 250 °C**

The results shown in Fig. 52 demonstrate the effluent gas concentrations for NO$_X$, NH$_3$, N$_2$O, CO and C$_3$H$_6$ during steady-state operation over the HPGM, Pd-only TWC (Fig. 52A) and LPGM, Pd/Rh TWC (Fig. 52B) as a function of the AFR. The inlet gas temperature, measured 1 cm in front of the TWC, was set to 250 °C. During operation, the lowest mid-core temperature under these conditions was approximately 430 °C, 180 °C higher than the inlet temperature, which demonstrates that co-feeding reductants in the presence of O$_2$ (where the O$_2$ conc. was adjusted in order to vary the AFR) resulted in a significant exotherm over TWCs. For stoichiometric operation (i.e., AFR = 14.59), the exotherm approached 250 °C.

Fig. 52 also shows that the product distribution obtained over TWCs was strongly dependent on the AFR. For stoichiometric operation, both the CO and NO$_X$ conversion exceeded 99.8% and the exiting concentrations of NO$_X$, CO and C$_3$H$_6$ were effectively zero. However, a slight change in the AFR resulted in dramatic changes in the concentrations of NO$_X$ and CO observed in the reactor effluent. C$_3$H$_6$, on the other hand, was not observed in the AFR.
range considered in this investigation, nor were any other hydrocarbons; however, it is expected that a significant amount of the C₃H₆ being fed is being converted to CO over these catalysts, especially under rich conditions. Tagliaferri et al. [378] previously reported similar results for C₃H₈ conversion under similar conditions. Even though the AFR was expected to dramatically affect the product distribution, the acute sensitivity of the TWCs to the operating conditions, especially for lean operation, was quite impressive. For example, when the AFR was tuned very slightly lean (e.g., AFR=14.63 or \(\lambda=1.003\)) over the HPGM catalyst, the NO\(_X\) conversion plummeted to 44%. Similar behavior was observed over the LPGM catalyst, but the NO\(_X\) conversion only dropped to 73% in that case. As Taylor [379] previously explained, Rh demonstrates high activity for the selective reduction of NO\(_X\) to N\(_2\), even under slightly lean environments. Therefore, the higher NO\(_X\) conversion over the LPGM case under lean conditions can most likely be attributed to the presence of Rh on the catalyst. The LPGM catalyst also produced less N\(_2\)O than the HPGM catalyst under slightly lean conditions, where significantly higher levels of N\(_2\)O formation over Pd/Al\(_2\)O\(_3\) in comparison to Rh/Al\(_2\)O\(_3\) have previously been reported [380]. The presence of CeO\(_2\) on the LPGM catalyst may have also suppressed N\(_2\)O formation, as previously reported by Oh [381].

During rich operation (i.e., AFR<14.59), both of the TWCs produced NH\(_3\) and slipped CO. Over the HPGM catalyst, the concentration of CO slipped as the AFR was tuned from 14.59 to 14.4 increased linearly, but subsequently richer operation resulted in an exponential increase in the concentration of CO slipped. NH\(_3\) formation over the HPGM catalyst similarly increased as the AFR was decreased from 14.59 to 14.4. Progressively richer operation did result in minimal increases in the NH\(_3\) yield, but >95.0% of the incoming NO\(_X\) had already reacted to form NH\(_3\) by an AFR of approximately 14.35. The results obtained over the LPGM
catalyst were generally similar, but the NH$_3$ yield was noticeably lower. For example at an AFR of 14.4, the NH$_3$ yield was only 54.0% over the LPGM catalyst in comparison to 90.0% over the HPGM catalyst under the same conditions. Even when operated under significantly richer environments, the LPGM catalyst never reached the high NH$_3$ yields observed over the HPGM catalyst. Conversely, the amount of CO slipped under rich conditions over the LPGM catalyst was lower in comparison to the HPGM case if compared at an AFR of 14.2.

It should be noted, that under these conditions of low NH$_3$ yield that neither N$_2$O or NO$_X$ were observed, which once again suggests that the N$_2$ yield was increasing for the Rh and CeO$_2$ containing LGPM. Schlatter et al. [120] previously explained that the main role of Rh in TWCs was to selectively reduce NO$_X$ to N$_2$ instead of NH$_3$. They demonstrated that Rh-only TWCs generated significantly less NH$_3$ than Pd/Rh or Pt/Rh TWCs under rich conditions. Furthermore, when the Pt and Rh TWCs were physically separated and the Rh catalyst was placed upstream of the Pt catalyst, significantly less NH$_3$ was generated than when Pt catalyst was placed upstream of the Rh catalyst. These results clearly demonstrate that Rh-only and Rh promoted TWCs more selectively reduce NO$_X$ to N$_2$ under rich conditions. This is in agreement with an earlier publication by Kobylinski et al. [382], where Pt and Pd catalysts mainly produced NH$_3$ under rich conditions, while Rh and Ru catalysts were significantly more selective towards N$_2$ formation.
Figure 52. Effluent gas concentrations for ( ) NO\textsubscript{X}, ( ) NH\textsubscript{3}, ( ) N\textsubscript{2}O, ( ) CO and ( ) C\textsubscript{3}H\textsubscript{6} over (A) HPGM, Pd-only TWC and (B) LPGM, Pd/Rh TWC, respectively. (S.V. 75,000 hr\textsuperscript{-1}, Inlet Temp. = 250 °C, Reaction conditions shown in Table. 12).
Figure 53. Effluent gas concentrations for (♦) NO\textsubscript{X}, (○) NH\textsubscript{3}, (X) N\textsubscript{2}O, (■) CO and (▲)C\textsubscript{3}H\textsubscript{6} over (A) Dual-Zone TWC and (B) LNT as TWC, respectively. (Same conditions as Fig. 52).
The presence of CeO$_2$ on the LPGM catalyst may also be significant as CeO$_2$ has previously been reported to: preserve noble metal dispersion, increase the thermal stability of the support, promote water gas shift (WGS) activity and steam reforming, store and release oxygen, and promote CO oxidation [383]. CeO$_2$ has also been reported to enhance NO decomposition, via spillover of oxygen onto the partially reduced CeO$_2$, and favorably alter the kinetics for CO oxidation and NO$_X$ reduction [379]. In this case, the CeO$_2$ on the LPGM catalyst appeared to affect the WGS activity, where the CO concentration at an AFR of 14.2 was approximately 4000 ppm instead of 5000 ppm for the LPGM and HPGM catalysts, respectively. Unfortunately, as discussed by Kaspar et al. [383], the role of CeO$_2$ in the NO/H$_2$ or NO/H$_2$/CO reaction on TWCs is still unclear and very few investigations have addressed the issue [384,385]. Therefore, further comments regarding the role of CeO$_2$ on NH$_3$ formation under rich conditions over the LPGM catalyst cannot be made. Given the extensive nature of research performed on TWCs, the reader is referred to the following reviews for a more exhaustive discussion on the effects of CeO$_2$ and Rh on TWC performance and/or specifics of TWC operation [2,279,379,383,385–387].

In summary, Fig. 52 clearly demonstrates that the AFR is a sensitive parameter that can be used to tune NH$_3$ generation over TWCs. This is important because in the passive NH$_3$, TWC-SCR approach, selective NH$_3$ generation over the close-coupled TWC will ultimately dictate operation conditions (i.e., cycle timing) for the downstream SCR catalyst. Additionally, the desired NH$_3$ yield can be balanced using a threshold limit for CO slip deemed to be tolerable. For example, steady-state operation of the HPGM catalyst at an AFR ratio of 14.2 would result in a slightly higher NH$_3$ yield, but the concentration of CO slipped from the TWC under these conditions would also be an order of magnitude higher than for operation at an AFR of 14.4.
Lastly, while CO slip can be minimized, it cannot be eliminated merely by tuning the AFR, as CO was observed under all conditions favorable for NH$_3$ generation over the TWCs.

Fig. 53 depicts the results collected over the Dual-Zone TWC (Fig. 53A) and over the LNT as TWC (Fig. 53B), respectively. As discussed in Section 4.2.1, the Dual-Zone TWC was a combination of the HPGM and LPGM catalysts placed in series, where the HPGM catalyst was always placed upstream of the LPGM catalyst. Interestingly, the NH$_3$ profile observed over the Dual-Zone catalyst was effectively identical, within experimental error, to the NH$_3$ profile observed over the HPGM catalyst (Fig. 52A). This is a strong indication that both NO$_x$ reduction and NH$_3$ formation occurred in the front section of the Dual-Zone catalyst over the HPGM section. While NH$_3$ formation over the downstream LPGM catalyst cannot be excluded, it is unlikely because, as previously discussed, this catalyst was significantly less selective for NH$_3$ formation. Furthermore, if the majority of NH$_3$ was indeed produced over the HPGM section, this indirectly suggests that NH$_3$ decomposition over the Rh and CeO$_2$ containing LPGM section did not occur, at least at these temperatures. While Kobylinski et al. [382] previously reported NH$_3$ decomposition over Rh and Ru containing TWCs, significant activity was not observed until 500 °C if CO was present in the gas mixture. In this case, the AFRs most favorable for NH$_3$ generation yielded corresponding catalyst temperatures below 470 °C and CO was always observed during NH$_3$ generation, as previously discussed. Conversely, the amount of CO slipped over the Dual-Zone catalyst under rich conditions was reduced and more closely resembled the results obtained over the LPGM catalyst (Fig. 52B), where higher WGS activity was previously suggested to account for the lower CO concentrations. These results are consistent with an earlier report by Schlatter et al. [120], where the NH$_3$ concentration profile as a function of the oxygen concentration obtained over a Rh catalyst placed upstream of a Pt
catalyst was nearly identical to the monometallic Rh catalyst. Similarly, the NH₃ profile obtained over a Pt catalyst placed upstream of a Rh catalyst was nearly identical to the monometallic platinum catalyst. Taken together, this indicates that the Dual-Zone catalyst may be able to combine the high NH₃ yield of the HPGM catalyst and lower CO slip of the LPGM catalyst, which are both desirable attributes of a TWC in the passive-NH₃, TWC-SCR approach.

The results obtained over the LNT as TWC are shown in Fig. 53B, where the NH₃, NOₓ and CO profiles generally mirror results obtained over the LPGM catalyst. Again, similarities in the LNT and LPGM catalyst formulations most likely explain why analogous behavior was observed. Unfortunately, C₃H₆ breakthrough was observed for AFRs below 14.3. This behavior was not expected, but could be explained because LNT catalysts are typically operated at significantly lower SVs than TWCs and the dip-coating procedure may have been altered accordingly. Additionally, the LNT catalyst contained Pt as a primary component instead of Pd, where Pd has long been reported to exhibit better activation of HCs than Pt [27,112,279].

**Quantified NH₃ Yield (150–550 °C)**

The results shown in Fig. 54 compare the quantified NH₃ yield as a function of the mid-core temperature at a constant AFR over the entire family of TWCs considered in this investigation. In all cases, the inlet temperature, prior to contacting the catalyst, was varied between 150 °C to 550 °C. As Fig. 54 demonstrates however, the mid-core temperature was always considerably higher than the set point temperature, as previously observed in Figs. 52 and 53. This shifted the temperature range of consideration from 150 to 550 °C to approximately 350 to 700 °C. While this may appear to be on the high side, close-coupled TWCs can experience temperatures as high as 900 – 1100 °C and operation from 350 – 700 °C was therefore viewed to be a representative temperature range [15]. Recent engine dynamometer
results collected using a federal test procedure (FTP) drive cycle (data omitted for brevity) confirmed that the average operating temperature for a close coupled TWC ranged from 400 – 500 °C, with excursions up to 700 °C.

Fig. 54A displays the richest condition considered (AFR = 14.0) and demonstrates that all of the TWCs considered in this investigation generated significant amounts of NH₃ over a broad temperature window if they are operated under sufficiently rich conditions. In this case, the HPGM, Pd-only TWC clearly generated the most NH₃, over the widest temperature range, but the Dual-Zone catalyst also generated significant amounts of NH₃ and was generally indistinguishable from the HPGM catalyst until the temperature exceeded 500 °C. Interestingly, the difference in the NH₃ yield between the HPGM and Dual-Zone catalyst occurred at approximately the same temperature as Kobylinski et al. [382] previously reported significant activity for NH₃ decomposition over Rh containing TWCs. Since the rear section of the Dual-Zone formulation was based on a Pd/Rh/CeO₂ combination, NH₃ decomposition over the downstream LPGM section could explain why lower NH₃ yields were observed at higher temperatures. Decreased NH₃ yield over the LPGM catalyst in comparison to the HPGM catalyst was also clearly evident, where the HPGM catalyst always produced more NH₃ than the LPGM catalyst even for the lowest temperatures considered. Similarly, decreased NH₃ yield over the LPGM catalysts was most likely caused by the presence of Rh and/or CeO₂ [120]. Fig. 54A also clearly demonstrates the similarities in operation between: (1) the HPGM and Dual-Zone catalyst and (2) the LPGM and LNT, as previously discussed (Figs. 52 and 53).
Figure 54. Quantified NH$_3$ yield as a function of catalyst temperature for AFRs of (A) 14.0, (B) 14.2 and (C) 14.4.
When the AFR ratio was increased from 14.0 to 14.2 (Fig. 54B), the differences in performance between the catalytic formulations became much more pronounced and only the HPGM catalyst maintained a high NH₃ yield over the entire temperature range. In all other cases, a significant decline in the NH₃ yield was observed. This is especially apparent for the LPGM and LNT catalysts for temperatures above 550 °C and reasonable NH₃ yields were only observed over a fairly narrow temperature range from 400 to 525 °C. Similarly, when the AFR was increased from 14.2 to 14.4 (Fig. 54C), even more significant impacts on the NH₃ yield were observed. Now, even the HPGM catalyst was unable to maintain a high NH₃ yield over the entire temperature range. In summary, Figs. 52-54 have shown that the AFR ratio, catalyst temperature and catalytic formulation are all sensitive parameters that dictate the amount of NH₃ that can be generated over TWCs. Generally, the NH₃ yield decreased as follows: HPGM ≥ Dual-Zone >> LPGM ≈ LNT, where tuning the AFR progressively closer to stoichiometric operation resulted in less NH₃ production in all cases. The differences between the catalytic formulations also became more pronounced as the operating conditions approached stoichiometric operation. This conclusion is more clearly seen in Fig. 55, where operation of the HPGM, Pd-only catalyst (i.e., the catalyst with the highest NH₃ yield used in this investigation) required subsequently richer and richer AFRs to achieve maximum NH₃ yield as the inlet gas temperature was increased.
The mechanism for NH$_3$ formation over Pt, Pd and Rh catalysts has long been reported to proceed via hydrogenation of a N adatom by dissociatively adsorbed H$_2$ [382,386,388–391]. For example, Pirug and Bonzel [388] reported an increase in the N$_2$, N$_2$O, NH$_3$ and H$_2$O concentrations at approximately 170 °C during reaction of NO + H$_2$ over a Pt foil for a H$_2$/NO ratio of 0.5. This temperature corresponded almost identically to the dissociation temperature for NO over the same foil and led the authors to conclude that NO dissociation must precede the formation of N$_2$, N$_2$O and NH$_3$. They also noticed little NH$_3$ formation for a H$_2$/NO ratio of 0.5, but significant NH$_3$ formation when the H$_2$/NO ratio was increased to 5, which indicated that a high H$_2$/NO ratio on the metal surface in addition to NO dissociation was required for NH$_3$ formation. Similar results have also been reported over Pd [389] and Rh [390]; but in the case of
Rh, NH₃ decomposition was observed by 325 °C. This is in excellent agreement with the CO-free results reported by Kobylniski et al. [382] over supported Rh catalysts. Gahndi et al. [392] similarly observed minimal NH₃ decomposition over Pt and Pd catalysts at approximately 500 °C, but significant (>80%) NH₃ decomposition over a Ru catalyst by 370 °C.

These features of the NH₃ formation mechanism are clearly evident in Figs. 52-55, where high reductant to NOₓ ratios favored NH₃ formation at intermediate temperatures. Under those conditions, NO dissociation occurs rapidly and NH₃ decomposition is slow. At elevated temperatures, higher NH₃ yields were observed for formulations where catalytic NH₃ decomposition was less likely. For temperatures below 400 °C, N₂O was also observed, but the yield was generally insignificant. This behavior was initially counterintuitive since rich operation implies a high H₂/NO ratio and N₂O formation should therefore be unlikely. However, as the temperature was decreased, NO dissociation most likely becomes rate-limiting – where the temperature for NO dissociation has been reported between 125 – 225 °C [388–390] – and the likelihood that a N adatom will react with a molecularly adsorbed NO instead of another N adatom increases.

4.4.2 NH₃ FORMATION DURING LEAN/RICH CYCLING

LEAN/RICH CYCLING PROFILES AND NH₃ YIELDS

The preceding sections demonstrated the potential for NH₃ formation over all four of the catalysts investigated, where changes in the catalyst formulation, temperature and AFR all affected the amount of NH₃ that could be formed. However, these results were obtained during steady-state operation under a constant rich environment. In the passive-NH₃, TWC-SCR approach, the TWC must also be able to generate significant amounts of NH₃ during lean/rich cycling. The results shown in Fig. 56 demonstrate lean/rich cycling over the HPGM, Pd-only
TWC for a rich period AFR ratio of 14.2. The top left pane shows the NO, NO₂ and NOₓ concentration profiles collected over 4 representative lean/rich cycles at 250 °C, where the first 40 s represents lean operation, followed by 20 s of rich operation. As previously discussed, this cycle timing was chosen in order to keep the total number of moles of NOₓ delivered during lean and rich periods the same. As shown, NOₓ breakthrough during lean operation (e.g., 0 - 40 s) occurred rapidly over the HPGM TWC. The sigmoidal shape of the NOₓ breakthrough curve indicated that some NOₓ storage was taking place, even though the HPGM TWC does not contain Ba as a NOₓ storage component. Furthermore, the effluent NOₓ concentration at the end of the lean period was only 680 ppm instead of 750 ppm, which provided additional evidence of NOₓ storage. At lower temperatures, NOₓ storage on the TWC might be expected, since significant NOₓ storage on Al₂O₃ has previously been reported for temperatures below 300 °C [33]. At 40 s, the conditions were switched back to rich operation. As in the case of LNT catalysts, a NOₓ spike was observed at the lean to rich interface. Over LNT catalysts, the decomposition of stored nitrites/nitrates has been reported to occur more rapidly than NOₓ reduction at these lean/rich interfaces [140,151]. Additionally, slower NOₓ reduction over partially oxidized metal sites has also been reported to contribute to NOₓ slip [6]. In this case, it would appear that similar NOₓ release mechanisms were occurring over the TWC and co-feeding NOₓ during the rich period may have made NOₓ release even more likely.

During rich periods, the effluent NOₓ concentration was always zero, excluding the brief period of NOₓ slip, which indicated that NOₓ reduction during rich periods even under lean/rich cycling was facile. The corollary N₂O, CO and NH₃ concentration profiles for lean/rich cycling
Figure 56. Lean/rich cycling over the HPGM, Pd-only TWC at 250 and 500 °C, respectively. (Reaction conditions shown in Table 13: Lean/Rich2 – AFR=14.2).

at 250 °C are shown in the bottom portion of the left-hand pane in Fig. 56. In this case, an N₂O spike was observed at the lean/rich transition, which rapidly decreased as the rich period continued. Again, N₂O formation over LNT catalysts has been shown to be a strong function of temperature and the ratio of adsorbed N and NO adatoms to reductants [140,151,346,349,351,356]. At the beginning of the rich period, the stored NOₓ was rapidly released and N₂O was formed until a net reducing environment was attained, where comparison between the concurrently decreasing N₂O and increasing CO concentrations supports this assessment. Significant amounts of NH₃ were also produced during the rich periods. In this
case, the peak concentration exceeded 2000 ppm. Since only 1500 ppm of NO\textsubscript{X} was fed during rich periods, peak values exceeding 1500 ppm implied that the NO\textsubscript{X} stored on the TWC could be converted to NH\textsubscript{3}. As the rich period progressed, the NH\textsubscript{3} concentration declined because all of the stored NO\textsubscript{X} had been consumed. If the rich period duration had been extended, the NH\textsubscript{3} and CO concentration values would have eventually reached the steady-state concentrations.

At 500 °C, NO\textsubscript{X} breakthrough occurred even more rapidly and a nearly-rectangular step-function for the NO\textsubscript{X} profile was observed, which implied that very little NO\textsubscript{X} was stored at this temperature. However, and surprisingly, minimal NO\textsubscript{X} storage was still observed. The transition from lean to rich conditions at 500 °C also resulted in a significantly higher NO\textsubscript{X} slip concentration, where any NO\textsubscript{X} stored over Al\textsubscript{2}O\textsubscript{3} under these conditions would most likely be released extremely rapidly. Similarly, N\textsubscript{2}O formation was observed at the lean/rich interface, but the concentration was significantly reduced, where higher temperatures generally favor less N\textsubscript{2}O formation during cycling [351]. The amount of CO slipped also decreased. This was most likely the result of higher activity for the water gas shift (WGS) reaction at this temperature. In both cases (250 and 500 °C), complete NO\textsubscript{X} conversion was observed during rich periods and therefore cannot explain increased CO consumption. Alternatively, deeper oxidation of the support and/or precious metals during lean periods could potentially contribute to increased CO consumption at higher temperatures [393]. At 500 °C, NH\textsubscript{3} production was delayed until approximately 5 s into the rich period. Then, the NH\textsubscript{3} concentration rapidly increased and the average concentration observed during the last 5 s of the rich period was approximately 1350 ppm. Under steady-state conditions, the average NH\textsubscript{3} concentration for an AFR of 14.2 was approximately 1300 ppm, while the average CO concentration was approximately 3600 ppm. As Fig. 56 demonstrates however, the CO concentration was still in a state of rapid transience when
the rich period was ended. If the rich period had been extended, the CO and NH₃ would eventually reach the steady-state values as previously discussed. Another key feature is that the NH₃ reaches its maximum value considerably faster than CO, which suggests that the timing can be adjusted to maximize NH₃ formation while reducing the CO slip. In summary, one particularly desirable feature of the HPGM TWC is its ability to rapidly produce significant amounts of NH₃ that are virtually identical to the steady-state values, even during cycling.

The NOₓ and NH₃ profiles observed in Fig. 56 were then integrated and averaged over four cycles to obtain the cycled averaged NOₓ slip and NH₃ yield. The ratio of these was then used as an additional metric for catalyst performance, as shown in Eqn. 27.

\[
\alpha = \frac{\int NH₃_{produced}}{\int NOₓ_{slipped}}
\]  

(27)

For example if \( \alpha = 1 \), the amount of NH₃ produced during the rich period is equal to the amount of NOₓ slipped during the lean period and a TWC-SCR system constructed using a “perfect” SCR catalyst (i.e., an SCR catalyst that could trap all of the NH₃ produced and then use 100% of that NH₃ for NOₓ reduction) would achieve 100% NOₓ conversion. In reality, a perfect SCR catalyst does not exist, but the cycle averaged \( \alpha \) was used to determine the most promising operating conditions and catalysts.

The results shown in Fig. 57 display the cycle averaged \( \alpha \) obtained for the HPGM catalyst as a function of temperature for rich AFRs of 14.4 and 14.2, respectively, where the solid dashed line demonstrates the critical \( \alpha \geq 1 \) threshold. Unfortunately for the AFR of 14.4 (with minimum associated fuel penalty), an \( \alpha \geq 1 \) was not observed for any of the temperatures considered, even though significant amounts of NH₃ could be formed under these same conditions during steady-state operation (Fig. 54C). In fact, NH₃ formation above 350 °C for the rich AFR of 14.4 was especially poor. This is an important result because it implies that richer
AFRs are required during cycling in comparison to steady-state operation. Generally, operation as close as possible to stoichiometric regime during rich periods is desired because it minimizes the rich period fuel penalty, but clearly an AFR of 14.4 will not suffice. The differences in NH₃ formation between cycling and steady-state can most likely be attributed to H₂/CO/C₃H₆ oxidation reactions that occur during the first few seconds of rich operation before a net reducing environment is achieved, where the reductants consumed during this time could otherwise be used for production of NH₃ under steady-state conditions. Reduction of OSC, reduction of oxidized precious metal sites and reaction of reductants in the concentration front that propagates through the catalyst bed during the lean/rich transition could all contribute to reductant consumption. As a side note, even the LNT (14.4 AFR data omitted for brevity) – where NOₓ storage capacity, as shown in Fig. 61, can dramatically increase the NH₃ to NOₓ ratio – never

**Figure 57.** The cycle averaged $\alpha$ as a function of temperature for rich period AFRs of 14.4 and 14.2, respectively.
achieved an $\alpha \geq 1$ for a rich AFR of 14.4. This provides even more substantial evidence that the slightly rich AFR of 14.4 will most likely never generate enough NH$_3$ during cycling to warrant operation under these conditions. For this reason, only results for rich AFRs of 14.2 were reported, with the exception of the results shown in Fig. 57.

For a rich AFR of 14.2, an $\alpha \geq 1$ was obtained from approximately 275 – 425 °C, which clearly demonstrates that the HPGM catalyst can generate enough NH$_3$ during cycling to theoretically operate a downstream SCR catalyst when operated under sufficiently rich conditions in an appropriate temperature range. At 350 °C, the cycle averaged $\alpha$ reached a maximum at 1.47, which further supports the previous conclusion of NO$_X$ storage capacity over the HPGM TWC (Fig. 56). In this case, an $\alpha > 1$ confirmed NO$_X$ storage because equivalent doses of NO$_X$ were fed in lean and rich periods and the upper limit for $\alpha$ would therefore be 1.0 unless some of the NO$_X$ fed during lean periods was stored and converted to NH$_3$ during a subsequent rich period. In a similar investigation, Li et al. [357] reported an AFR of 14.2 to be the optimum rich condition for lean/rich cycling, which agrees well with the results reported here.

The results shown in Figs. 58 and 59 depict corollary lean/rich cycling experiments conducted over the LPGM and LNT as TWC, respectively. The NO$_X$ profiles obtained during lean periods over the LPGM catalyst (Fig. 58) were very similar to the profiles obtained over the HPGM catalyst, which implied that the loading and ratio of precious metals on the TWCs did not have a significant impact on performance during lean periods. However, the results obtained over the LPGM catalyst during rich periods were dramatically different. For example at 250 °C, the peak NH$_3$ concentration approached 1700 ppm, which was above the feed NO$_X$ concentration (1500 ppm) and additionally confirmed NO$_X$ storage over the LPGM catalyst, but was substantially
lower than the peak \( \text{NH}_3 \) concentration observed for the HPGM catalyst. The corresponding cycle averaged \( \alpha \) for the LPGM catalyst at this temperature was 0.9, where the cycle averaged \( \alpha \) for the HPGM catalyst under the same conditions was 1.47. This indicated that the LPGM formulation would either require a longer rich time or a richer, rich period to generate the same amount of \( \text{NH}_3 \) as the HPGM catalyst. Li et al. [358] previously reported similar results for a Pd-only and Pd/Rh TWC and concluded that the Pd-only catalyst may be preferred in the TWC-SCR even though Pd/Rh catalysts have long been used for TWC-only configurations. The CO concentration profile obtained over the LPGM catalyst also displayed interesting behavior, where CO breakthrough occurred rapidly and approached 7000 ppm before declining briefly to 2000 ppm and then increasing back to 7000 ppm. The dip in the CO concentration can most likely be explained by the OSC capacity provided by \( \text{CeO}_2 \) on the LPGM catalyst, where Feio et al. [394] previously reported that reduction of \( \text{CeO}_2 \) on a Pd/\( \text{CeO}_2/\text{Al}_2\text{O}_3 \) catalyst did not begin until approximately 300 °C. Since the furnace temperature in this case was set to 250 °C, it is likely that reduction of \( \text{CeO}_2 \) was delayed until the catalyst temperature reached a temperature high enough to reduce \( \text{CeO}_2 \). Fig. 60 displays the temperature profiles for the four TWCs considered in this investigation and demonstrates the increase in temperature as a function of the rich period duration. In all cases, a 150 °C exotherm was observed by the end of the rich period. At 250 °C, light-off for the HPGM and Dual-Zone catalyst occurred more rapidly than light-off for the LPGM and LNT catalyst, respectively. At 500 °C, a dip in the CO concentration was not observed. Above 300 °C, temperature inhibited CO consumption should not occur since the catalyst temperature is well above 300 °C. \( \text{NH}_3 \) formation at this temperature was also substantially suppressed, where the peak concentration was only 200 ppm and declined throughout the rich period. This corresponded to a cycle averaged \( \alpha \) of only 0.08. Clearly,
lean/rich cycling conducted over the LPGM catalyst at elevated temperatures resulted in very poor NH$_3$ yields, which further indicates that the LPGM formulation may be a particularly poor candidate for the TWC-SCR approach. Substantially lower NH$_3$ yields for the Rh containing LPGM TWC were also observed for the steady-state experiments, as previously discussed (4.4.1), and were previously attributed to higher rates of NO dissociation and/or NH$_3$ decomposition over Rh [43,47].

**Figure 58.** Lean/rich cycling over the LPGM, Pd/Rh TWC at 250 and 500 °C, respectively. (Same conditions as Fig. 56).
The results for lean/rich cycling over the LNT are shown in Fig. 59, where a substantial number of publications [4,6] provide detailed examples of cycling results obtained over LNT catalysts. However in this case, the required cycle timing was substantially different from the usual LNT cycle timing protocol. We additionally wanted to clearly contrast cycling over TWCs in comparison cycling over LNT catalysts, since a relatively small number of publications [56,62,235,358,362] have provided examples of cycling over TWCs. For example at 250 °C, the NO\textsubscript{X} profile over the LNT (Fig. 59) visibly depicts storage, where considerable storage was expected since the LNT catalyst contains Ba as a NO\textsubscript{X} storage component. By the end of the
lean period, the outlet NOX concentration was only 500 ppm and integration of the NOX profile confirmed that approximately 75% of the NOX fed during the lean period was stored. During the subsequent rich period, a significant amount of NH3 was generated and the corresponding α was 1.82, where the α for the HPGM catalyst under the same conditions was 1.47. This is quite a significant result because a review of the steady-state results (Fig. 54B) would lead to the expectation of lower NH3 yields over the LNT in comparison to the HPGM catalyst. This was not the case and demonstrates that NOX storage capacity on the TWC is one way to alter the catalytic formulation to increase NH3 formation during rich periods. A dip in the CO concentration was also observed, where reduction of stored NOX in addition to reduction of OSC on the LNT could account for the additional CO consumption during rich periods. It is encouraging to note that this delay is not observed with all reductants, particularly NH3. It may suggest that the reduction of the OSC occurs more preferentially with CO than with NH3. At 500 °C, the LNT catalyst still stored NOX, but significantly less (approximately 50% of the NOX fed during the lean period was stored). This translated in to an improved NH3 yield during the subsequent rich period in comparison to the LPGM catalyst (which mirrored the LNT catalysts under steady state operation), but the cycle averaged α was still only 0.20, while the α for the HPGM catalyst under the same conditions was 0.65. Again, a comparison of the results collected under steady-state condition would lead to the expectation of lower NH3 yields over the LNT in comparison to the HPGM catalyst, as observed at 500 °C. In summary, incorporation of NOX storage capacity could not overcome the inherently lower NH3 production capabilities of the LNT catalyst at elevated temperatures.
As previously mentioned, the results in Fig. 60 depict the mid-core catalyst temperature profiles for the four catalysts under consideration at 250 and 500 °C, respectively, as also shown in Figs. 56, 58 and 59. In both cases, the catalyst cooled during the first 40 s (e.g., lean
operation) to the furnace set point. At 40 s, the catalyst was switched back to rich operation and a rapid exotherm was observed. By the end of the 20 s rich period, the catalyst had approximately reached the temperature measured under steady-state conditions, which indicated that a rich period lasting longer than 20 s would be expected to yield both the product distribution and catalyst temperature exhibited under steady-state operation.

The results shown in Fig. 61 summarize the cycle averaged $\alpha$ values measured for all four catalysts as a function of temperature, where the dashed line again indicates the critical $\alpha \geq 1$ threshold. The LPGM catalyst generally exhibited the lowest NH$_3$/NO$_X$ yields of all the catalysts considered in this investigation. The LPGM catalysts also exhibited a narrow temperature region for an $\alpha \geq 1$, where sufficient NH$_3$ could only be produced from approximately 325 °C to 400 °C. The Dual-Zone catalyst and HPGM catalyst exhibited nearly identical NH$_3$/NO$_X$ yields, with the HPGM catalyst being slightly better at lower temperatures. The HPGM and Dual-Zone catalyst also exhibited a very similar temperature region with favorable NH$_3$/NO$_X$ yields. However at higher temperatures, the Dual-Zone catalyst became noticeably inferior to the HPGM catalyst. Again, NH$_3$ decomposition over the downstream Pd/Rh/ CeO$_2$ TWC likely consumed some of NH$_3$ formed on the upstream HPGM portion of the Dual-Zone catalyst [382]. While subtleties existed between the TWCs, a maximum $\alpha$ was generally observed between 300 – 400 °C with an optimum operation window between 275 – 425 °C. The maximum $\alpha$ for the TWCs also never exceeded 1.47 (HPGM), under these conditions. The LNT catalyst on the other hand, exhibited a maximum $\alpha$ at 400 °C and was able to maintain an $\alpha \geq 1$ for a larger temperature range from approximately 275 to 500 °C. The cycle averaged $\alpha$ near the optimum was especially pronounced and almost 5 times more NH$_3$, in comparison to the amount of NO$_X$ slipped, was produced over the LNT catalyst. This is
additionally encouraging because this dramatic improvement was observed over a catalyst that demonstrated relatively poor NH₃ generation capabilities under steady-state operation, especially when compared to the HPGM catalyst. Therefore, the results in Fig. 61 clearly demonstrate that adding an “optimal” amount of NOₓ storage capacity to a TWC could substantially increase the NH₃/NOₓ yield and make the operation of passive TWC-SCR more efficient. Currently, the “optimal” amount of NOₓ storage capacity has not been investigated. Sulfur poisoning of Ba sites at elevated temperatures [35,105] and long-term, high-temperature stability of the Ba storage component (e.g., formation of BaAl₂O₄) [162,192] will also need to be addressed, where the addition of CeO₂ may decrease losses in NOₓ storage capacity in both cases [180,234,395].

**Figure 61.** The cycle averaged α as a function of temperature for the HPGM, LPGM, Dual-Zone and LNT catalysts. (Rich period AFR = 14.2).
**CYCLE AVERAGED NO\textsubscript{X}, CO AND C\textsubscript{3}H\textsubscript{6} CONVERSIONS AND N\textsubscript{2}O YIELD**

The results shown in Fig. 62 summarize the cycle averaged NO\textsubscript{X}, CO and C\textsubscript{3}H\textsubscript{6} conversion for all of the catalysts considered in this investigation. In the TWC-SCR system, the NO\textsubscript{X} (and potentially C\textsubscript{3}H\textsubscript{6} [334]) conversion would be improved by the inclusion of a downstream SCR catalyst. Conversely, the CO conversion would most likely not improve in the TWC-SCR system because additional CO oxidation/conversion over the downstream SCR catalyst under a net rich environment is highly unlikely unless the WGS reaction [396] and NH\textsubscript{3}-SCR reaction occur simultaneously. For example, even in the presence of O\textsubscript{2}, CO oxidation over a Cu-ZSM5 catalyst at 250 °C was minimal [397], while CO oxidation over a Pd/CeO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3} (0.155/20%, w/w) catalyst under similar conditions had approximately reached complete conversion [398]. Therefore, the cycled average NO\textsubscript{X} conversion for the TWC-SCR system would be higher, but the CO and C\textsubscript{3}H\textsubscript{6} conversions will most likely be very similar to the values reported here.

As previously discussed, cycle averaged NO\textsubscript{X} conversions exceeding 50%, as designated by the dashed line, confirmed NO\textsubscript{X} storage on the catalysts. The results obtained over the LNT were most pronounced and a cycled averaged NO\textsubscript{X} conversion of approximately 90% was measured near the optimum operating temperature for that particular catalyst [376]. Generally, NO\textsubscript{X} was stored on all of the catalysts considered, at least up to 500 - 550 °C; by 600 °C, the NO\textsubscript{X} storage capacity had been eliminated even for the LNT catalyst. Direct NO decomposition over reduced precious metal sites could also occur after the catalyst was switched back to lean operation, but if occurring, this phenomenon would be expected to occur for a very brief period and account for minimal increases in the amount of NO reduced, since Amirnazmi, Benson and Boudart [399] reported a strong inhibiting effect for O\textsubscript{2} on NO decomposition.
Figure 62. The cycled averaged NO\textsubscript{X}, CO and C\textsubscript{3}H\textsubscript{6} conversion as a function of temperature for the HPGM, LPGM, Dual-Zone and LNT catalyst. (Rich period AFR = 14.2).
Below 300 °C, the LPGM and LNT catalyst exhibited especially poor overall performance in comparison to the HPGM and Dual-Zone catalyst and correspondingly lower cycle averaged NO\textsubscript{X}, CO and C\textsubscript{3}H\textsubscript{6} conversions were measured. In this case, the lower PGM loadings on the LPGM and LNT catalyst most likely explain this behavior. For example, it is generally accepted that the easiest way to improve the low-temperature activity of a TWC is to increase the PGM loading [279]. As a result, the HPGM and Dual-Zone catalyst offered more robust performance as the temperature was decreased and complete NO\textsubscript{X} conversion during rich periods was still observed for the lowest temperatures considered. Alternatively, the LPGM and LNT catalysts slipped significant amounts of NO\textsubscript{X} during rich period, which explains why the NO\textsubscript{X} conversion dropped below 50% for these catalysts. Additionally, complete light-off was not observed below 250 °C and in both cases the rich period temperature exotherm was below 100 °C, while the HPGM and Dual-Zone catalysts exhibited a temperature exotherm of approximately 150 °C. For complete light-off, an exotherm of approximately 150 °C was expected, as further demonstrated in Fig. 60. This further indicated that the LPGM and LNT catalyst underwent a longer and slower light-off process at the lowest temperatures considered, which ultimately resulted in poor overall performance.

The results obtained for the cycle averaged CO conversions were quite complex. As discussed, the poor CO conversion below 300 °C for the LPGM and LNT catalyst can most likely be explained by the lower activity of those catalysts at low temperatures. For the HPGM and Dual-Zone catalyst, this is not the case and the higher CO conversion was most likely a combination of rapid CO oxidation and NO\textsubscript{X} reduction. As the temperature was increased above 300 °C, the WGS reaction most likely explains the additional increase in CO conversion that was observed. Light-off for the WGS reaction over a Pt/Al\textsubscript{2}O\textsubscript{3} catalyst was previously reported to
occur around 275 °C [383]. Nova et al. [64] similarly reported significant WGS activity over a Pt/Ba/Al₂O₃ LNT catalyst by 300 °C. Reduction of stored NOₓ, especially for the LNT catalyst at lower temperatures, could also contribute to CO consumption, and therefore makes deconvolution of the different effects even more difficult. As the temperature was increased above 450 °C, the CO conversions for all of the catalysts were effectively identical. This behavior was not surprising since all of the catalysts were highly active for CO oxidation, NOₓ reduction and the WGS reaction under these conditions. The NOₓ storage capacity also begins to decrease at these temperatures and the controlling factor for the measured CO conversion becomes the equilibrium conversion of the WGS reaction. The results for C₃H₆ conversion demonstrate a more typical light-off curve profile even though these results were collected under cycling conditions, which demonstrated that C₃H₆ conversion is primarily controlled by temperature. Abdulhamid et al. [27] previously reported significant activity for C₃H₆ above 350 °C, but poor utilization of the HC for lower temperatures, as also observed here. Again, differences in the C₃H₆ conversion measured at low temperature were most likely due to differences in PGM loadings.

In summary, comparison of the results in Fig. 61 with the results of Fig. 62 imply an optimum operating temperature for the TWC between 400 to 450 °C. In this fairly narrow regime, the cycled averaged NOₓ conversion was high, all of the catalysts could stored some NOₓ, the cycled averaged \( \alpha \) was generally \( \geq 1 \) (expect for the LPGM catalyst), a maximum in CO conversion was observed and lastly propylene conversion was 100%. Above 500 °C, the increased NOₓ conversion provided via NSC was eliminated, the CO conversion began to decline (since both the WGS equilibrium conversion declines and less NOₓ is stored) and only the HPGM catalyst generated enough NH₃ to yield a reasonable cycle averaged \( \alpha \). At lower
temperatures (275 – 400 °), the cycled averaged \( \alpha \) was generally higher, but the CO conversion was significantly lower and \( \text{C}_3\text{H}_6 \) slip also became a problem under these conditions. Crocker et al. [334] previously reported that the conversion of \( \text{NO}_x \) by \( \text{C}_3\text{H}_6 \) and \( \text{NH}_3 \) was additive, but the amount of \( \text{C}_3\text{H}_6 \) stored in comparison to \( \text{NH}_3 \) was quite low so the majority of \( \text{C}_3\text{H}_6 \) might still be slipped from the SCR under these conditions. Therefore, operation at lower temperatures would only be feasible if the lean/rich cycle timing could be increased as a result of increased \( \text{NH}_3 \) production, which would limit the amount of CO and \( \text{C}_3\text{H}_6 \) released because less time would be spent operating rich.

The results shown in Fig. 63 depict the cycle averaged \( \text{N}_2\text{O} \) yield measured for all of the catalysts considered in this investigation. At low temperatures, a fairly significant amount of \( \text{N}_2\text{O} \) was formed, especially for the LPGM catalyst. Pihl et al. [351] previously observed that low temperatures favored \( \text{N}_2\text{O} \) formation over LNT catalysts. Burch and coworkers [3,16,400] similarly explained that at lower temperatures, NO dissociation occurs more slowly and therefore favors \( \text{N}_2\text{O} \) formation either through coupling of an adsorbed N and NO adatom or through an adsorbed \( \text{(NO)}_2 \) dimer. Bowker et al. [401] measured the sticking coefficient for NO on a Pd(110) surface and observed a decrease in the sticking coefficient with increasing temperatures and proposed that \( \text{N}_2\text{O} \) formation was favored at lower temperatures because the lifetime of molecular NO on the surface was longer. Obuchi et al. [389] similarly observed \( \text{N}_2\text{O} \) formation over a Pd foil at low temperatures, but \( \text{N}_2\text{O} \) formation over a Rh foil [390] was below the detection limit. The effect of catalyst formulation on \( \text{N}_2\text{O} \) formation has also been observed by Macleod et al. [380]. More recently, Ji et al. [140] discussed the role of the regeneration/oxidation front on \( \text{N}_2\text{O} \) formation, where transition from lean/rich or rich/lean
results in a reaction front that passes over the catalyst bed and alters the H/NO ratio on the metal surface.

In this case, the LNT catalyst generally produced the most N$_2$O, with the exception of results collected at the lowest temperature considered. Since the LNT is basically a TWC with Ba, it would appear that the addition of NSC increased the amount of N$_2$O formed. One potential reason for this behavior could be the “sea” of stored NO$_X$ present on the catalyst when regeneration begins, which in turn increases the likelihood of high NO$_X$/H ratios during this transition. As the temperature was increased, the formation of N$_2$O decreased. By 400 °C, the formation of this undesirable global warming pollutant was substantially decreased. At the highest temperatures considered, N$_2$O formation was negligible. While N$_2$O was formed, the downstream SCR catalyst may actually further decrease the N$_2$O yields in the combined TWC-SCR system, as Wang and Crocker et al. [335] recently reported N$_2$O reduction over Cu-zeolite catalysts. Lastly, the simultaneous low N$_2$O yields for high NH$_3$ yields offered by the TWC-SCR system is potentially one of the most attractive aspects of this system because similar screening investigations conducted for LNT-SCR systems concluded that NH$_3$ and N$_2$O yields peaked under almost identical conditions for LNT catalysts [340,376].
Figure 63. The cycled averaged N₂O yield as a function of temperature for the HPGM, LPGM, Dual-Zone and LNT catalyst. (Rich period AFR = 14.2).

4.5 CONCLUSIONS

NH₃ formation under steady-state and lean/rich cycling conditions was investigated using a HPGM, LPGM, Dual-Zone and LNT catalyst operated as a TWC. NH₃ formation during steady-state operation was dependent on the AFR, temperature and catalytic formulation. Generally, the NH₃ yield decreased as follows: HPGM ≥ Dual-Zone >> LPGM ≈ LNT. While all of the formulations could produce significant amounts of NH₃ if operated under sufficiently rich conditions, the selectivity to NH₃ for the LPGM and LNT and was always lower than the selectivity to NH₃ for the HPGM and Dual-Zone catalyst, respectively. The presence of Rh and/or CeO₂ in these formulations could explain why less NH₃ was observed. At higher temperatures, the Dual-Zone catalyst also produced less NH₃ than the HPGM catalysts and NH₃ decomposition over Rh and/or CeO₂ most likely explains why lower NH₃ yields were observed. The AFR was determined to be a sensitive parameter that could be used to control NH₃ generation and CO slip, where CO was always observed under conditions favorable for NH₃.
formation. As the temperature was increased, a richer AFR was necessary to achieve the same NH₃ yield observed at lower temperatures.

For cycling, a significantly richer AFR was required to produce a similar amount of NH₃ observed during the steady-state experiments. Consumption of CO, and other reductants, in the lean/rich front that propagates through the catalyst bed, reduction of oxidized precious metal sites and oxygen storage capacity (OSC), especially for CeO₂ containing formulations, could explain why a richer AFR was necessary during cycling. The optimum catalysts and conditions were determined using a new parameter defined as the cycle averaged α (ratio of NH₃ produced to NOₓ slipped). The HPGM catalyst demonstrated the most robust α over the entire temperature range considered, with an optimum between 275 to 400 °C. At moderate temperatures (275 – 500 °C), inclusion of NOₓ storage capacity (i.e., results collected for the LNT) dramatically increased the amount of NH₃ produced in relation to the amount of NOₓ slipped, even though the LNT catalyst generally exhibited the lowest NH₃ yields for steady-state operation. This implied that inclusion of an “optimum” amount of NOₓ storage capacity could dramatically improve the performance of the TWC-SCR system. Above 500 °C, only the HPGM produced enough NH₃ to theoretically operate a TWC-SCR system. When the CO and C₃H₆ conversions were considered in addition to the NH₃ formation, the optimum temperature for this system was determined to be approximately 400 – 450 °C, but CO slip continue to be a concern. N₂O formation, on the other hand, was insignificant for temperatures above 400 °C, which is a unique advantage of TWC-SCR system.
4.6 ACKNOWLEDGEMENTS

A portion of this research was sponsored by the U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy, Vehicle Technologies Program. The authors thank program managers Ken Howden and Gurpreet Singh for their support. This manuscript has been co-authored by UT-Battelle, LLC, under Contract No. DE-AC05-00OR22725 with the U.S. Department of Energy. The United States Government retains and the publisher, by accepting the article for publication, acknowledges that the United States Government retains a non-exclusive, paid-up, irrevocable, world-wide license to publish or reproduce the published form of this manuscript, or allow others to do so, for United States Government purposes. Additionally, the authors would like to acknowledge the contributions of Wei Li, Chang Kim and Kushal Narayanaswamy of General Motors in addition to Davion Clark and Christopher Owens of Umicore for discussions and guidance in this portion of our research.
CHAPTER 5. CONCLUSIONS

Lean-burn gasoline engines are more fuel efficient than conventional, stoichiometric-burn ones. Although the improvements are relatively modest, if implemented across the entire U.S. automotive fleet, lean-burn engines could have far-reaching implications on the amount of gasoline imported in the country on an annual basis. However, the development of cost-effective catalytic converter catalysts capable of meeting emission regulations for lean-burn vehicles still represents a major technical challenge. Currently, three-way (TWC), lean \( \text{NO}_x \) trap (LNT) and selective catalytic reduction (SCR) and combinations thereof represent the possible solutions. In this dissertation, the three most promising configurations were considered (i.e., TWC+LNT, TWC + LNT + SCR, and TWC + SCR).

In Chapter 2, a fundamental investigation of the \( \text{NO}_x \) reduction mechanism by CO and \( \text{C}_3\text{H}_6 \) in the presence of water was performed over \( \text{Pt/BaO/Al}_2\text{O}_3 \) and \( \text{Rh/BaO/Al}_2\text{O}_3 \) model LNT catalysts using \textit{in situ} FTIR spectroscopy. Quantification of the FTIR results was then performed using corollary experiments monitored using mass spectroscopy. The FTIR results indicated that surface nitrites were the predominant \( \text{NO}_x \) storage form at 250 °C, while surface nitrates became the predominant storage form at 350 °C. The presence of water did not have a significant effect during storage. Surface isocyanates (NCO) were formed under a variety of conditions and their concentration was dependent on the temperature, the reductant selected, the presence of \( \text{H}_2\text{O} \) and the type of precious metal used. The reaction of surface NCO species with
NO and O₂ was fast and catalyzed by precious metals, with no difference observed between Pt and Rh. A similarly fast reaction was also observed with H₂O, even in the absence of the noble metal component. Comparison of N₂ evolution amounts during the rich phase and subsequent reaction of residual NCO species with O₂ and NO confirmed that reaction of NCO species could contribute significantly to the total amount of N₂ formed, when CO is used as the reducing agent.

In Chapter 3, a commercial LNT catalyst – obtained from a BMW 120i, lean-burn gasoline engine exhaust tailpipe – was evaluated during lean/rich cycling for potential application in an LNT-SCR system. The NH₃ yield in comparison to the NOₓ was carefully tracked as a function of lean/rich cycle timing and temperature in order to determine if the cycle timing could be used as a parameter for concerted NH₃ generation. Two lean/rich cycling regimes were clearly identified. At low temperatures, NOₓ release and reduction were kinetically limited. Therefore, a longer, lower concentration rich dose favored increased cycle averaged NOₓ conversions. For example, extending the rich period from 5 to 15 s at 250 °C, while holding the reductant dose constant, resulted in an increase in cycle averaged NOₓ conversion from 59 to 87%, respectively. At high temperatures, the opposite was true and shorter, higher concentration rich doses resulted in higher NOₓ conversions. The selectivity to NH₃ and N₂O was shown to primarily be a function of temperature and the selectivity generally increased as the temperature decreased. NH₃ and N₂O yields, on the other hand, were significantly affected by the cycling timing any combination of changes in the lean/rich timing protocol or reductant concentrations that resulted in increased NOₓ conversion also resulted in increased NH₃ and N₂O yield. Lastly, concerted control of NH₃ formation by varying the lean/rich cycle timing was demonstrated. While tuning the lean/rich timing could improve the
amount of NH$_3$ formed in comparison to the amount of NO$_X$ slipped, the N$_2$O yield also increased under the same conditions.

In Chapter 4, NH$_3$ formation under steady-state and lean/rich cycling conditions was investigated using a three commercial TWCs and the LNT catalyst from Chapter 3 for application in a TWC-SCR system. NH$_3$ formation during steady-state operation was dependent on the AFR, temperature and catalytic formulation, but all of the formulations could produce significant amounts of NH$_3$ if operated under sufficiently rich conditions. The selectivity to NH$_3$ was always lower for the Rh and/or CeO$_2$ containing formulations. In all cases, the high precious metal loading, Pd-only TWC produced the most NH$_3$ during steady-state operation. For cycling, a significantly richer AFR was required to produce similar amount of NH$_3$ as observed during the steady-state experiments. Again, the Pd-only catalyst demonstrated the most robust NH$_3$ formation over the entire temperature range considered, with an optimum between 275 to 400 °C. However, inclusion of NO$_X$ storage capacity (i.e., results collected over the LNT catalyst) demonstrated that NO$_X$ storage capacity could significantly increase the amount of NH$_3$ produced in relation to the amount of NO$_X$ slipped, even though the LNT catalyst generally exhibited the lowest NH$_3$ yields for steady-state operation. This implied that inclusion of an “optimum” amount of NO$_X$ storage capacity could significantly improve the performance of the TWC-SCR system. When CO and C$_3$H$_6$ conversions were considered in addition to the NH$_3$ formation, the optimum temperature for this system was determined to be approximately 400 – 450 °C, but CO slip will still need to be addressed. N$_2$O formation, on the other hand, was insignificant for temperatures above 400 °C, which is a unique advantage of TWC-SCR system.
REFERENCES


202

204


APPENDICES

A.1 PRELIMINARY IN SITU FTIR RESULTS COLLECTED OVER AL₂O₃, Pt/Al₂O₃, Ba/Al₂O₃ AND Pt/Ba/Al₂O₃

A.1.1 EXPERIMENTAL METHODS

MATERIALS AND PREPARATION

All catalysts were prepared by incipient wetness impregnation using aqueous solutions of barium acetate (Alfa Aesar) and tetraammineplatinum (II) nitrate (Sigma-Aldrich), as summarized in Table A1. Prior to impregnation, Catalox® SBa-200 γ-Al₂O₃ (Sasol) was calcined for 24 hr at 600 °C. Ba was deposited first, dried for 24 hr at R.T., dried for 12 hr at 120 °C and calcined in air for 12 hr at 600 °C. Then, Pt was deposited, dried for 24 hr at R.T., dried for 12 hrs at 120 °C and calcined in air for 5 hr at 500 °C.

Table A1. List of catalysts prepared for the preliminary in situ FTIR investigation.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Pt (wt %)</th>
<th>Ba (wt %)</th>
<th>Al₂O₃ (wt %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al₂O₃</td>
<td>-</td>
<td>-</td>
<td>Bal.</td>
</tr>
<tr>
<td>Pt/Al₂O₃</td>
<td>1.0</td>
<td>-</td>
<td>Bal.</td>
</tr>
<tr>
<td>Ba/Al₂O₃</td>
<td>-</td>
<td>17.0</td>
<td>Bal.</td>
</tr>
<tr>
<td>Pt/Ba/Al₂O₃</td>
<td>1.0</td>
<td>17.0</td>
<td>Bal.</td>
</tr>
</tbody>
</table>
Spectra were collected on a Nexus 470 FTIR spectrometer operated in transmission mode with 2 cm\(^{-1}\) resolution, where 30 scans per spectra were collected for storage experiments (30 s collection time) and 19 scans per spectra were collected for cycling experiments (20 s collection time). The catalysts were pressed into self supported wafers (\(\approx 15-20 \text{ mg cm}^{-2}\)) using a die from International Crystal Laboratories. Analysis was performed in a homemade cell consisting of a stainless steel tube (1.5” ID X 4.5” L) with cooling water flanges welded to each end. The flanges were machined to accommodate polished windows (NaCl 32mm x 3mm – Alfa Aesar) that were held in place by Viton gaskets. Cooling water was passed through the flanges to keep the Viton gasket temperature below 100 °C. The cell was wrapped in a 400 W, 4 ft heating cord (Glas-Col), which allowed heating up to 400 °C. A thermocouple was placed in close proximity to the sample for determination of catalyst temperature. A gas manifold with five mass flow controllers (Brooks 5890E – CO, Tylan – NO, NO\(_2\), O\(_2\), He, H\(_2\), C\(_3\)H\(_6\)) and two needle valves (Swagelok – He) delivered the mixed gas to the cell, where appropriate gases were purified by high capacity water and moisture traps (Restek). Certified gas mixtures were purchased from National Welders and included: 1% NO in He, 1% H\(_2\) in He, 1% NO\(_2\) in He, 1% C\(_3\)H\(_6\) in He, 3% CO in He, 10% O\(_2\) in He, pure H\(_2\) and pure He. Flow through the cell was maintained at 100 cm\(^3\) min\(^{-1}\) throughout all experiments.

Two types of experiments were performed (conditions shown in Table A2). First, the catalysts were characterized by adsorption of NO, NO\(_2\), NO+O\(_2\) or CO at RT or 350 °C for 20 min. These experiments are referred to as “storage experiments” and were used to compare storage capacity and assign peaks. Then, samples were investigated under more realistic cycling conditions in order to observe intermediate species. Cycling was performed using 2 min. lean
phases (Table A2), followed by a 2 min He flush to remove all O$_2$ and lastly, a 2 min rich phase (Table A2). Reductants were investigated separately (i.e., Rich CO refers to cycling with CO as the reductant and Rich H$_2$ refer to cycling with H$_2$ as the reductant). Prior to experiments, samples were reduced for 30 min. in H$_2$ at 400 °C, flushed for 15 min in He, oxidized for 5 hr in 10% O$_2$ in He at 400 °C, flushed for 1 hr in He at 400 °C and cooled to either RT or 350 °C for experiments. The same sample was used to complete one set of data. Fresh samples underwent additional pretreatment to remove stable carbonates species, where the catalyst was treated in 0.5% NO, 5% O$_2$ in He mixture at 400 °C for 5 hr, reduced in pure H$_2$ for 1 hour, and subsequently treated as described above. After all pretreatments, a background spectra was collected and used for subtractions.

Table A2. Gas concentrations (mole %) during storage and cycling Experiments.

| Storage |
|---|---|---|---|---|---|---|---|---|
| **Experiment** | NO (%) | NO$_2$ (%) | CO (%) | H$_2$ (%) | C$_3$H$_6$ (%) | O$_2$ (%) | He (%) |
| NO | 0.1 | - | - | - | - | - | Bal. |
| NO + O$_2$ | 0.1 | - | - | - | - | 5.0 | Bal. |
| NO$_2$ | - | 0.1 | - | - | - | - | Bal. |
| CO | - | - | 0.1 | - | - | - | Bal. |

| Cycling |
|---|---|---|---|---|---|---|---|
| **Experiment** | Lean | Rich CO | Rich H$_2$ | Rich C$_3$H$_6$ | NO (%) | NO$_2$ (%) | CO (%) |
| Lean | 0.1 | - | - | - | - | - | 5.0 | Bal. |
| Rich CO | - | - | - | - | - | - | - | Bal. |
| Rich H$_2$ | - | - | - | - | - | - | 0.9 | Bal. |
| Rich C$_3$H$_6$ | - | - | - | - | - | - | 0.1 | Bal. |
A.1.2 \textit{in situ} FTIR Storage Experiments

Storage of NO, NO + O₂, NO₂ and CO at room temperature (RT) and 350 °C was investigated by \textit{in situ} FTIR spectroscopy on pre-oxidized Al₂O₃, Pt/Al₂O₃, Ba/Al₂O₃ and Pt/Ba/Al₂O₃ samples in order to confirm observations and mechanisms presented in the literature \cite{21,22,24,27,31,33,34,37,38,41,43,112,179}. While RT spectra were included, a higher emphasis was placed on spectra collected at 350 °C since this represents a relevant storage temperature. Many bands assignments should be considered tentative since overlapping bands from a variety of possible nitrite and nitrate species makes definitive assignments difficult, if not impossible \cite{50–52,402}.

\textbf{NO}

Exposure of pre-oxidized Al₂O₃ catalyst to NO at RT resulted in the formation of low intensity bands at 1650, 1581, 1463, 1322, 1232 and 1080 cm⁻¹ (Fig. A1). The bands at 1650 and 1581 cm⁻¹ were assigned to nitrates, where a bridging bidentate nitrate, monodentate nitrate or chelating bidentate nitrate could all account for bands in this region of the spectra \cite{22,31,33,34}. The band at 1463 cm⁻¹ was assigned to a linear nitrite, while the bands at 1322 and 1232 cm⁻¹ were assigned to a bridged bidentate nitrite. Similarly, exposure of pre-oxidized Pt/Al₂O₃ to NO at RT resulted in formation of low intensity bands at 1783, 1652, 1582, 1465, 1322, 1232 and 1078 cm⁻¹. The band at 1783 cm⁻¹ was consistent with a Pt mononitrosyl, where the other bands correspond to previously assigned nitrogen oxide species adsorbed on Al₂O₃.

Exposure of Ba/Al₂O₃ to NO at RT resulted in formation of bands at 1647, 1560, 1448 and 1390 cm⁻¹. Assignment of these bands was difficult and it was unclear if bands at 1647, 1560 and 1448 cm⁻¹ were associated with the Al₂O₃ and/or BaO-BaCO₃ storage component. It is
worth mentioning that the relative intensity between the 1650 and 1582 cm\(^{-1}\) changes when Ba is added to the \(\text{Al}_2\text{O}_3\) support. This may infer storage to be occurring on Ba or Ba may occupy sites previously accessible to NO\(_X\) on the bare alumina support. The band at 1390 cm\(^{-1}\) was not assigned, as it was only observed for the Ba/\(\text{Al}_2\text{O}_3\) sample during exposure to NO in the absence of O\(_2\).

Addition of Pt to the Ba/\(\text{Al}_2\text{O}_3\) sample completely changed the spectra and bands at 1541, 1443, 1417, 1373, 1314, 1209 cm\(^{-1}\) were observed after exposure to NO at RT. The band at 1541 cm\(^{-1}\) was most likely associated with a monodentate nitrate or bidentate nitrate on Ba, while bands at 1443, 1417, 1373 and 1314 cm\(^{-1}\) could be assigned to monodentate nitrates, monodentate nitrites, linear nitrites, or hyponitrites on Ba [22,31,33,34]. Additionally, these bands could be associated with NO\(_X\) species adsorbed on \(\text{Al}_2\text{O}_3\) or on sites in close proximity to Ba, where definitive assignments is difficult because a large number of NO\(_X\) species adsorbed on both Ba and \(\text{Al}_2\text{O}_3\) at room temperature. The band at 1209 cm\(^{-1}\) was assigned to a bridging bidentate nitrite on Ba.

Assignment of NO\(_X\) species adsorbed on \(\text{Al}_2\text{O}_3\), Pt/\(\text{Al}_2\text{O}_3\), Ba/\(\text{Al}_2\text{O}_3\) and Pt/Ba/\(\text{Al}_2\text{O}_3\) at 350 °C was more straightforward as seen in Fig. A2. Exposure of \(\text{Al}_2\text{O}_3\) to NO at 350 °C resulted in very weak bands at 1312 and 1229 cm\(^{-1}\), which were assigned to bridged bidentate nitrites (Fig. A2). For Pt/\(\text{Al}_2\text{O}_3\), a band at 1555 cm\(^{-1}\) was observed in addition to bands 1297 and 1234 cm\(^{-1}\).

The band at 1234 cm\(^{-1}\) was assigned to bidentate nitrites, while the band at 1555 cm\(^{-1}\) was most likely associated with bridging bidentate nitrates, chelating nitrates or monodentate nitrates, with another vibration occurring around 1297 cm\(^{-1}\). The nitrate peak was centered at 1555 cm\(^{-1}\), but contained shoulders at higher and lower wavenumbers. Storage of NO on Pt/\(\text{Al}_2\text{O}_3\) at
Elevated temperatures probably included a combination of bridging bidentate nitrates, chelating nitrates and monodentate nitrates, which would account for the shoulders. Exposure of Ba/Al$_2$O$_3$ to NO at 350 °C resulted in formation of a band at 1211 cm$^{-1}$, which was previously assigned to a bridging bidentate nitrite on Ba. While storage of NO$_X$ was observed for Ba/Al$_2$O$_3$, the storage capacity was low and occurred mainly in the form of nitrites.

Exposure of Pt/Ba/Al$_2$O$_3$ to NO at 350 °C resulted in formation of a band at 1213 cm$^{-1}$, which was assigned to a bridged nitrite on Ba (Fig. A2). With increased time of exposure, bands at 1742, 1418 and 1306 cm$^{-1}$ also formed and grew in intensity. Furthermore, the Pt/Ba/Al$_2$O$_3$ catalyst was the only catalyst tested to show appreciable storage when exposed to NO in the absence of O$_2$. Fanson et al. [43] also observed significant storage of NO on Pt/Ba/Al$_2$O$_3$ catalysts, but their results were obtained at RT. In our case, significant storage was only observed at elevated temperatures.

The band at 1742 cm$^{-1}$ was assigned to a NO$_X$ species coordinated on Pt, where the shift to lower wavenumbers could be explained by elevated temperatures, the state of Pt or the chemical environment of Pt (i.e., Pt deposited on Ba may have different electronic properties) [37]. The bands at 1418 and 1306 cm$^{-1}$ were assigned to “bulk-like” ionic nitrates on Ba [21,24,34,40,187,188,191].

This data corroborates well with other results, where Pt increases storage capacity and catalyzes the transition from nitrites to nitrates [22,86]. It also supports the mechanism involving nitrites as intermediate species in the formation of nitrates [21,22,31,34,39]. However, an alternative mechanism, as previously suggested by Fanson et al. [43], where NO directly interacts with the Ba and the main role of Pt is to provide atomic oxygen, possibly through NO decomposition, cannot be ruled out.
Figure A1. Adsorption of 1000 ppm NO in He at RT on (A) Al₂O₃, (B) Pt/Al₂O₃, (C) Ba/Al₂O₃, (D) Pt/Ba/Al₂O₃. Spectra shown after 0, 0.5, 1, 2, 3, 5, 10 & 20 min., respectively.

Figure A2. Adsorption of 1000 ppm NO in He at 350 °C on (A) Al₂O₃, (B) Pt/Al₂O₃, (C) Ba/Al₂O₃, (D) Pt/Ba/Al₂O₃. Spectra shown after 0, 0.5, 1, 2, 3, 5, 10 & 20 min., respectively.
Addition of oxygen to the feed drastically increased the concentration of nitrite and nitrate species for all of the catalysts investigated both at RT and 350 °C, as shown in Figs. A3 and A4. Fridell et al. and others previously established the beneficial role O₂ plays in NOₓ storage [22,62]. Admission of NO+ O₂ over Al₂O₃ and Pt/Al₂O₃ at RT resulted in formation of bands at 1792, 1585, 1548, 1466, 1316, 1230 and 1077 cm⁻¹ (Fig. A3). The band at 1792 cm⁻¹ was previously assigned to mononitrosyls on Pt and bands at 1585, 1548, 1466, 1316, and 1230 cm⁻¹ were assigned to monodentate or chelating nitrates, linear nitrites, and bridging nitrites, respectively. The band previously observed at 1650 cm⁻¹ was no longer resolved, but seemed to be present as a shoulder on the 1585 cm⁻¹ band. The strong band at 1077 cm⁻¹ could be assigned to a bridged N-coordinated nitrite, a chelating bidentate nitrate or a bridged bidentate nitrate.

Exposure of Ba/Al₂O₃ to NO + O₂ at RT resulted in formation of bands at 1549, 1478, 1347, and 1212 cm⁻¹. It is worth noting the large differences observed between NO and NO + O₂ exposure, as shown in Fig. A1 and A3, respectively. In the presence on O₂, storage occurred mainly as a bridged bidentate nitrite species, while in the absence of O₂ a series of bands at 1647, 1560, 1448 and 1390 cm⁻¹ were observed. In this case, the bands at 1549, 1478 and 1347 cm⁻¹ in Fig. A3 were assigned to monodentate nitrates/nitrites on Ba or Al, linear nitrites on Ba or Al or hyponitrites on Ba or Al.

Exposure of Pt/Ba/Al₂O₃ to NO + O₂ at RT resulted in formation of bands at 1543, 1420, 1331 and 1212 cm⁻¹ (Fig. A3). While the primary feature was the bidentate nitrite species at 1212 cm⁻¹, formation of ionic nitrate species at 1310 and 1420 cm⁻¹ and bidentate nitrate species at 1543 cm⁻¹ indicated the transition from surface nitrites to surface and bulk nitrates with increasing time even at RT and demonstrated the influential role of Pt.
At 350 °C, exposure of Al₂O₃ to NO + O₂ resulted in formation of low intensity bands at 1552 and 1231 cm⁻¹, where the band at 1552 cm⁻¹ was consistent with a bridged bidentate nitrate, chelating nitrate or monodentate nitrate and the band at 1231 cm⁻¹ was consistent with a bidentate nitrite. Interestingly, nitrate formation was observed over Al₂O₃ even in the absence of a precious metal. Significantly higher storage was observed for Pt/Al₂O₃ exposed to NO + O₂ at 350 °C (Fig. A4). Bands at 1574, 1296 and 1245 cm⁻¹ were consistent with nitrate features, where storage most likely occurred as a bridging bidentate nitrate or chelating bidentate nitrates. Monodentate nitrates were also possible, but lack of a band in the 1400-1300 cm⁻¹ region inferred storage in this form to be unlikely. Additionally, storage of NOₓ as a bidentate nitrite was only observed at shorter times. With increased time of exposure, the band at 1230 cm⁻¹ disappeared. This further demonstrated the critical role of Pt, where nitrites stored on the surface were not observed because Pt catalyzed rapid conversion from nitrites to nitrates either by providing atomic oxygen or oxidizing NO to NO₂, which could further oxidize the nitrites to nitrates.

Exposure of Ba/Al₂O₃ to NO + O₂ at 350 °C demonstrated a similar trend as Al₂O₃, where storage occurred primarily as nitrites with formation of nitrates at increased times of exposure (Fig. A4). The primary band at 1208 cm⁻¹ was assigned to bidentate nitrites, while less intense bands at 1300 and 1415 cm⁻¹ were assigned to ionic nitrates. A band also appeared between 1600 -1500 cm⁻¹, but it was masked by a negative band at 1560 cm⁻¹ associated with decomposition of BaCO₃. It is worth mentioning that exposure of Ba/Al₂O₃ to NO at 350 °C resulted solely in the formation of nitrites (1210 cm⁻¹). Therefore, the presence of oxygen facilitated storage as nitrates and conversion from nitrites to nitrates, but total storage capacity remained low in comparison to Pt/Ba/Al₂O₃ catalysts.
Exposure of Pt/Ba/Al$_2$O$_3$ to NO + O$_2$ at 350 °C resulted in significant storage of NO$_x$, as demonstrated by Fig. A4. Intense bands at 1744, 1547, 1418 and 1306 cm$^{-1}$ were observed and corresponded to nitrosyls on Pt, bidentate nitrates, and ionic nitrates (1418 and 1306 cm$^{-1}$) on Ba, respectively. Initially, a band at 1223 cm$^{-1}$, assigned to a nitrite on Ba, was observed. However, this peak was no longer evident at longer times. It is possible that the nitrite was still present, but its vibration was masked by the much larger band at 1306 cm$^{-1}$. In conclusion, Pt/Ba/Al$_2$O$_3$ exposed to NO + O$_2$ at 350 °C stored significantly more NO$_x$ than Al$_2$O$_3$, Pt/Al$_2$O$_3$ and Ba/Al$_2$O$_3$, where storage occurred primarily as ionic nitrates. Conversion from nitrites to nitrates was observed at shorter times (<30 sec), but nitrites were no longer observed at longer times, which provided further evidence for a nitrite to nitrate storage mechanism.

Figure A3. Adsorption of 1000 ppm NO + 5% O$_2$ in He at RT on (A) Al$_2$O$_3$, (B) Pt/Al$_2$O$_3$, (C) Ba/Al$_2$O$_3$, (D) Pt/Ba/Al$_2$O$_3$. Spectra shown after 0, 0.5, 1, 2, 3, 5, 10 & 20 min., respectively.
Figure A4. Adsorption of 1000 ppm NO + 5% O$_2$ in He at 350 °C on (A) Al$_2$O$_3$, (B) Pt/Al$_2$O$_3$, (C) Ba/Al$_2$O$_3$, (D) Pt/Ba/Al$_2$O$_3$. Spectra shown after 0, 0.5, 1, 2, 3, 5, 10 & 20 min., respectively.

NO$_2$

Exposure of Al$_2$O$_3$, Pt/Al$_2$O$_3$, Ba/Al$_2$O$_3$ and Pt/Ba/Al$_2$O$_3$ to NO$_2$ was also performed. It is worth noting that exposure to NO$_2$ instead of NO or NO + O$_2$ effectively negates the beneficial role of Pt, where the main role of Pt is to adsorb and oxidize NO to NO$_2$. Additionally, many groups have stressed the importance of the Pt/BaO interface in NO$_X$ storage, where Pt acts like a bridge for NO$_X$ to adsorb and spillover onto the Ba component where storage ultimately occurs [8,21,29,46,66,69,73,74]. Sakamoto et al. [71] suggested storage and reduction of NO$_X$ to occur within a few micrometers of the Pt particle and mentioned that preferential adsorption and reduction of NO$_X$ occurring in close vicinity to Pt particles could explain why only 20% of the deposited Ba participates in storage [72]. Therefore if NO$_2$ is selected as the NO$_X$ source, all storage sites essentially become equivalent because oxidation of NO to NO$_2$ is no longer the rate determining step for storage and nitrate formation should be facile according to the
disproportionation mechanism presented by Prinetto et al. [40] and others [38,41,42], where disproportionation proceeds through oxidation of BaO to BaO₂ by gas phase NO₂ which subsequently adsorbs two molecules of NO₂ to form Ba(NO₃)₂.

Figs. A5 and A6 demonstrate exposure of NO₂ at RT and 350 °C, respectively for Al₂O₃, Pt/Al₂O₃, Ba/Al₂O₃ and Pt/Ba/Al₂O₃. In all cases, formation of intense bands assigned to nitrates on Al₂O₃ or Ba were observed. Initially, nitrites were observed, but they were rapidly oxidized to nitrates. Prinetto et al. [34] and Nova et al. [21] previously reported that exposure of NSR catalysts to NO₂ only yielded nitrates. However, Sedlmair et al. [31] observed nitrite species when Pt/Ba/Al₂O₃ catalysts were exposed to NO₂.

While nitrites were observed, storage occurred mainly as nitrates on Al₂O₃ or BaO. For Al₂O₃ and Pt/Al₂O₃, bands at 1600 – 1500 and 1300 – 1200 cm⁻¹ were assigned to bridged bidentate nitrates, monodentate or chelating bidentate nitrates on Al₂O₃. For Ba/Al₂O₃ and Pt/Ba/Al₂O₃, bands at 1552, 1420 and 1310 cm⁻¹ were assigned to bridging nitrates on Ba and ionic nitrates on Ba, respectively. It is worth noting that adsorption of NO₂ was qualitatively very similar to adsorption of NO + O₂, but yielded higher intensity bands at equivalent storage times, which was expected since the Pt/BaO interface was no longer important. Additionally, since nitrites were observed during exposure of NO₂, a mechanism involving a nitrite to nitrate route could not be excluded even though NO₂ was used as the NOₓ source.
Figure A5. Adsorption of 1000 ppm NO\textsubscript{2} in He at RT on (A) Al\textsubscript{2}O\textsubscript{3}, (B) Pt/Al\textsubscript{2}O\textsubscript{3}, (C) Ba/Al\textsubscript{2}O\textsubscript{3}, (D) Pt/Ba/Al\textsubscript{2}O\textsubscript{3}. Spectra shown after 0, 0.5, 1, 2, 3, 5, 10 & 20 min., respectively.

Figure A6. Adsorption of 1000 ppm NO\textsubscript{2} in He at 350 °C on (A) Al\textsubscript{2}O\textsubscript{3}, (B) Pt/Al\textsubscript{2}O\textsubscript{3}, (C) Ba/Al\textsubscript{2}O\textsubscript{3}, (D) Pt/Ba/Al\textsubscript{2}O\textsubscript{3}. Spectra shown after 0, 0.5, 1, 2, 3, 5, 10 & 20 min., respectively.
Exposure of pre-oxidized samples to CO was performed because nitrates/nitrites absorb infrared light in the same region as carbonates, carboxylates and formates and band assignments can be even more difficult when carbon containing species were present in the gas mixtures.

Exposure of Al$_2$O$_3$ and Pt/Al$_2$O$_3$ to 1000 ppm CO in He at RT resulted in formation of low intensity bands at 2092, 1653, 1470, 1436, 1266 and 1230 cm$^{-1}$ (Figs. A7 and A8). The band at 2092 cm$^{-1}$ was assigned to a CO carbonyl on Pt. Bands at 1653, 1470, 1436, 1266 and 1230 cm$^{-1}$ were most likely associated with bidentate carbonates and unidentate carbonates [37,179]. Detailed bands assignments were not attempted since the bands were insignificant at 350 °C, a relevant storage temperature. Exposure of Ba/Al$_2$O$_3$ and Pt/Ba/Al$_2$O$_3$ to 1000 ppm CO at RT resulted in formation of bands at 2087, 1656, 1567, 1379, 1321 and 1230 cm$^{-1}$, which could similarly be assigned to Pt carbonyls and bidentate carbonates and unidentate carbonates respectively.

Exposure of Al$_2$O$_3$ and Pt/Al$_2$O$_3$ to 1000 ppm CO at 350 °C resulted in formation of low intensity bands at 1585, 1515, 1521, 1441, 1392 and 1296 cm$^{-1}$ and were assigned to weakly bound carbonate species on Al$_2$O$_3$ (Fig. A8). Notice that storage of CO occurred negligibly at 350 °C on Al$_2$O$_3$. These results were in agreement with storage of 1000 ppm NO, in absence of O$_2$, at 350 °C (Fig. A2). The more intense band at 2049 cm$^{-1}$ was assigned to linearly bound CO carbonyl on reduced Pt.

Exposure of Ba/Al$_2$O$_3$ and Pt/Ba/Al$_2$O$_3$ to 1000 ppm CO resulted in formation of much more intense bands at 1570 and 1335 cm$^{-1}$, which were assigned to bidentate carbonates [37,179]. A band at 1450 cm$^{-1}$ was not observed in the absence of H$_2$O and O$_2$, where the band at 1450 cm$^{-1}$ was previously assigned to bulk BaCO$_3$. This indicated that under the conditions of
the experiment only surface carbonates were formed. Formation of a band at 1450 cm\(^{-1}\) would likely indicate deterioration of NSR ability since bulk-like BaCO\(_3\) is highly stable and is believed to be inactive for NO\(_X\) storage. The band at 2016 cm\(^{-1}\) was assigned to a carbonyl on Pt and bands at 2230 and 2162 cm\(^{-1}\) were assigned to isocyanate species bound to Al\(_2\)O\(_3\) and BaO, respectively [24]. The formation of NCO species even in the absence of NO\(_X\) indicated that the Ba storage component contained some residual NO\(_X\) stored on the surface even though a high-temperature reduction using H\(_2\) was performed.

**Figure A7.** Adsorption of 1000 ppm CO in He at RT on (A) Al\(_2\)O\(_3\), (B) Pt/Al\(_2\)O\(_3\), (C) Ba/Al\(_2\)O\(_3\), (D) Pt/Ba/Al\(_2\)O\(_3\). Spectra shown after 0, 0.5, 1, 2, 3, 5, 10 & 20 min., respectively.
In situ cycling experiments were performed using model NO\textsubscript{X} storage and reduction conditions, where the lean period contained 1000 ppm NO + 5 % O\textsubscript{2} and the rich period contained 9000 ppm H\textsubscript{2}, 9000 ppm CO or 1000 ppm C\textsubscript{3}H\textsubscript{6} in He. The duration of the periods lasted 2 min with a 2 min He flush in between the lean and rich period. The He flush was used to ensure complete removal of O\textsubscript{2} from the IR cell before introduction of the reductant. Spectra were collected in 20 s intervals for 3 complete NO\textsubscript{X} storage and reduction cycles. The following sections present results from Pt/Al\textsubscript{2}O\textsubscript{3}, Ba/Al\textsubscript{2}O\textsubscript{3} and Pt/Ba/Al\textsubscript{2}O\textsubscript{3} samples. The extensive storage characterization experiments presented in Section A.1.2 aided in interpretation of the results because numerous bands were observed during cycling experiments and assignment of these bands would have been difficult without the storage experiments.
In situ cycling using H\textsubscript{2} as a reductant on a Pt/Al\textsubscript{2}O\textsubscript{3} catalyst yielded bands at 1551, 1295 and 1241 cm\textsuperscript{-1} during the first lean period, as shown in Fig. A9. These bands were previously assigned to bridging or chelating bidentate nitrates on Al\textsubscript{2}O\textsubscript{3} and they continued to grow in intensity for the duration of the lean period. Removal of NO and O\textsubscript{2} during the subsequent He flush destabilized these species and a slow decrease in intensity of the 1551, 1296 and 1241 cm\textsuperscript{-1} bands was observed. Notice the clear maximum obtained for the 1551 cm\textsuperscript{-1} band in Fig. A9. Introduction of 9000 ppm H\textsubscript{2} during the rich periods caused rapid removal of the nitrate bands, where spectra collected during rich periods were nearly flat. This indicated that the reduction period effectively returned the catalyst to its clean “pre-cycled” state. Since effluent gases from the IR cell were not analyzed, it was not possible to determine if the species were reacting on the surface or merely desorbing into the gas phase, but Fridell et al. [62] performed similar experiments over a Pt-Rh/Al\textsubscript{2}O\textsubscript{3} catalyst and complete reduction of NO\textsubscript{X} was observed during rich periods.

Similarly, cycling using CO and C\textsubscript{3}H\textsubscript{6} as reductants on a Pt/Al\textsubscript{2}O\textsubscript{3} catalyst yielded bands assigned to bridging or chelating bidentate nitrates on Al\textsubscript{2}O\textsubscript{3} during the first storage period, as shown in Figs. A10 and A11. However when CO or C\textsubscript{3}H\textsubscript{6} were used as reductants, bands in the region of 1600 – 1200 cm\textsuperscript{-1} appeared. These bands were previously assigned to carbonates on Al\textsubscript{2}O\textsubscript{3}. Careful inspection of the spectra collected during reduction demonstrated that nitrate species were either reacting or desorbing while CO\textsubscript{X} type species were adsorbing on the Al\textsubscript{2}O\textsubscript{3}. The nitrate feature at 1551 cm\textsuperscript{-1} decreased in intensity while a band assigned to a broad CO\textsubscript{X} peak appeared in the 1650 – 1360 cm\textsuperscript{-1} region and grew in intensity. Similarly, the nitrate bands
at 1295 and 1241 cm\(^{-1}\) decreased in intensity, while a CO\(_X\) band appeared at 1285 cm\(^{-1}\) and grew in intensity.

Reduction by CO also resulted in formation of intense bands at 2230 and 2041 cm\(^{-1}\). The band at 2230 cm\(^{-1}\) was assigned to an isocyanate (NCO) on Al\(_2\)O\(_3\) and the band at 2041 cm\(^{-1}\) was assigned to a CO-carbonyl on Pt. Cycling using C\(_3\)H\(_6\) as the reductant also resulted in formation of a band around 2020 cm\(^{-1}\). The nature of this band appeared to be quite complex and might involve transience of the oxidation state of Pt or an adsorbed CO\(_X\) type species on Pt. Initially this band was centered at 2028 cm\(^{-1}\) with a shoulder at 2090 cm\(^{-1}\). Increased time of exposure caused the band to grow in intensity and shift to 2022 cm\(^{-1}\). Further exposure resulted in decreased intensity and a shift to 2005 cm\(^{-1}\), then 1993 cm\(^{-1}\). The shoulder at 2090 cm\(^{-1}\) was always observed. The mobility and intensity of this peak has not been discussed in the literature and was only observed for Pt/Al\(_2\)O\(_3\) and it is not clear if multiple species are responsible for this behavior. A more detailed investigation regarding this phenomenon was not conducted, as it was not immediately relevant to NSR catalysts.

In summary, Pt/Al\(_2\)O\(_3\) catalysts exhibited minor storage of NO\(_X\) as nitrates on Al\(_2\)O\(_3\) during lean periods and the stored nitrates demonstrated limited stability in He at 350 °C. Removal of nitrates during rich periods occurred rapidly for H\(_2\), CO and C\(_3\)H\(_6\) and resulted in formation of CO\(_X\) type adspecies when CO and C\(_3\)H\(_6\) were used as reductants.
Figure A9. *In situ* cycling over Pt/Al$_2$O$_3$ at 350 °C using 9000 ppm H$_2$ as the reductant.

Figure A10. *In situ* cycling over Pt/Al$_2$O$_3$ at 350 °C using 9000 ppm CO as the reductant.
Figure A11. *In situ* cycling over Pt/Al$_2$O$_3$ at 350 °C using 1000 ppm C$_3$H$_6$ as the reductant.

**Ba/Al$_2$O$_3$**

*In situ* cycling using H$_2$ as the reductant on a Ba/Al$_2$O$_3$ catalyst yielded a band at 1206 cm$^{-1}$ during the first lean period, which was previously assigned to bridging bidentate nitrite on Ba (Fig. A12). The intensity of this band remained constant during the subsequent He flush, which demonstrated the increased stability of nitrites formed on Ba in comparison nitrates/nitrites formed on Al$_2$O$_3$. Interestingly, exposure of the nitrated Ba/Al$_2$O$_3$ catalyst to 9000 ppm of H$_2$ did not result in removal of the stored NO$_X$ species. Instead, the band at 1206 cm$^{-1}$ continued to grow slowly during each subsequent lean period throughout the experiment. This implied that Ba/Al$_2$O$_3$ was inactive during reduction. Fig. A12(B) more clearly demonstrates this concept, where the band at 1206 cm$^{-1}$ remained stable even after exposure to H$_2$ for 2 min. For Pt/Al$_2$O$_3$, the nitrate bands were removed completely during rich periods.

*In situ* cycling using CO and C$_3$H$_6$ as the reductants yielded similar results to cycling using H$_2$, where nitrites were initially formed and stable in He. However, exposure to CO or
C₃H₆ resulted in the formation of carbonates, as shown in Figs A13 and A14. Notice how the bands at 1560 and 1350 or 1335 cm⁻¹ grew rapidly during the first rich period. During the following lean period, COₓ adspecies were desorbed in favor of nitrite formation. This type of behavior was expected since both NOₓ and COₓ are acidic species and compete for the same adsorption sites on the basic BaO. Fridell et al. [41] previously demonstrated the poor storage and reduction properties of Ba/Al₂O₃ catalysts, where transient reactor measurements demonstrated insignificant storage and conversion of NOₓ to N₂. Nova et al. [63] observed conversion of NOₓ using NH₃ as the reductant for a Ba/Al₂O₃ catalyst beginning at 320 °C. Conversion of NO on a Pt/Ba/Al₂O₃ began around 100 °C when NH₃ was used a reductant and around 60 °C when H₂ was used as reductant. The considerably lower NOₓ conversion temperature demonstrated the advantage of adding Pt to Ba/Al₂O₃.

Fig. A13 appears to demonstrate higher stability of nitrites in comparison to carbonates, where bands 1562 and 1338 cm⁻¹ decreased when CO was removed during lean periods, but the nitrite bands at 1210 cm⁻¹ appeared to grow with each lean period, as observed for H₂ cycling. Weak bands at 2224 and 2164 cm⁻¹ were also observed, as seen in Fig. A13(B). These bands were assigned to NCO species on Al₂O₃ and Ba, respectively [24]. Formation of isocyanates in the absence of Pt was unexpected because these species have been reported to form only on the surface of precious metals [403]. So, the presence of NCO species indirectly implied that minimal reduction was occurring even in the absence of Pt.

Figure A14 demonstrates that when C₃H₆ was used, lower intensities of COₓ adspecies were formed. Additionally, no isocyanate species were observed. These results implied that C₃H₆ was less effective than CO, which was in agreement with results reported by other groups [27].
Figure A12. *In situ* cycling on Ba/Al$_2$O$_3$ at 350 °C using 9000 ppm H$_2$ as the reductant. (A) The 3D representation showing all 56 spectra collected during the cycling experiment and (B) Depicts spectra collected during the 2$^{nd}$ rich period.
Figure A13. *In situ* cycling on Ba/Al$_2$O$_3$ at 350 °C using 9000 ppm CO as the reductant. (A) The 3D representation showing all 56 spectra collected during the cycling experiment and (B) Depicts spectra collected during the 2$^{nd}$ rich period.
Figure A14. *In situ* cycling on Ba/Al$_2$O$_3$ at 350 °C using 1000 ppm C$_3$H$_6$ as the reductant. (A) The 3D representation showing all 56 spectra collected during the cycling experiment and (B) Depicts spectra collected during the 2$^{nd}$ rich period.
**Pt/Ba/Al$_2$O$_3$**

*In situ* cycling over Pt/Ba/Al$_2$O$_3$ catalyst resulted in 3 distinct regions in the FTIR spectra, as shown in Fig. A15. During the first lean period, bands at 1420 and 1310 cm$^{-1}$ formed and grew rapidly. These bands were previously assigned to ionic nitrates on Ba and were stable in He at 350 °C. Admission of H$_2$ to IR cell resulted in rapid removal of these nitrate species. Fig. A15 (B) demonstrates the reduction process for H$_2$, where nitrates were completely removed after 80 s in H$_2$. The negative bands at 1526 and 1370 cm$^{-1}$ were difficult to assign. They could represent decomposition of BaCO$_3$, but previous CO + O$_2$ adsorption experiments (omitted for brevity) yielded bands at 1570 and 1335 cm$^{-1}$. Another possibility could be partial reduction of the BaO surface. Roedel et al. [404] demonstrated that BaO exhibits bands at 1693, 1467 and 1370 cm$^{-1}$ if studied by DRIFTS and bands at 1641 and 1433 cm$^{-1}$ if studied by transmission IR. Later cycling experiments (Fig. A16 and A17) exhibited bands at 1562 and 1350 cm$^{-1}$ for reduction of NO$_X$ by CO and bands at 1556 and 1367 cm$^{-1}$ for reduction of NO$_X$ by C$_3$H$_6$.

While some aspects remain unclear, the synergistic effect of incorporating both a precious metal and storage component was clear. The cycling experiments on Pt/Al$_2$O$_3$ showed poor storage, but implied complete reduction. The cycling experiments on Ba/Al$_2$O$_3$ showed both poor storage and poor reduction. Combining Pt and Ba on Al$_2$O$_3$ demonstrated much higher storage capacity and implied complete reduction during rich periods. Since operando methods were not employed, it was not possible to determine the cycle averaged NO$_X$ conversion or selectivity to N$_2$, but effective removal of nitrates during rich periods at 350 °C was clearly established.

*In situ* cycling using CO as the reductant yielded a more complex picture than cycling in H$_2$, as seen in Figure A16. This was due to simultaneous formation of CO$_X$ adspecies as nitrates
were removed/reduced. Interestingly, the bidentate carbonates formed during reduction were more completely removed in subsequent lean periods over Pt/Ba/Al₂O₃ catalysts than Ba/Al₂O₃ catalysts. Careful examination of the bands at 1565 and 1310 cm⁻¹ demonstrates this phenomenon, where the band at 1565 corresponds to COₓ adspecies and the band at 1310 represents ionic nitrates.

The second major difference between cycling in H₂ and cycling in CO was the formation of intense bands at 2220 and 2162 cm⁻¹. These bands were previously assigned to isocyanate species on Al₂O₃ and Ba, respectively. The presence of these bands and their intensity has led many groups to the conclusion that isocyanate species are intermediates in the reduction on nitrates to N₂ [16,24,27,64,289,290]. While this is one possibility, researchers investigating NOₓ reduction mechanisms on three-way catalysts concluded that reaction through isocyanate intermediates only accounted for 5% of the total NOₓ conversion observed [2]. However, the conditions and catalysts used for NSR applications are different than those used for TWCs and general conclusions made for these systems do not necessarily extend to NSR catalysts. Fig. A16 (B) depicts the 2nd reduction period, where nitrates were removed/reduced and carbonates/formates and isocyanate species formed. A band at 2020 cm⁻¹ also appeared and was assigned to a CO carbonyl on Pt. The isocyanate species and carbonyls were removed almost immediately in subsequent lean periods.

Fig. A17 demonstrates in situ cycling when C₃H₆ was used as the reductant. The results were very similar to cycling in CO, but less carbonate/formate species were formed and lower concentrations of isocyanate species were observed. In fact, the band at 2220 was no longer observed.
Figure A15. *In situ* cycling on Pt/Ba/Al$_2$O$_3$ at 350 °C using 9000 ppm H$_2$ as the reductant. (A) The 3D representation showing all 56 spectra collected during the cycling experiment and (B) Depicts spectra collected during the 2$^{\text{nd}}$ rich period.
Figure A16. *In situ* cycling on Pt/Ba/Al₂O₃ at 350 °C using 9000 ppm CO as the reductant. (A) The 3D representation showing all 56 spectra collected during the cycling experiment and (B) Depicts spectra collected during the 2<sup>nd</sup> rich period.
Figure A17. In situ cycling on Pt/Ba/Al$_2$O$_3$ at 350 °C using 1000 ppm C$_3$H$_6$ as the reductant. (A) The 3D representation showing all 56 spectra collected during the cycling experiment and (B) Depicts spectra collected during the 2$^\text{nd}$ rich period.
A.1.4 CONCLUSIONS

Exposure of pre-oxidized $\text{Al}_2\text{O}_3$, Pt/$\text{Al}_2\text{O}_3$, Ba/$\text{Al}_2\text{O}_3$ and Pt/Ba/$\text{Al}_2\text{O}_3$ to NO, NO + O$_2$ or NO$_2$ at RT or 350 °C resulted in formation of nitrites and/or nitrates for all catalysts investigated. The relative concentration between nitrates and nitrites, the total concentration of NO$_X$ adspecies and the coordination of NO$_X$ to $\text{Al}_2\text{O}_3$ or Ba was dependent on the storage temperature, the NO$_X$ source (e.g. NO, NO$_2$ or NO + O$_2$), addition of Pt to $\text{Al}_2\text{O}_3$, addition of Ba to $\text{Al}_2\text{O}_3$, and addition of Pt and Ba to $\text{Al}_2\text{O}_3$. Storage of NO + O$_2$ at 350 °C on the Pt/Ba/$\text{Al}_2\text{O}_3$ catalyst occurred as ionic nitrates on Ba, with bands at 1420 and 1310 cm$^{-1}$, and as a bridging nitrate on Ba with a band around 1560 cm$^{-1}$. At short times, a bridging nitrite coordinated to Ba was observed for the Pt/Ba/$\text{Al}_2\text{O}_3$ catalyst, where Pt catalyzed conversion from nitrites to nitrates. In the absence of O$_2$, storage as nitrates was observed for the Pt/Ba/$\text{Al}_2\text{O}_3$ catalyst at 350 °C, but the transition from storage as nitrites to storage as nitrates occurred at longer times. O$_2$ increased storage capacity and facilitated conversion from nitrites to nitrates. Similarly, exposure of pre-oxidized $\text{Al}_2\text{O}_3$, Pt/$\text{Al}_2\text{O}_3$, Ba/$\text{Al}_2\text{O}_3$ and Pt/Ba/$\text{Al}_2\text{O}_3$ to CO at RT and 350 °C resulted in formation of CO$_X$ adspecies for all catalysts investigated. Exposure of the Pt/Ba/$\text{Al}_2\text{O}_3$ catalyst to CO at 350 resulted in formation of bidentate carbonates with bands at 1560 and 1335 cm$^{-1}$. Storage experiments of both NO$_X$ and CO$_X$ demonstrated numerous bands, where overlap between bands corresponding to NO$_X$ species on $\text{Al}_2\text{O}_3$ and Ba and CO$_X$ species on $\text{Al}_2\text{O}_3$ and Ba greatly complicated definitive band assignments.

In situ cycling at 350 °C on Pt/$\text{Al}_2\text{O}_3$, Ba/$\text{Al}_2\text{O}_3$ and Pt/Ba/$\text{Al}_2\text{O}_3$ catalysts clearly demonstrated the synergistic effect of adding both Pt and Ba to NSR catalysts. Cycling on Pt/$\text{Al}_2\text{O}_3$ yielded low storage of NO$_X$ and the nitrites/nitrates exhibited poor thermal stability. However, complete removal of nitrite/nitrate features was observed during rich phases when
employing H₂, CO or C₃H₆ as the reductant. Cycling on Ba/Al₂O₃ also yielded low storage, but the nitrites/nitrates were thermally stable. However, insignificant removal of stored nitrites/nitrates was observed during rich periods. Cycling on Pt/Ba/Al₂O₃ yielded appreciable storage of NOₓ, high thermal stability of the nitrates/nitrites and rapid removal of nitrates/nitrites during reduction. Comparison of the cycling results on Pt/Al₂O₃, Ba/Al₂O₃ and Pt/Ba/Al₂O₃ led to the conclusion that Ba provided high storage capacity of NOₓ as thermally stable nitrates/nitrites and Pt catalyzed both the storage and reduction period, where poor activity of the Ba/Al₂O₃ catalysts inferred precious metals to be an integral component of NSR catalysts. Reduction of stored nitrites/nitrates using CO and C₃H₆ led to the formation of isocyanate species, especially for Pt/Al₂O₃ and Pt/Ba/Al₂O₃. This again inferred Pt to play an influential role during reduction, as discussed at length in Chapter 2.
A.2 REVIEW: THE ROLE OF ISOCYANATE (NCO) INTERMEDIATES IN THE REDUCTION OF NO\textsubscript{X} BY CO

A.2.1 PREFACE

Recently, there has been considerable interest regarding NO\textsubscript{X} reduction mechanisms occurring on noble metal supported lean NO\textsubscript{X} traps (LNT) or NO\textsubscript{X} storage and reduction (NSR) catalysts. It is generally accepted that storage on these catalysts is preceded by oxidation of NO to NO\textsubscript{2} on metal sites, followed by spillover and storage on BaO/BaCO\textsubscript{3}. However, much less is known about the reduction mechanism. The generally accepted mechanism for reduction by H\textsubscript{2} proceeds through an NH\textsubscript{3} intermediate, where NH\textsubscript{3} is ultimately responsible for the reduction of stored NO\textsubscript{X}. Similarly, the mechanism for reduction by CO and hydrocarbons (HCs) reportedly proceeds through an isocyanate intermediate, which can be oxidized to N\textsubscript{2} and CO\textsubscript{2} or undergo hydrolysis to produce NH\textsubscript{3}. The NH\textsubscript{3} could then further react, as observed for H\textsubscript{2}, and ultimately form N\textsubscript{2}. While this mechanism for CO and HCs seems reasonable, considerable skepticism has been expressed in past regarding this route. This review summarizes the current mechanisms proposed for reduction of NO\textsubscript{X} over NSR catalysts when CO and C\textsubscript{3}H\textsubscript{6} are used as reductants and discusses why isocyanate intermediates could potentially play more of a role than previously reported for other lean NO\textsubscript{X} reduction catalysts.

A.2.2 REDUCTION OF NO\textsubscript{X} BY CO AND HCS ON NSR CATALYSTS

Investigation of the rich period occurring on NSR catalysts is an inherently difficult process. Firstly, the reduction period is very short, which makes it very difficult to obtain accurate information regarding the state of catalytic sites during operation and in situ or
operando techniques with good temporal resolution are required. For example, understanding how the oxidation state of the metal changes during reduction may infer some mechanisms to be more likely than others, but collection of *in situ* XPS data during reaction may not be feasible due to the small time increments required. XPS spectra could be obtained by briefly exposing the catalyst to pulses of reductant, followed by subsequent evacuation and scanning, but it is unclear how this process would affect the surface chemistry and stability of species observed at ambient pressures. Experiments of this nature would be of great importance though because NOX slip, an undesirable process describing the release of NOX that exits the catalytic converter before reduction can occur, has been attributed to the inability of oxidized precious metals to reduce NOX [38,72]. Olsson and Fridell [56] reported formation of Pt oxides on Pt/Al2O3 and Pt/Ba/Al2O3 catalysts after exposure to NO + O2. Higher amounts of Pt oxides were formed on Pt/Ba/Al2O3 catalysts, which the authors attributed to the basic nature of BaO. So, if Pt supported on Ba/Al2O3 is especially susceptible to oxide formation and reduction of NOX on oxidized Pt is slow or negligible, the length of the reduction period becomes very important because short reduction periods (≈1 -2 s) may be dominated by a metallic state not favorable for NOX reduction.

Second, and more importantly, there are two processes occurring simultaneously during reduction that affect the net behavior observed. They include: 1.) release of NOX from the storage sites and 2.) reduction of the released NOX to N2. Unfortunately, it is not possible to study these separately, which drastically complicates efforts in understanding the reduction mechanisms occurring on NOX storage catalysts. Figure A18 is a general overview of the reduction of stored NOX by CO and C3H6. Both the water gas shift (WGS) reaction and NH3
formation were excluded for clarity. NH$_3$ is also a possible product, especially in the presence of water, as discussed in the following sections [290].

![Figure A18](image.png)

**Figure A18.** Overview of NO$_X$ reduction (t=0 + $\Delta$) on a Pt/Ba/Al$_2$O$_3$ catalyst after the storage period has ended (t=0). This figure is intended for clarification purposes only and should not be referenced as an actual representation of the real processes occurring during operation. These subtleties are still unclear and are the topic of this paper. Note: The role of NH$_3$ as a product and intermediate was excluded for clarity.

### A.2.3 Release Mechanisms

Understanding the release mechanism of stored NO$_X$ is critical because it determines the chemical nature of the NO$_X$ that interacts with the reductants (i.e., NO vs. NO$_2$) and where the reduction actually initiates (i.e. on the surface of the support, storage material or metal). Several possibilities have emerged in the literature and include: 1.) thermal release due to heat evolved from oxidation of reductants during the switch from lean to rich conditions, 2.) destabilization of...
stored NO\textsubscript{X} due to removal of O\textsubscript{2} from the feed, 3.) destabilization of stored NO\textsubscript{X} due to establishment of a net reducing environment, 4.) spillover of NO\textsubscript{2} from BaO to Pt and subsequent reduction, 5.) competition between NO\textsubscript{2}, CO\textsubscript{2} and H\textsubscript{2}O for the same storage sites, and lastly 6.) direct reaction of NO\textsubscript{X} with the reductant on the surface of the storage component [59–61].

Kabin et al. [61] demonstrated that a significant exotherm can be generated by introduction of the reductant to lean exhausts. Although the authors were attempting to perform the experiment at 300 °C, the heat generated during oxidation of the reductant increased the average temperature to over 350 °C, with sharp spikes up to approximately 500 °C when the reductant was introduced, as shown in Figure A19.

**Figure A19.** Temperature profile of the catalyst bed during 60 s lean, 10 s rich periods over 2.2\%Pt/16.3\%BaO/Al\textsubscript{2}O\textsubscript{3} (w/w), where lean: 500 ppm NO, 5\% O\textsubscript{2}, 1000 ppm C\textsubscript{3}H\textsubscript{6} and rich: 500 ppm NO, 5\% O\textsubscript{2}, 1.4\% C\textsubscript{3}H\textsubscript{6}. Reprinted from Kabin et al., 2004 [18].

Additionally, Scotti et al. [405] performed temperature programmed desorption (TPD) of NO\textsubscript{2} stored at 350 °C, a relevant storage temperature, and determined that thermal evolution of NO\textsubscript{2} reached a maximum around 460 °C and thermal evolution of NO reached a maximum around 550 °C on Ba/Al\textsubscript{2}O\textsubscript{3}, as shown in Fig. A20. NO\textsubscript{2}-TPD performed on Pt/Ba/Al\textsubscript{2}O\textsubscript{3} catalyst resulted in the release of mainly NO at temperatures slightly lower than 460 °C, where evolution as NO instead of NO\textsubscript{2} for Pt containing samples was explained by reduction
of NO\textsubscript{2} to NO over Pt. A decrease in the thermal stability of Ba nitrates due to addition of precious metals was also reported by Prinetto et al. [34].

![Figure A20](image)

**Figure A20.** TPD profiles of (A) 20\%Ba/Al\textsubscript{2}O\textsubscript{3} (w/w) and (B) 1\%Pt/20\%Ba/Al\textsubscript{2}O\textsubscript{3} (w/w) after exposure to 1000 ppm NO\textsubscript{2} in He at 350 °C, Scotti et al. [405].

Since Kabin et al. [61] routinely observed temperatures above 500 °C for cycling and Scotti et al. [405] reported that thermal evolution began below 500 °C, one could argue that thermal evolution of NO\textsubscript{X} from Ba is a reasonable release mechanism. However, Nova et al. tested the validity of a thermal release mechanism by performing temperature programmed surface reaction (TPSR) measurements on Ba/Al\textsubscript{2}O\textsubscript{3} and Pt/Ba/Al\textsubscript{2}O\textsubscript{3} (20/100 and 1/20/100 w/w, respectively) catalysts under near-isothermal conditions [60]. Both catalysts were saturated using NO + O\textsubscript{2} or NO\textsubscript{2} mixtures at 350 °C, flushed with He, cooled to room temperature, and then ramped at 15 °C/min in 2000 ppm H\textsubscript{2}. If thermal evolution of NO\textsubscript{X} was crucial for reduction to occur, reaction of the stored nitrates would not be expected to begin until approximately 350 °C. This was indeed the case for Ba/Al\textsubscript{2}O\textsubscript{3}, as consumption of hydrogen did not begin until approximately 350 °C. As a side note, establishment a net reducing environment
did not seem to dramatically change the thermal stability of the stored nitrates (≈ a 20 °C shift to lower temperatures). However, it did affect the product distribution, most likely through Reactions A1 and A2. Ba/Al₂O₃ unexpectedly catalyzed this reaction, but it was unclear how.

In the absence of a catalyst, consumption of H₂ in NO₂ (g) was not observed even when the temperature was increased to 500 °C. The authors speculated that stored NOₓ may have played a role.

\[
NO_2 + H_2 \rightarrow NO + H_2O \quad (A1)
\]

\[
NO + H_2 \rightarrow \frac{1}{2}N_2 + H_2O \quad (A2)
\]

Alternatively, consumption of hydrogen during H₂-TPSR on the Pt/Ba/Al₂O₃ sample began at 150 °C, which was significantly lower than the temperature required for thermal release. Several mechanisms were proposed that could explain this behavior including: 1.) adsorption and activation of hydrogen on metal sites, where hydrogen could then spill over onto the support and destabilize stored NOₓ, 2.) direct reduction of NOₓ by activated hydrogen on the support, or lastly, 3.) NO₂ released from the storage component could diffuse to the metal, where reduction by hydrogen could occur. The role of the reactions occurring directly on the support is unclear, but Forzatti et al. [290] observed formation of weak bands assigned to isocyanates adsorbed Ba and Al on a Ba/Al₂O₃ catalysts, which essentially proved that reaction on the support was possible even without the presence of a precious metal to activate reductants. Figure A21 depicts the dramatic changes observed between H₂-TPSR on Ba/Al₂O₃ and Pt/Ba/Al₂O₃ catalysts.
The first two release mechanisms proposed by Nova et al. [60] are easily visualized, while the latter is harder to grasp. Liu and Anderson [59] explained this mechanism more clearly and argued that the release of NO\textsubscript{X} was based on the law of microreversibility. In other words, equilibrium is established between the NO\textsubscript{X} stored on the Ba at the Pt/Ba interface. When hydrogen is introduced, it reacts with the NO\textsubscript{X} on Pt, which then desorbs and essentially opens the gate and allows more NO\textsubscript{X} to pour onto the Pt surface where it can react with additional hydrogen. This process would continue until the supply of hydrogen was exhausted or all the NO\textsubscript{X} stored on the surface was consumed.

NO\textsubscript{X} release due to removal of oxygen from the gas phase was also suggested as a release mechanism, according to Reactions 3 and 4 [59]. However, this is very unlikely since NO\textsubscript{X} species adsorbed on the surface survived evacuation even at 500 °C [34]. Su and Amiridis [22] reported similar results regarding the stability of stored nitrite/nitrate species in He at 350 °C.

\[
(NO_3^-)_2 \rightleftharpoons O^{2-} + \frac{1}{2} O_2 + 2NO_2 \quad \text{(A3)}
\]
The last NO\textsubscript{X} release mechanism worth mentioning involves competitive adsorption between CO\textsubscript{2}, NO\textsubscript{2}, H\textsubscript{2}O and SO\textsubscript{2}. Generally, BaSO\textsubscript{4} >> BaCO\textsubscript{3} ≥ Ba(NO\textsubscript{3})\textsubscript{2} in terms of thermodynamic stability [44,105]. Therefore, if Ba(NO\textsubscript{3})\textsubscript{2} was exposed to CO\textsubscript{2} in the absence of NO\textsubscript{X}, you would expect exchange between Ba(NO\textsubscript{3})\textsubscript{2} in favor of BaCO\textsubscript{3} and the rate of exchange would depend on the concentration of CO\textsubscript{2} and the temperature. Similarly if BaCO\textsubscript{3} was exposed to NO\textsubscript{X} in the absence of CO\textsubscript{2}, you would expect to exchange BaCO\textsubscript{3} for Ba(NO\textsubscript{3})\textsubscript{2}. In reality, this is exactly what you observe experimentally and this type of methodology is used to remove bulk-like BaCO\textsubscript{3} from samples for FTIR measurements because BaCO\textsubscript{3} strongly absorbs infrared light at 1450 cm\textsuperscript{-1} [179,290]. SO\textsubscript{2}, on the other hand, essentially irreversibly binds to BaO under the temperatures and conditions present during typical NSR operation. This leads to deactivation of the catalyst, where the degree of deactivation was observed to be directly proportional to the amount sulfur to which the catalyst has been exposed and harsh regeneration treatments must be employed to recover activity [105,197]. While competitive adsorption is almost certainly occurring, it is probably not the most dominant release mechanism for stored NO\textsubscript{X}. Instead, it is more likely that the working capacity (defined here as the total number of sites available for NO\textsubscript{X} storage) of the catalyst decreases, which impairs performance as observed by Epling et al. [181] when CO\textsubscript{2} and water were included in the reaction mixture.

In conclusion, the most likely mechanisms for release of NO\textsubscript{X} are as follows: (1) adsorption and activation of reductant molecules on metal sites, which then spill over onto to the support and destabilize stored NO\textsubscript{X}, 2.) direct reduction of NO\textsubscript{X} on the support by activated reductant molecules and lastly, 3.) spillover of NO\textsubscript{2} from BaO to Pt, according to the law of

\[
(NO_3^-)_2 \Leftrightarrow O^{2-} + \frac{1}{2} O_2 + NO
\]
microreversibility, and subsequent reduction on precious metal sites. Thermal release due to heat evolved during oxidation of reductants and competitive adsorption of CO\textsubscript{2} could aid in the release of NO\textsubscript{X}, but these mechanisms are not expected to be the driving force behind the release of stored NO\textsubscript{X}. Release due to removal of O\textsubscript{2} or NO from the feed are expected to contribute very little (or not at all) to the total amount of NO\textsubscript{X} released during storage.

A.2.4 REDUCTION MECHANISMS

A considerable amount of effort was donated to the mechanism of NO\textsubscript{X} release because the NO\textsubscript{X} reduction mechanism is intimately tied to NO\textsubscript{X} release. For example, a reduction mechanism that proceeds through a reductant that is activated over a precious metal that subsequently spills onto the support and reacts with stored NO\textsubscript{X} is much different than a reduction mechanism that proceeds through NO\textsubscript{2} migration from the storage sites to the metal and subsequent reduction over the metal. While the differences between these two processes seems obscure, elucidation of the release and reduction mechanism will not only provide fundamental understanding of the chemistry occurring on these materials; it will allow researchers to target specific areas for improvement during systematic design of new catalysts better suited to carry out this chemistry (i.e. stabilization of activated hydrocarbon adspecies on the support may facilitate reduction if the process mainly proceeds though reactions taking place on the support). The following sections focus on NO\textsubscript{X} reduction mechanisms for deNO\textsubscript{X} catalysts and NSR catalysts.

A.2.4.1 REDUCTION MECHANISMS ON DE-NO\textsubscript{X} CATALYSTS

Removal of NO\textsubscript{X} from both stationary and mobile sources has generated an immense amount of research activity because NO\textsubscript{X} release can lead to acid rain, smog, and destruction of
ozone layer [1–3,5,7]. Therefore, regulations were introduced to control the release of NOX into the environment and a vast array of catalysts have been proposed and tested for activity in the reduction of NOX under an assortment of operating conditions including: NH3-SCR on base oxides (e.g. V2O5 and Cr2O3), NH3-SCR on metal zeolites (e.g. Cu-ZSM5), HC-SCR on precious metals and zeolites (e.g. Ag/Al2O3, Pt/Al2O3, Cu-ZSM5), reduction of NO in the presence of H2, CO or HCs (TWCs) on supported metals (e.g. Cu2O/Al2O3, Pt/Al2O3, Pd/Al2O3, Rh/Al2O3, Ir/Al2O3 and Ru/Al2O3) and lastly, direct decomposition of NO (e.g. Cu-Zeolites) [1–3,5,7].

This section briefly highlights mechanistic details for reduction of NOX by CO and HCs on the catalysts relevant to this review. Many details were omitted for brevity since a complete review of all deNOX catalysts is out of the scope of this paper.

**Reduction Mechanisms Occurring on HC-SCR Catalysts**

Reaction 5 describes the desirable reaction products after a lean NOX mixture has been treated using a HC-SCR catalyst, where zeolite based, non-zeolitic oxide-based and noble metal based catalysts have all been investigated for their potential use in this application [2,3,5].

\[
NO (g) + O_2(g) + HC \xrightarrow{HC-SCR Catalyst} N_2 + CO_2 + H_2O
\]

Zeolite based catalysts are generally composed of Cu supported/exchanged on mordenite or ZSM5 and can only achieve high activity (conversion of 66%) in a narrow temperature range (150-230 °C) and are highly susceptible to deactivation by water [3]. Therefore, application in automotive exhaust systems is unlikely and these catalysts will not be discussed further.

Non-zeolitic oxide-based catalysts are generally composed of Co, Ni, Cu, Fe, Sn, Ga, In, or Ag supported on Al2O3, TiO2, ZrO2 or MgO [5]. Of these, Ag/Al2O3 has generated the most
interest because it offers the highest activity and selectivity [5]. While the reduction mechanism occurring on these catalysts is still unclear, several observations have been reached regarding the activity of these materials and include: 1.) The ability of the material to form adsorbed NO\textsubscript{X} species, which is most likely preceded by oxidation of NO to NO\textsubscript{2} and subsequent spillover, 2.) The ability of the material to form partially oxidized hydrocarbon adspecies, and 3.) The ability of adsorbed NO\textsubscript{X} and hydrocarbon species to react with one another to form organo-nitrogen intermediates, where decomposition leads to cyanides, isocyanates, NH\textsubscript{3} and activated NH\textsubscript{3} (-\textsubscript{2}NH), which can then further react with other adsorbed NO\textsubscript{X} species, or gas phase NO [3,5]. When NO\textsubscript{2} was used instead of NO as the NO\textsubscript{X} source, the rate increased and implied that NO\textsubscript{2} may play a critical role in the overall mechanism. Additionally, reaction of NO\textsubscript{X} with oxygen containing HC species (e.g. alcohols instead of propylene) increased the rate, which suggested that adsorbed, partially oxidized hydrocarbon intermediates may also be an important intermediate. Lastly, isocyanate and cyanide species were observed spectroscopically, which supported their role as intermediates. Fig. A22 summarizes this mechanistic scheme. Thibault-Starzyk et al. [304] also recently reported that the transition from a cyanide to isocyanate intermediate was an integral step in this reduction mechanism [26]. Fig. A23 summarizes the updated mechanism based on their results.
Figure A22. Possible reaction scheme of HC-SCR of NO occurring on Ag/Al$_2$O$_3$ catalysts, Burch et al. [5].

Figure A23. Updated HC-SCR of NO reaction mechanism occurring on Ag/Al$_2$O$_3$ when CO was used as the reductant molecule, Thibault-Starzyk et al., 2009 [26].
Noble metal based catalysts were also investigated for activity in the HC-SCR reaction, where Ir and Pt supported catalysts seemed to be most active [2,3,5]. Three possible NO\textsubscript{X} reduction mechanisms emerged for noble metal based HC-SCR catalysts including: 1.) a reduction of NO\textsubscript{X} mainly through formation of cyanides or isocyanates, 2.) reduction through the formation of organo-nitrogen intermediates, or 3.) reduction through decomposition of NO on the surface of precious metals.

As opposed to previous investigations on Ag/Al\textsubscript{2}O\textsubscript{3} catalysts, researchers have been much more reticent to propose that the main route for NO\textsubscript{X} reduction on Pt/Al\textsubscript{2}O\textsubscript{3} catalysts proceeds through cyanide, isocyanate or organo-nitrogen intermediates and controversy on the importance of these mechanisms persists. Both of these routes were proposed based on species observed spectroscopically (FTIR and XPS), but as Breen et al. point out, differentiation between spectator species and true reaction intermediates can be difficult [5]. Generally, the lack of kinetic data tied to cyanide, isocyanate and organo-nitrogen concentrations makes elucidation of their role in the reduction of NO\textsubscript{X} difficult. However, these species cannot be excluded as potential reaction intermediates and the presence of water may greatly alter their relative importance since –NCO species can readily react with water. Reactions involving NCO adspecies can be described as follows [5]:

\[ -NCO + NO \rightarrow N_2 + CO_2 \]  \hspace{1cm} (A6)

\[ -NCO + NO \rightarrow N_2O + CO \]  \hspace{1cm} (A7)

\[ -NCO + NO_2 \rightarrow N_2O + CO_2 \]  \hspace{1cm} (A8)

\[ -NCO + NO_2 \rightarrow N_2 + CO + O_2 \]  \hspace{1cm} (A9)
\[-NCO + [O] \rightarrow N_2 + CO_2\]  \hspace{1cm} (A10)

\[-NCO + H_2O \rightarrow NH_3 + CO_2 + O_2\]  \hspace{1cm} (A11)

The last mechanism proposed for HC-SCR on platinum group metal involves reduction of the oxidized metal surface by hydrocarbons, followed by adsorption and decomposition of NO, where N(ads) combines with another N(ads) species to form N\(_2\) [2,3,5]. Fig. A24 demonstrates this pathway. In conclusion, a variety of mechanisms have been proposed for HC-SCR of \(NO_X\) and the true mechanism is still unknown. Ag based systems are usually represented by mechanisms where isocyanate/organo-nitrogen intermediates dominate, but platinum group metal systems are preferentially described by NO decomposition mechanisms. In reality, some or all of these mechanisms may be operating simultaneously, where the relative contribution of each pathway is dependent on the temperature, concentration of NO/NO\(_2\), concentration of reductant, concentration on O\(_2\), particle size and the inherent properties of the metal and the support. In fact Meunier et al. [297] predicted drastically different behavior for Ag particles of varying sizes, where small particles oxidize NO to NO\(_2\) and large particles dissociate NO. Fig. A25 depicts this behavior. Notice how the NO decomposition and reaction through isocyanate/organo-nitrogen intermediates mechanisms are both occurring simultaneously, but the Ag particle size selectively activates one process over another.
Figure A24. NO decomposition mechanism for HC-SCR of NO\textsubscript{X} on platinum group metal supported catalysts, where the main role of the reductant is to remove adsorbed oxygen that can come from either adsorption of oxygen from the gas phase or decomposition of NO, Parvulescu et al. [2].
**Figure A25.** Example of how Ag particle size could activate one mechanism over another. Notice that large Ag particles can participate in NO decomposition, where the role of adsorbed HC species is to scavenge O(ads) from the metal surface. Small particles are reported to exist in an oxidized state and can only oxidize NO to NO\(_2\). These sites are responsible for catalyzing the NCO/organo-nitrogen route, Meunier et al. [297].

**REDUCTION MECHANISMS BY CO AND HCS ON TWCs**

The reduction of NO\(_X\) under conditions where the concentration of NO\(_X\) and available reductants is very close to the stoichiometric equivalent (i.e., TWCs) is generally accepted to proceed through decomposition of NO on the surface of a platinum group metal [2,3,5]. These catalysts are almost exclusively formulated using Pt or Pd supported on Al\(_2\)O\(_3\), and promoted using Rh and/or ceria. Rh and Ru are thought to be highly active metals since they selectively decompose NO to N(ads) and O(ads). Ruthenium, while active, is poisoned by small amounts of gas phase O\(_2\) and is therefore not relevant for TWCs or NSR catalysts [2]. Ir on the other hand has been reported to decompose NO even in the presence of large amounts of gas phase oxygen and may be interesting for future study [2,132]. Reactions A12 – A15 describe reduction of NO by CO on TWCs [2].

\[
CO + M \rightarrow M - CO
\] (A12)
\[ NO + M \rightarrow M - NO \]  
\[ M + M - NO \rightarrow M - N + M - O \]  
\[ M - N + M - N \rightarrow N_2 + 2M \]  
\[ M - N + M - NO \rightarrow N_2O + 2M \]  
\[ M - N + NO \rightarrow N_2O + M \]  
\[ M - O + CO \rightarrow CO_2 + M \]  
\[ M - N + CO \leftrightarrow M - NCO \]  

Notice that Reaction 19 also describes the formation of isocyanate species, where M-NCO could further react as described previously in Reactions A6-A11. Parvalescu et al. suggested that formation of these species, while observed spectroscopically, constituted only 5% of the overall \( N_2 \) production [2]. However, in a more recent review, Burch [3,5] suggests that this mechanism may be responsible for more \( N_2 \) production than initially thought. In summary, the mechanisms occurring on TWCs are pretty much identical to mechanisms presented for HC-SCR catalysts.

**Reduction Mechanisms by CO and HCs on NSR Catalysts**

Early reports on NSR catalysts mention the formation of isocyanates during reduction with carbon containing compounds, but their role in the reduction mechanism was not discussed [62]. Later, Fanson et al. [43] observed formation of strong bands at 2163 cm\(^{-1}\), which they assigned to isocyanates on Ba. The intensity of the bands correlated well with the NO\(_X\) storage
capacity of the catalysts, which was suggested to imply their role as intermediates. However, if \(-\text{NCO}\) adspecies are spectators and account for only 5% of the total \(\text{N}_2\) produced, as suggested by Parvalescu et al. [2], it is logical that increasing or decreasing the amount of \(\text{NO}_X\) stored on the catalysts would directly influence the concentration of isocyanate species as shown in Reaction A20.

\[
[\text{\(-NCO\)}] = \phi [\text{Ba(NO}_3\text{)}_2] \tag{A20}
\]

Reaction A20 is meant for instructional clarification only and demonstrates the case where isocyanate species are formed via a side-route mechanism not responsible for production of \(\text{N}_2\), where \(\phi\) is the fraction of \(\text{Ba(NO}_3\text{)}_2\) that participates in this reaction (\(\phi=0.05\) if you assume Parvalescu is correct). While the true value for \(\phi\) is unknown, use of this Reaction infers that the concentration of isocyanate species should be directly proportional to the amount of \(\text{NO}_X\) stored by the catalyst, as observed by Fanson et al [43]. However, this does not establish these species as intermediates. It only infers that their relative concentration is dependent on the amount of total \(\text{NO}_X\) stored. To more conclusively assign these species as intermediates, the intensity of isocyanate species needs to be tied to the concentration of \(\text{N}_2\) or other reduction products observed in the gas phase.

Lesage et al. [145] attempted to compare the formation of isocyanate species to evolution of \(\text{N}_2\) by studying the NSR process on a Pt-Rh/Ba/Al\(_2\)O\(_3\) catalyst using \textit{operando} FTIR spectroscopy. Isocyanate species were observed, even in the presence of water, but their intensity was much lower in comparison to experiments conducted under dry conditions. Additionally, their formation was not convincingly tied to production of \(\text{N}_2\). Figure A26 (A) depicts the formation of isocyanates during rich conditions and their removal during the subsequent lean period. Figure A26 (B) depicts the associated chemigrams and mass
spectrometer data. Notice that production of \( \text{N}_2 \) occurs mainly during the first few seconds of the rich periods (shown in grey) and drops off as the isocyanate species intensity increases. This led the authors to imply that isocyanates poisoned the catalyst and led to deactivation during reduction. Lesage et al. [145,146] reported that formation of isocyanate species was undesirable and suggested development of catalytic formulations to minimize formation of these species.

**Figure A26.** NSR mechanism on Pt-Rh/Ba/Al\(_2\)O\(_3\) studied by *operando* FTIR spectrometry. (A) FTIR spectra demonstrating the formation of nitrates, carbonates and isocyanates during periodic lean/rich operations (Lean: 500 ppm NO, 10% O\(_2\), 10% CO\(_2\), 2% H\(_2\)O; Rich: 2% CO, 1% H\(_2\), 10% CO\(_2\), 2% H\(_2\)O). (B) Chemigrams and mass spectra data corresponding to (A), where m=28 corresponds to \( \text{N}_2 \) and m=30 corresponds to NO, Lesage et al. [145].

In a later work, Lesage et al. [146] compared the Pt-Rh/Ba/Al\(_2\)O\(_3\) to their newly formulated Pt/K/CeO\(_2\)-Al\(_2\)O\(_3\) catalyst and suggested that higher stability of nitrates on K resulted in a shift to longer times regarding formation of isocyanates. Figure A27 represents this shift. While nitrates on K are generally thought to be more stable, increased consumption of reductants due to the oxygen storage capacity of ceria could also be used to explain the shift to longer times [151,164]. Generally, Lesage et al. [145,146] seem to favor the route of NO decomposition leading to production of \( \text{N}_2 \), where formation and reaction of isocyanates could either poison the
catalyst or provide a supplementary route to N\textsubscript{2}. Either way, isocyanate intermediates were not suggested as the main route to production of N\textsubscript{2}.

![Figure A27](image)

**Figure A27.** Chemigrams and mass spectra during periodic lean/rich cycling (Lean: 500 ppm NO, 10% O\textsubscript{2}, 10% CO\textsubscript{2}, 2% H\textsubscript{2}O; Rich: 2% CO, 1% H\textsubscript{2}, 10% CO\textsubscript{2}, 2% H\textsubscript{2}O) performed on a Pt/K/CeO\textsubscript{2}-Al\textsubscript{2}O\textsubscript{3} catalyst, where m=28 corresponds to N\textsubscript{2} and m=30 corresponds to NO. Reprinted from Lesage et al. [146].

In the absence of water, Abdulhamid et al. [27] observed formation of strong IR bands at 2220 and 2162 cm\textsuperscript{-1} on M/Ba/Al\textsubscript{2}O\textsubscript{3} (M=Pt, Pd, or Rh) catalysts using both CO and C\textsubscript{3}H\textsubscript{6} as reductants. These peaks have been confidently assigned to isocyanate species on Al and Ba, respectively [24,27]. Since NCOs were observed during cycling using CO and C\textsubscript{3}H\textsubscript{6}, Abdulhamid et al. [27] concluded similar mechanistic pathways must operating for both reductants, but were reticent to suggest a reduction mechanism based on their data. Deterioration of Pt based catalysts was observed and was attributed to the formation of carbonyls on Pt or isocyanates on Al (2230-2220 cm\textsuperscript{-1}) or Ba (2162 cm\textsuperscript{-1}). Interestingly, this behavior was not observed on Pd or Rh based catalysts.
Szailer et al. [24] on the other hand, proposed a fairly detailed mechanism based on their results using Pt/Al₂O₃ and Pt/Ba/Al₂O₃ catalysts. At low temperatures, decomposition of NO and reaction of N(ads) with CO to form NCO(ads) was active, but production of N₂ was low (<473 K). At higher temperatures (>573 K), NCO(ads) could react with stored NOₓ to produce N₂. Addition of water drastically increased production of N₂. The following mechanism was proposed to explain these observations:

\[
P_{\text{t}} - O + H_2 \rightarrow Pt^* + H_2O \tag{A21}
\]

\[
2Pt - N \rightarrow 2Pt^* + N_2 \tag{A22}
\]

\[
(x + 1)Pt^* + NO_X \rightarrow xPt - O + Pt - N \tag{A23}
\]

\[
Pt - N + Pt - H \rightarrow Pt - NH_X + Pt - H \rightarrow NH_3 \tag{A24}
\]

\[
Pt - N + Pt - CO \rightarrow Pt^* + Pt - NCO \tag{A25}
\]

\[
Pt - O + CO \rightarrow Pt^* + CO_2 \tag{A26}
\]

\[
NCO(ads) + NO_X \rightarrow N_2 + CO_2 \tag{A27}
\]

\[
NCO(ads) + H_2O \rightarrow NH_2(ads) + OH(ads) \tag{A28}
\]

\[
NH_3 + NO_X + H_2O \rightarrow [NH_4NO_X] \rightarrow N_2 + H_2O \tag{A29}
\]

*Note: Pt* represent a free Pt site and X(ads) represent a molecule adsorbed on a nondescript site*

Reactions A21-A24 describe reduction by H₂ and were included to demonstrate that reduction of NOₓ by H₂ or CO is preceded by decomposition of NO (Reaction A23). For H₂, the N adatom can either combine with another N adatom to form N₂ (Reaction A22) or react with H₂.
to form ammonia (Reaction A24), where NH$_3$ can desorb un-reacted or selectively reduce NO$_X$ (Reaction A29). Similarly for CO, the decomposed N adatom can either combine with another N adatom or react with CO(ads) to form isocyanates (Reaction A25). The authors admitted that reaction of two N adatoms cannot be excluded as a pathway for production of N$_2$ when CO is used as a reductant, but suggested that the main route proceeded through formation of isocyanates that react with water, oxygen or stored NO$_X$ to ultimately form N$_2$. This claim is based on the observation that adding water and CO to the reactor during reduction increased production of N$_2$.

Two particularly important subtleties of this mechanism are worth mentioning. First, NO must decompose to an N adatom before it can react with CO to form an isocyanate. Therefore, both NO reduction mechanism share NO decomposition as a primary step. Second, isocyanate species were not observed on metal surfaces, but on the support – both Ba (2162 cm$^{-1}$) and Al$_2$O$_3$ (2220-2250 cm$^{-1}$) [24,27,62,64,145,146,289,290]. So, were isocyanate species reacting on the support with stored NO$_X$, or must they diffuse back to the surface of the metal to undergo reaction?

Recently, Breen et al. [16] reported reactor data consistent with the mechanism presented by Szailer et al., where a series of catalyst were tested in a fast transient reactor capable of 200 ms time resolution. This allowed the NO$_X$ reduction process to be studied under realistic operating conditions (e.g., 60 s lean and 1.2 s rich). In this case, N$_2$ evolved in two distinct periods during reduction, the first occurred immediately after the switch from lean to rich and the second occurred immediately after the switch back to lean conditions. Fig. A28 describes this behavior for a series of typical NSR catalysts, where the precious metal loading and type of precious metal greatly affected the behavior observed.
Figure A28. Evolution of reaction products during a rich event (CO + H\textsubscript{2} + H\textsubscript{2}O + CO\textsubscript{2}) at 350 °C on a series of NSR catalysts formulated from commonly used precious metals including: (A) 0.5% Pt, (B) 1.6% Pt, (C) 1.1% Rh and (D) 0.5% Pt-0.8% Rh supported on 17%Ba/Al\textsubscript{2}O\textsubscript{3} (w/w), Breen et al. [16].

Figure A29 demonstrates how changing the reductant affected N\textsubscript{2} evolution. Notice the large N\textsubscript{2} spike when CO was used as a reductant in the absence of H\textsubscript{2}, where approximately 90% of the total N\textsubscript{2} evolved on this catalyst came from the 2\textsuperscript{nd} N\textsubscript{2} evolution period. This suggested that isocyanates were formed on the catalyst during rich periods and were quickly oxidized to N\textsubscript{2} or hydrolyzed to NH\textsubscript{3} during subsequent lean periods. Breen et al. concluded that the first N\textsubscript{2} peak was formed by rapid reduction of NO\textsubscript{X} on the surface of reduced Pt or Rh and the second N\textsubscript{2} peak was formed by reaction of stored NH\textsubscript{3} with stored NO\textsubscript{X} from by hydrolysis of isocyanates. The authors omitted the possibility of oxidation of stored NH\textsubscript{3} to produce N\textsubscript{2} and reaction of isocyanates with NO/O\textsubscript{2} to form N\textsubscript{2} as another route to N\textsubscript{2} production. However, storage of NH\textsubscript{3} at elevated temperatures is very unlikely, as recently shown by Bahrami et al. [175]. Lastly, Breen et al. [16] used fairly high concentrations of reductants, which could also
alter the reduction mechanism. For example, a high concentration of CO in the gas phase may facilitate isocyanate intermediates because the probability of an N adatom reacting with an adsorbed CO species before it can react with another N adatom may increase if the concentration of CO on the surface increases proportionally to the concentration of CO in the gas phase.

![Figure A29](image)

**Figure A29.** Reaction products during a rich event over a 0.5%Pt-0.8%Rh/17%Ba/Al\textsubscript{2}O\textsubscript{3} (w/w) NSR catalyst at 250 °C, where the rich phase contained 6% CO, 6%H\textsubscript{2} or 1.5% H\textsubscript{2} and 4.5% CO, Breen et al. [16].

Nova et al. [64,289] also proposed that the reduction of NO\textsubscript{X} could proceed through isocyanate intermediates, but pointed out that the water gas shift reaction (Reaction A30) could also create large amounts of H\textsubscript{2} from CO in the presence of water. When a Pt/Ba/Al\textsubscript{2}O\textsubscript{3} catalyst
was exposed to CO and H₂O, the light-off temperature for the WGS reaction occurred slightly above 200 °C. Above 300 °C, H₂ and CO₂ were the only products observed, as shown in Fig. A30. Scholz et al. [28,319,320] have also mentioned the WGS reaction as a potentially important reaction occurring on NSR catalysts. This conclusion was reached because CO and H₂ were equally effective reductants in the presence of water, but H₂ was much better than CO in the absence of water.

\[
CO + H₂O \rightarrow H₂ + CO₂ \quad \text{(A30)}
\]

**Figure A30.** Temperature programmed surface reaction (TPSR) of 2000 ppm CO + 1% (v/v) H₂O over a 1%Pt/20%Ba/Al₂O₃ (w/w) NSR catalyst, Nova et al. [64,289].

Forzatti et al. also suggested that formation of N₂ proceeds through formation of isocyanate intermediates, where the isocyanates could then react with adsorbed NOₓ species, NO, O₂ or H₂O as shown in Fig. A31 [290]. However, an alternative mechanism for reduction of surface nitrates with CO in the absence of water was also proposed. Reactions A31 – A35 highlight this mechanism.
\[ -Ba - ONO_2 + Pt - CO \rightarrow -Ba - ONO + CO_2 + Pt^* \] (31)

\[ -Ba - ONO + Pt - CO \rightarrow -Ba - OCONO + Pt^* \] (32)

\[ -Ba - OCONO + Pt - CO \rightarrow -Ba - OCNO + CO_2 + Pt^* \] (33)

\[ -Ba - OCNO + Pt - CO \rightarrow -Ba - NCO + CO_2 + Pt^* \] (34)

\[ -Ba - NCO + Ba - ONO \rightarrow -Ba - O - Ba - + N_2 + CO_2 \] (35)

The first step involves decomposition of barium nitrate to nitrite. Next, CO spills over from Pt onto Ba and inserts itself into barium nitrite forming an organo-nitrogen-like compound. Reaction with another CO molecule reduces this complex ultimately forming an NCO adspecies on Ba. This species can then undergo reactions A6-A11, A27-A28, or reaction A35 to produce \( N_2 \).

**Figure A31.** Proposed reaction network for reduction of \( \text{Ba(NO}_3\text{)}_2 \) by CO in the absence of water. Reprinted from Forzatti et al., 2010 [15].

In summary, reduction of \( \text{NO}_X \) by CO and \( \text{C}_3\text{H}_6 \) has many potential reaction pathways and the overall reduction mechanism operating on these catalysts remains elusive. Additionally, the role of isocyanate intermediates is still unclear. While a considerable number of investigations have observed isocyanate species in FTIR spectra, evidence tying their presence to
the production of $N_2$ is still lacking, where parallel reactions like WGS greatly complicate understanding. In the presence of $H_2O$ production of $H_2$ from CO and $H_2O$ could dramatically change the reduction mechanism and could favor the currently proposed reduction mechanism for $H_2$, which involves NH$_3$ an intermediate [60,286,346].

A.2.5 CONCLUSIONS

NO$_X$ storage and reduction catalysts are very promising for use in lean-burn engine exhausts because they are capable of converting high amounts of harmful NO$_X$ to $N_2$ and have already been implemented in Japan. Since their inception, many advances have been made and the current materials are more thermally resistant and sulfur tolerant than their predecessors. However, the reduction mechanisms occurring on these catalysts are still unclear. Since these catalysts are often limited by their inability to completely reduce NO$_X$ stored during the short times necessary for these systems to operate, better understanding of the reduction mechanism is crucial for optimization of this aspect of the catalyst.

While the specific reduction mechanism is still unclear, this review has exposed some of the more significant conclusions available in the literature. Mainly, release of stored NO$_X$ most likely proceeds through adsorption of reductant molecules that either react with NO$_X$ on the metal surface or spillover onto the support and destabilize/react with adsorbed NO$_X$. Reduction by CO or hydrocarbons most likely proceeds through NO decomposition to N adatoms that react with other N adatoms to form $N_2$ or react with adsorbed to form isocyanates, where isocyanates could then react with NO, O$_2$, H$_2$O or stored NO$_X$ to produce $N_2$, N$_2$O or NH$_3$, where NH$_3$ is an excellent molecule for SCR of NO$_X$. Additionally, the role of the WGS reaction cannot be
excluded and CO may react with water to produce H₂, which has long been considered a better reductant than CO or C₃H₆. The role of C₃H₆ in the reduction of stored NOₓ is still unclear.