Influence of Coordination Environment on Catalyst Structure and Function for CO2 Hydrogenation and Ethane Partial Oxidation

Juan D. Jimenez

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INFLUENCE OF COORDINATION ENVIRONMENT ON CATALYST STRUCTURE AND FUNCTION FOR CO₂ HYDROGENATION AND ETHANE PARTIAL OXIDATION

by

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DEDICATION

To my family
ACKNOWLEDGEMENTS

First and foremost, I would like to thank my advisor, Prof. Jochen Lauterbach. Without your guidance and leadership, I am sure I would have never become half the scientist I am today. In your group I developed a strong sense of scientific autonomy, where I could pursue anything that crossed my mind unimpeded.

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Most importantly, to my family, thank you. Without your encouragement I would have surely lost my mind. Your encouragement and support allowed me to focus entirely on my work, where I have grown to become a capable scientist.
ABSTRACT

In this work, we set out to establish strong structure/activity relationships for various catalytic compositions and reactions. Through in situ spectroscopic approaches, specifically DRIFTS, Raman XPS, and XAFS, we were able to discern the reactive species in CO$_2$ hydrogenation over highly active cobalt nanostructures, the relevant ensemble size and composition of single site catalysts for CO$_2$ hydrogenation, and active vibrational modes of mixed oxide catalysts for ethane partial oxidation (EPO).

First, we illustrate how tailoring surface orientations of Co$_3$O$_4$ catalysts on the nanoscale results in control over catalytic performance via the preferential formation of active surface species during CO$_2$ hydrogenation. This resulted in over an order of magnitude increase in the methane turnover frequency on Co$_3$O$_4$ nanorods with the exposed {110}/{001} family of surface facets, as opposed to conventional Co$_3$O$_4$ nanoparticles with the exposed {111}/{001} family of surface facets. We found via in situ DRIFTS studies that this difference in catalytic performance for the Co$_3$O$_4$ nanorods was due to the inhibition of the formate spectator species. Furthermore, by studying the second hydrogenation step in CO$_2$ hydrogenation, which is CO hydrogenation, we were able to discern that the formation of bridged CO was the key difference between the two catalyst.

Second, cobalt and ruthenium single site catalyst were explored due to their highly uniform active sites; allowing for definitive claims as to which surface species are responsible for the reaction mechanisms. To characterize the structure and dispersion of the single-site catalysts, techniques such as UV-vis, XAFS, XPS, TPR, and Raman were
utilized under ambient conditions as well as under reductive environments to simulate reaction conditions. For the case of cobalt single sites, the surface moieties under ambient and reductive environments coupled with their corresponding catalytic performance during CO$_2$ hydrogenation allowed us to discern how the transition between isolated atoms to small nanoparticles affects the reaction mechanism. For ruthenium single site catalysts supported on boronitride, we found atomic and/or subnanometer clusters to be over an order of magnitude more active than their analogous nanoparticles.

Finally, we utilize a statistical Design of Experiments (DOE) methodology to elucidate the relationship between different synthesis parameters and their effect on the catalytic activity and selectivity of EPO. Specifically, we explored the effects of dopant addition to a base MoVNbO catalyst, which has shown promising activity for EPO and other hydrocarbon partial oxidations. To capture a multitude of the convoluted effects arising from changes to the synthesis parameters we provide a detailed characterization of the crystalline structure, relative crystalline phase abundance, composition, and the catalytic activity/selectivity of EPO. By capturing multiple trends afforded to the DOE parameter space, we developed heuristics and guided synthesis parameters for the development of novel catalyst for ethane partial oxidation. Furthermore, the most active catalysts were chosen for detailed in situ Raman spectroscopy, where in these studies we found that the active Raman band under reaction conditions is the $\nu=940$ cm$^{-1}$ band while the $\nu=870$ cm$^{-1}$ band was found to be structurally dependent and not dependent on the reaction.
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Figure A.6 Copyright Permission for J. Jimenez, K. Mingle, T. Bureerug, C. Wen, and J. Lauterbach, "Statistically Guided Synthesis of MoV-Based Mixed-Oxide Catalysts for Ethane Partial Oxidation," Catalysts, vol. 8, p. 370, 2018 ........................................244
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LIST OF ABBREVIATIONS

AA ........................................................................................................... Acetic Acid
AC-TEM ............................................................ Aberration Corrected Transmission Electron Microscopy
BIXAFS .............................................................. Back-Illuminated X-Ray Absorption Spectroscopy
BPR ........................................................................................................... Back Pressure Regulator
CoNP ....................................................................................................... Cobalt Nanoparticles
CoNR ....................................................................................................... Cobalt Nanorods
CTAB ................................................................................................. Hexadecyltrimethylammonium bromide
CV ........................................................................................................... Cyclic Voltammogram
D/H ........................................................................................................... Dopant to Host Ratio
DI .............................................................................................................. De-Ionized Water
DMF .......................................................................................................... Dimethylformamide
DOE ......................................................................................................... Design of Experiments
DRIFTS .......................................................... Diffuse Reflectance Infrared Fourier Transformed Spectroscopy
DWF .......................................................................................................... Debye-Waller Factor
EDS .......................................................................................................... Energy Dispersive Spectroscopy
EPO .......................................................................................................... Ethane Partial Oxidation
EXAFS ............................................................. Extended X-Ray Absorption Fine Structure
FCC .......................................................................................................... Face centered cubic
FID ............................................................................................................. Flame Ionization Detector
FTIR .............................................................. Fourier Transformed Infrared Spectroscopy
FWHM ..................................................................................................... Full-Width Half-Max
GC ................................................................. Gas Chromatography
GHSV ............................................................ Gas Hourly Space Velocity
GQD ............................................................... Graphene Quantum Dots
HAADF ............................................................ High Angular Annular Dark Field
hBN .............................................................. hexagonal boron nitride
HCP ................................................................. Hexagonal close packed
HERFD ............................................................ High Energy Resolution Fluorescence Detection
HOPG ............................................................. Highly Orientated Pyrolytic Graphite
HRTEM ............................................................ High Resolution Transmission Electron Microscopy
ICP-MS ........................................................... Inductively Coupled Plasma-Mass Spectroscopy
ICP-OES ........................................................ Inductively Coupled Plasma-Optical Emission Spectroscopy
IMP ............................................................... wet impregnated catalysts
LHS ................................................................. Left Hand Side
MFC ............................................................... Mass Flow Controller
MS ................................................................. Mass Spectroscopy
NGQD ............................................................ Nitrogen Doped Graphene Quantum Dots
ODH ............................................................... Oxidative Dehydrogenation
pBN ............................................................... porous boron nitride
PPIR ............................................................... Primary Phase Intensity Ratio
PTFE .............................................................. Polytetrafluoroethylene
R/A ................................................................. Redox to Acid Ratio
RGA ............................................................... Residual Gas Analyzer
RWGS ........................................................... Reverse Water Gas Shift
S (fx) ............................................................... Selectivity
SEM ............................................................... Scanning Electron Microscopy
SPIR ...................................................................................... Secondary Phase Intensity Ratio
SSC ...................................................................................... Single Site Catalysts
STEM .................................................................................. Scanning Transmission Electron Microscopy
TBOT ..................................................................................... Titanium (IV) butoxide
TCD ..................................................................................... Thermal Conductivity Detector
TEM .................................................................................... Transmission Electron Microscopy
TEOS ..................................................................................... Tetraethylorthosilicate
TOF ........................................................................................ Turnover Frequency
TPD ........................................................................................ Temperature Programmed Desorption
TPR ........................................................................................ Temperature Programmed Reduction
UV-vis .................................................................................... Ultraviolet-visible absorption spectroscopy
X (fx) ........................................................................................ Conversion
XAFS ..................................................................................... X-Ray Absorption Spectroscopy
XANES .................................................................................. X-Ray Absorption Near Edge Spectroscopy
XPS ...................................................................................... X-Ray Photoelectron Spectroscopy
XRD ........................................................................................ X-Ray Diffraction
Heterogeneous catalysts consist of materials that drive down the activation barrier of chemical reactions, that is facilitate the kinetics, while maintaining the final thermodynamic endpoint, i.e. A+B→C. Heterogenous catalysts, much like any catalyst, undergo various elementary steps that when combined constitute the transition from reactant to product [4]. The distinguishing feature on heterogeneous catalysts is the reaction mechanism, which predominantly occurs via a Langmuir-Hinshelwood mechanism [5]. Regardless of the phase of the reactant, be it gas or liquid, on a solid catalyst the reactant must first contact the surface of the catalyst, after which it will be in an adsorbed state such that species A will become species A* and species B will become B*. This is the fundamental driving force that allows for the reaction to take place with a lower activation barrier; where the adsorbed species are much more reactive than they were in the bulk phase. At this point the reaction will take place given a sufficient input of energy, be it voltage for electrochemical reactions, light for photochemical or heat for thermo-chemical reaction. This ultimately leads to the production of the end adsorbed product, C*, which will desorb from the surface and re-enter the reactant phase as the final product C. Throughout this thesis, several reactions will be discussed in detail with respect to their overall mechanism and how it both pertains to the catalyst structure and performance. Specifically, the catalyst performance will be monitored as a consequence of carefully
perturbing the reactive surface for CO₂ hydrogenation and ethane partial oxidation over a host of different catalyst compositions to ultimately elucidate the structure-activity relationship between the selected catalysts and their corresponding reactions.

1.2 CO₂ Hydrogenation

As the field of carbon dioxide capture and storage is expanding as a means of mitigating CO₂ emissions, transforming carbon dioxide into value added chemicals or fuels represents an economically viable approach to carbon fixation[6-10]. Various means of upgrading CO₂ have been explored, most notably electrochemical conversion and catalytic conversion.[8] Cobalt, ruthenium, and nickel catalysts have been shown to favor the complete reduction of CO₂ to methane,[11, 12] while other metals, such as Cu/ZnO, can partially reduce CO₂ into methanol.[13, 14] Recently the direct production of olefins from CO₂ has been reported using a variety of different catalyst compositions such as Indium supported on zeolites [15, 16] or alkali promoted Fe catalysts [17, 18]. The cause of the variety in production distribution on different catalysts is partially due to the highly surface structure sensitive nature of CO₂ hydrogenation, where both DFT and experimental studies struggle to elucidate the reaction mechanism due to the complex nature of nanoscale catalysts.[6, 19-21]. The generally agreed upon mechanism in literature is that CO₂ initially dissociates into CO and then undergoes an associative hydrogenation into the final reduced product, such as methanol or methane [19, 22-24]. Chain growth into C₂⁺ products can occur during the intermediate CO hydrogenation after the initial CO₂ C-O cleavage, however due to the operating conditions of CO₂ hydrogenation which favor hydrogen rich feedstocks (either 3:1 H₂:CO₂ or 4:1 H₂:CO₂ ratios) chain growth is typically limited to an upper limit of C₃⁺ in the presence of transition metal catalysts such as Co, Ni, or Ru [24-
The relevant reactions occurring during CO$_2$ hydrogenation are CO$_2$ methanation and the reverse water gas shift, which are shown in Equations (1) and (2); respectively [8].

\[
(1) \ CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \Delta H^0 = -165kJ/mol
\]

\[
(2) \ CO_2 + H_2 \rightleftharpoons CO + H_2O \Delta H^0 = 21kJ/mol
\]

Cobalt catalysts have shown immense potential due to their high catalytic activity and affordability. A typical cobalt catalyst for CO$_2$ hydrogenation consists of supported cobalt nanoparticles on the order of 5-15 nm.[27, 28] However, at the nanoscale a high degree of heterogeneity is found on the catalytically relevant surface structures, arising from changes in particle size[27], surface crystal faceting[24, 28, 29], or point defects[30]. Studies performed on single crystal surfaces in ultra-high vacuum conditions mitigate the heterogeneity of the active sites by rigorously characterizing the surface[19], however, such degree of characterization is not feasible on powder catalysts at the 5-10nm scale. Furthermore, nanoscale catalysts are also subject to surface reconstruction, which becomes increasing difficult to characterize under reaction conditions and can lead to changes in activity that are not captured by correlating catalytic activity and particle size, requiring the need for rigorous in situ techniques such as environmental TEM, in situ XAFS, or ambient pressure XPS.

1.3 Single Site Catalysts

Single-site catalysts (SSCs) have been recently studied due to the highly uniform surface they offer.[1, 20, 31-34] Single site catalysts generally consist of atomically isolated active sites, where there is no long-range ordering of catalytically active atoms. Such an example would be single-site cobalt supported on silica, where the cobalt is grafted
onto the surface oxide groups of the silica support, resulting in atomically dispersed cobalt cations with no observable Co-O-Co bonding.[33, 35] Recent advances in SSCs have been focused on determining their catalytic activity for a host of different reactions. Most notably, single-site platinum on various different supports have been studied for CO oxidation[36]. Platinum is a preferred element to study due to the ease of characterizing the atomic isolation via either Scanning Transmission Electron Microscopy (STEM) or CO adsorption infrared studies. Palladium has also been studied for hydrogenation reactions, where single-site palladium was shown to be active for the hydrogenation of 1-hexane[37] as well as for the cyclotrimerization of acetylene.[38]. SSCs have been shown to yield remarkably stable product selectivity for reactions such as propane dehydrogenation[33] and the hydrogenation of hexane[37], which can be attributed to the uniform active site. For SSCs, the metal-support interaction is a key factor governing the catalytic activity of SSCs. Since the active sites on SSCs are completely surrounded by the support, reaching an atomic efficiency of 100%[31], the choice of support plays a drastic role in the structure, stability, and activity of the SSC.[1, 35, 36, 39] Recent work has shown that Pt/La-Al2O3 remains in an atomically isolated state in the presence of ceria polyhedrons and nanorods after being aged at 800°C for a week, while in the presence of ceria nanocubes the Pt completely sinters after the aging procedure[36]. Platinum single site catalysts supported on HZSM-5 are shown in Figure 1.1, alongside the associated CO adsorption that verified the formation of single site catalysts.

Given the success of noble metal SSCs in promoting various different kinds of reactions, work has been recently turned to the use of transition metals for SSCs. While transition metals would be expected to have a lower activity than noble metals due to their
electron configuration, they have the advantage of being more stable in the atomically isolated state. While palladium is slightly oxophillic and tends to form PdO when in contact with oxygen, or in this case on an oxide support, it interacts with the surface oxide leading to stable atomic centers up to approximately 300°C in a reducing environment. As for platinum, it tends to interact very weakly with the support and does not form an oxide, meaning it remains in either a metallic state or a Pt^+1 state, which is highly unstable and tends to aggregate into clusters or nanoparticles readily under reaction conditions.

Figure 1.1. Identification of Pt single sites via (left) CO adsorption and (right) electron microscopy for Pt/HZSM-5 catalysts. Adapted from reference [1]

One of the main advantages of using SSCs is their ability to probe reaction mechanisms. Since the surface that is created consists of a uniform active site that can be well characterized, one can definitively link changes in surface structure to changes in catalytic activity. Since atomically dispersed sites are not trivial to characterize, one must turn to several surface science techniques to confidently claim the surface is uniform and highly dispersed. Such techniques include X-Ray Photoelectron Spectroscopy (XPS), X-Ray Absorption Spectroscopy (XAS), Infrared Spectroscopy, Raman Spectroscopy, and
electron microscopy. With the information afforded by these techniques on the surface structure of the catalyst, we can gain insight into the CO$_2$ hydrogenation reaction mechanism and how it depends on the local coordination environment of the studied catalytic site. Herein we studied cobalt single-site catalysts due to its activity in various reactions, such as propane hydrogenation/dehydrogenation[33], water oxidation,[34, 35] and the electrochemical reduction of CO$_2$[20]. Additionally, cobalt has been shown to be stable in an atomically dispersed state up to 500°C in a reducing environment, which is sufficiently stable to resist sintering into nanoparticles, which would complicate the mechanistic understanding due to the introduction of heterogeneous active sites.

There are three typical pathways towards confining metal atoms on supporting materials: extraneous (e.g. coordinating Ti by titanocene dichloride), intrinsic ligands (e.g. oxygen or heteroatoms connecting metal atom) by forming coordination, and micropore-confined structures (e.g. metal organic frameworks) by physical restriction.[40, 41] Due to its effectiveness and simplicity, intrinsic ligand coordination has been widely applied to prepare single atom catalysts such as single Fe, Co and Ni atoms immobilized on N-doped carbon through metal-N coordination.[42-45]. Intrinsic ligand coordination can be accomplished via the coordination between surface OH groups and reactive cationic species, i.e. precursor salts such as hexammine based metal salts. When using sufficiently low loading (~0.1-0.7wt% metal) of metal precursor onto a high surface area support (>300 m$^2$/g), the formation of single sites via intrinsic ligand formation is statistically favorable[33, 34]. Therefore, intrinsic ligand coordination was adopted for the preparation of both sets of single site catalysts herein due to the precise synthesis it provides.
1.4 Ethane Oxidative Dehydrogenation

The catalytic conversion of ethane into olefins and chemicals has been a subject of much research over the past several decades [46, 47]. Conversion of ethane into value added products goes through either ethane deoxyhydrogenation, whose main product is ethylene [48-50], or ethane partial oxidation, which produces a various value added C2 components, such as ethylene [51, 52] and acetic acid [2, 53-56]. Currently, the development of efficient heterogeneous catalysts for ethane conversion into its value-added products, acetic acid and ethylene, is of interest due to the high abundance of low-cost ethane from shale gas. The overall reaction schematic is shown in Figure 1.2 for the oxidation of ethane into either ethylene, acetic acid, or combustion products. Generally, ethane partial oxidation occurs sequentially, with ethylene being the primary product and acetic acid being the secondary product. To preferentially form ethylene the reaction is carried using fast residence time to dampen the secondary acetic acid formation, which occurs under low space velocities. Under low residence time ethylene can undergo a secondary oxidation with either adsorbed oxygen, lattice oxygen, or adsorbed water via a Wacker mechanism to form acetic acid. It is important to note that combustion products such as CO2 and CO can form from either ethylene or acetic acid depending on the nature of the catalysts; where combustion products are often the most difficult aspect of the reaction to mitigate. Furthermore, the rate limiting step for ethane oxidation is often the initial C-H scission, where the subsequent step to form olefins, oxygenates, or combustion products occurs rapidly.
Figure 1.2. Overall ethane partial oxidation reaction scheme. Adapted from reference [2]

State of the art catalysts for the partial oxidation of short alkanes are typically based on molybdenum and vanadium mixed oxides, which have been shown to preferentially form value added products, such as acrylic acid and acetic acid [2, 56-64]. A schematic representation of the structure of the Mo-V catalysts is shown in Figure 1.3, which is referred to as the M1 structure consisting of Mo, V, and Nb octahedrons in a specific configuration of five, six and seven membered rings.

Elements such as niobium and antimony have been added to these Mo-V-O structures with the objective of increasing their structural stability and maintaining the desired Mo-V phase[54]. Additionally, the stabilization of the active Mo-V-M-O (M = Al,
Co, Cr, Fe, and Bi) phase through interactions between the molybdenum and M species resulting in the formation of a solid solution during the hydrothermal treatment has been explored as a means of forming a uniform phase[65]. Overall, Nb was found to be the most effective stabilizing agent for the Mo-V-M-O structure resulting in the mitigation of phase segregation and increased activity in both ethane partial oxidation[54, 60, 66] and ethane oxidative dehydrogenation[64, 67].

In addition to studies focused on stabilizing the Mo-V-O catalyst, recent studies have been dedicated to improving the catalytic performance through the incorporation of promoters. Such promoters are typically either acid/base elements, such as tellurium[54, 58], calcium, potassium[68] or transition metals with varying redox properties, such as palladium, nickel and titanium[48, 65, 66]. Optimal loadings of acid/base elements are typically on the same order of magnitude as the loading of niobium into the base catalyst, such as Mo$_6$V$_2$Te$_1$O$_x$ and Mo$_6$V$_2$Sb$_1$O$_x$ [69], where the acid/base elements in this case were tellurium and antimony in place of the niobium. Similarly, in cases where both the niobium and an additional acid/base element is present, their atomic ratio remains at approximately unity, such as Mo$_1$V$_{0.22}$Nb$_{0.15}$Te$_{0.23}$ [59, 68, 70]. Interestingly, in some cases the destabilization of the primary Mo-V-O phase has not resulted in decreased catalytic activity, possibly due to the formation of new active sites in lieu of the Mo-V-O phase. One such example is the incorporation of small amounts of alkali metals, such as potassium or basic metals, such as bismuth to MoVTeNbO[68]. Due to extensive segregation of the crystalline structure of mixed oxide catalysts upon addition of dopants, forming a clear correlation between catalyst structure, dopants and performance is currently challenging when comparing varied literature[68, 71-74].
Contrary to findings for acid-element doping, optimal loadings of redox elements vary based on the reducibility of the metal. For example, incorporating noble metals such as palladium dramatically affects the catalytic activity to favor acetic acid production with the addition of only 0.0025 wt% Pd metal to a Mo$_{0.61}$V$_{0.31}$Nb$_{0.08}$O$_x$/TiO$_2$ catalyst [56]. However, less reducible transition metals, such as nickel and titanium, appear to require higher loadings to have a comparable effect on activity, where optimal ethylene production was achieved using a Ni$_{0.85}$Nb$_{0.15}$O$_x$ catalyst [75] and high acetic acid production was achieved using a Mo$_6$V$_2$Al$_1$Ti$_{0.5}$O$_x$ catalyst [63]. While the doping of acid/base elements into Mo-V-O structures has been addressed in depth in several studies [76-78], a comprehensive understanding of how co-incorporating both reducible and acidic species at varying levels affects both catalytic activity and structure, specifically in terms of the required balance between reducibility and acidity, remains unclear.
CHAPTER 2
METHODS & THEORY

2.1 CO₂ Hydrogenation and Catalytic Activity Testing

CO₂ hydrogenation is the thermo-catalytic reduction of CO₂ into either methane, CO, methanol, or higher order olefins. For illustration, a list of elementary steps is shown below in Figure 2.1 for the conversion of CO₂ into methane:

![Figure 2.1. Schematic of CO₂ methanation following two competing mechanisms](image)

CO₂ methanation generally requires the use of strongly adsorbing transition metal, such as Co, Ni, Fe or Ru [6, 20]. The methanation reaction typically requires the presence of metallic species as opposed to their cationic counterparts due to the ability of metallic transition metals to dissociate hydrogen, which is required for the complete reduction. Oxides generally favor the incomplete reduction of CO₂ into CO via the RWGS reaction; where the weaker binding energy between the cationic species and the adsorbed CO
intermediate coupled with the reduced amount of spillover hydrogen compared to a metal surface allow for the desorption at CO from oxides. In practice, the relevant parameters that are drawn from catalytic measurements are the temperature, outlet concentration of effluent stream, and pressure. From these, one can calculate the conversion and product distribution: shown in the equation 2.1 and 2.2; respectively

\[
X = 1 - \frac{(\frac{C_{CO_2}}{C_{Ar}})_{outlet}}{(\frac{C_{CO_2}}{C_{Ar}})_{inlet}} \tag{2.1}
\]

\[
S = \frac{c_i}{\Sigma_{i=0}^n v c_i} \tag{2.2}
\]

To increase the accuracy of the measurement, an inert standard is introduced into the feedgas in a known concentration. This allows one to use the relative ratio of reactant to inert to compensate for gas expansion, since neither moles or volume of reactant is conserved in a chemical reaction. Additionally, the selectivity for all reactions is calculated on a carbon basis. A representative schematic for the reactor configuration used throughout the work presented in this thesis is shown in Figure 2.2. Two tandem, high pressure reactors ran simultaneous reactions which were independently sampled by a Shimadzu GC-2014 equipped with an internal switching valve to keep the effluent flow from each reactor isolated. The GC had a TCD and FID detector with a ShinCarbon Column for light gases (inert gases and carbon species below C_3) and a 30m 0.25mm ID capillary column for higher chain hydrocarbons. For CO_2 hydrogenation test, generally the catalysts was packed in a 6:1 ratio of sand: catalysts to mitigate the exothermicity of reaction and avoid hot spot formation; where the K-type thermocouple was inserted into the catalyst bed to measure temperature accurately. Pressure was regulated via the use of a BPR and brought up to the specified pressure indicated for each catalytic test, which was generally 10 bar. The gas
hourly space velocity, which is defined as the amount of time required to fill one complete volume of catalyst was reported in terms of the total flow rate divided by the amount of catalyst loaded such that units were mL·g\textsuperscript{-1}·hr\textsuperscript{-1}. The reactor itself consisted of a stainless-steel plug flow reactor, where the catalysts was held in position with a support rod directly in the center of the furnace, to ensure uniform heating of the bed. Unless otherwise specified, the feed gas used was a mixture of stoichiometric methanation gas which has a 4:1 ratio between H\textsubscript{2} and CO\textsubscript{2}; respectively, where Ar acted as the inert standard (gas composition: 18% CO\textsubscript{2}/72% H\textsubscript{2}/10% Ar)

Figure 2.2. Dual high-pressure reactor schematic with variable gas inlet compositions

The apparent activation energy measurements were carried out under differential conversion conditions to avoid contribution from mass transfer limitations, which can
influence the measured activation energy. Equation 2.3 shows the Arrhenius expression of the catalytic activity as a function of inverse temperature.

\[ r = a \exp \left( \frac{-E_a}{RT} \right) \]  \hspace{1cm} (2.3)

Equation 2.3 is then linearized by taking the natural log of the rate of reaction as a function of the corresponding inverse temperature and the resultant slope yield the apparent activation energy for the given catalyst.

2.2 Ethane Partial Oxidation

The same reactor schematic shown in Figure 2.2 was used for the catalytic testing of ethane partial oxidation, with a few differences in the reactor type and downstream treatment. As ethane oxidation is a highly reactive process, quartz tube instead of stainless steel was used for the plug flow reactor construct to avoid excess ethane oxidation on the wall of the steel. The feedgas for the reaction consisted of either 4:5:1 ethane to oxygen to inert; respectively, or 2:1:3 ethane to oxygen to inert; respectively. For the gas composition of 4:5:1 ethane to oxygen to inert a space velocity of 1200 hr\(^{-1}\) was used to maximize the production of AA. The reaction was carried over a temperature ramp from 120-460\(^{\circ}\)C with 30\(^{\circ}\)C step sizes while temperature was measured inside the catalysts with a K type thermocouple. The BPRs in this configuration were removed in order to prevent condensation of acetic acid, where the effluent lines were all heated to 125\(^{\circ}\)C to allow acetic acid to uniformly reach the GC for accurate detection. The selectivity for all ethane oxidation reactions was calculated on a carbon basis, where ethane was taken as a basis unit. The conversion of ethane, selectivity towards acetic acid, ethylene, carbon monoxide, carbon dioxide, and methane are shown in equations 2.4, 2.5, 2.6, 2.7, 2.8, 2.9; respectively.

\[ X(C_2H_6) = \left( 1 - \frac{C_2H_6\text{out}}{C_2H_6\text{in}} \right) \times 100 \]  \hspace{1cm} (2.4)
\[ S(AA) = \frac{AA_{\text{out}}}{C_2H_4_{\text{out}} + 0.5CO_{\text{out}} + 0.5CO_2_{\text{out}} + AA_{\text{out}} + 0.5CH_4_{\text{out}}} \] (2.5)

\[ S(C_2H_4) = \frac{C_2H_4_{\text{out}}}{C_2H_4_{\text{out}} + 0.5CO_{\text{out}} + 0.5CO_2_{\text{out}} + AA_{\text{out}} + 0.5CH_4_{\text{out}}} \] (2.6)

\[ S(CO) = \frac{CO_{\text{out}}}{C_2H_4_{\text{out}} + 0.5CO_{\text{out}} + 0.5CO_2_{\text{out}} + AA_{\text{out}} + 0.5CH_4_{\text{out}}} \] (2.7)

\[ S(CO_2) = \frac{CO_2_{\text{out}}}{C_2H_4_{\text{out}} + 0.5CO_{\text{out}} + 0.5CO_2_{\text{out}} + AA_{\text{out}} + 0.5CH_4_{\text{out}}} \] (2.8)

\[ S(CH_4) = \frac{CH_4_{\text{out}}}{C_2H_4_{\text{out}} + 0.5CO_{\text{out}} + 0.5CO_2_{\text{out}} + AA_{\text{out}} + 0.5CH_4_{\text{out}}} \] (2.9)

For the reaction run with a 2:1:3 ratio of ethane to oxygen to inert, the production of ethylene was the desired product, where the same carbon-based selectivity was adopted. However, for these tests a stainless-steel reactor was used instead of quartz. The justification for the switch from quartz to steel was due to the low space velocity required for AA formation, which was no longer required for ethylene production as the space velocity was increased an order of magnitude from 1200 hr\(^{-1}\) to 12000 hr\(^{-1}\). A blank steel tube was probed for catalytic performance and we found no activity from the blank tube.

2.3 Catalyst Synthesis

_Wet Impregnation_

Catalysts prepared via wet impregnation were used as control samples throughout several of the work presented herein. The principles of wet impregnation are the dissolution of soluble precursor salts in either DI water or organics, such as ethanol, and adding this solvated mixture to the supporting materials, typically an oxide. The suspension is stirred, often at elevated temperatures that are below the boiling point of the solvent, until the solution completely evaporates. The resultant precursor is deposited onto the support in a non-uniform coating. This synthesis often results in a large particle size distribution, and in the case of multiple metal species being added, result in the phase segregation of the said
species. This preparation method is used as a benchmark for catalyst synthesis, as wet impregnation is the most documented synthesis method.

The impregnated Co/SiO$_2$ catalyst (Co/SiO$_2$ IMP) was prepared by solvating cobalt nitrate (65 mg, 99%, Sigma-Aldrich) in deionized water (50 mL) and directly added to the silica support (3.0 g, Davisil 646, 35-60 mesh, 300$m^2$/g and 1.1 cm$^3$/g, Sigma-Aldrich). This solution was mixed at 200 rpm until the water evaporated. The resulting catalyst was then dried overnight at 125 °C and then heated under air to 300 °C using a 10 °C/min ramp rate and held at 300 °C for 3 hours. The catalyst loading was determined to be 2.05±0.10 wt% Co/SiO$_2$ via ICP-OES.

**Strong Electrostatic Adsorption**

Strong electrostatic adsorption was utilized to prepare cobalt single site catalyst. The principles of strong electrostatic adsorption is that the supporting material suspension, in this case a silica suspension in water, has it’s pH either increased or decreased. By increaseing its pH above it’s point of zero charge, the surface is deprotonated, allowing for the uniform uptake of cationic precursor salts. If the solution is brought below its point of zero charge, it will become protonated, allowing for the uptake of anionic species. The discussion of strong electrostatic adsorption is thorughly discussed in literature [33, 79, 80]and will not be discuss in exhaustive detail herein. The benefits of strong electrostatic adsorption is that it allows for a uniform monolayer of metal to be deposited onto to surface, since the charged species have strong repulsive forces coupled with a hydration sheathe that serves to sterically hinder adjacent metal deposition. This often results in precise particle size distribution and highly uniform particles.
The cobalt single site samples (Co/SiO$_2$ SSC), were synthesized via strong electrostatic adsorption. Hexaaminecobalt (III) chloride (4.0 g, 99%, Sigma-Aldrich) was dissolved in deionized water (100mL), where the pH of this solution was raised to 11 using ammonium hydroxide (28% NH$_3$ in H$_2$O ≥ 99.99%, Sigma-Aldrich). In a separate container, the silica support (10.0 g, Davisil 646, 35-60 mesh, 300m$^2$/g and 1.1 cm$^3$/g, Sigma-Aldrich) was suspended in deionized water (200 mL) and then adjusted to a pH of 11 using ammonium hydroxide. The cobalt precursor solution was added to the silica suspension and allowed to stir for 10 minutes. The resulting catalyst was washed several times with deionized water to remove excess precursor and dried overnight in air at 125 °C. Once dried, the catalyst was calcined under air at 300 °C using a 10 °C/min ramp rate and held at 300 °C 3 hours. The catalyst loading was determined to be 1.82±0.08 wt% Co/SiO$_2$ via inductively coupled plasma-optical emission spectroscopy (ICP-OES).

**Cobalt Nanostructure Synthesis**

The Co$_3$O$_4$ nanorods were synthesized using a co-precipitation method by following previous literature report.[29, 81] In a typical synthesis, Co(OAc)$_2$·4H$_2$O (4.98g) was added to ethylene glycol (60mL) under a N$_2$ atmosphere to remove residual O$_2$. The solution was then heated to 80 or 160 °C, for nanoparticles or nanorods; respectively. Afterward, an aqueous solution of Na$_2$CO$_3$ (200mL, 0.2 mol·L$^{-1}$) was injected into the cobalt precursor solution at a speed of 1.11 mL min$^{-1}$. The mixture was further aged at the synthesis temperature for one more hour. The overhead solvent was decanted out and the solid product was collected via vacuum filtration and washing with ethanol. The filtered product was vacuum dried at 50 °C overnight, then calcined at 450°C for 4h. For supported nanorod synthesis, the dried nanorods were coated with 0.02M CTAB solution.
**Supported CoNR/MO\textsubscript{x} catalyst**

CoNR/Si\textsubscript{2}O\textsubscript{2} was synthesized by immersing 1g of coated nanorods in 100ml of a 0.1M sodium hydroxide solution while stirring, then injecting 10ml of tetramethyloorthosilicate (TEOS) at a rate of 1ml/hr. After vacuum filtering and washing with water, the catalyst was dried at 50°C under vacuum overnight and then calcined in air at 450°C for 4 hours.

CoNR/Ti\textsubscript{2}O\textsubscript{2} was synthesized by mixing 1g of the coated nanorods in 100ml of DI water and injecting a solution of 5ml ethanol mixed with 1ml titanium (IV) butoxide, TBOT, at a rate of 0.5ml/min. The cobalt/titanium mixture was brought up to and held at 85°C for 90min. Afterwards, the catalyst was vacuum filtered and washed with water, then dried at 50°C under vacuum overnight and calcined in air at 450°C for 4 hours.

The aluminum precursor was made by mixing 6.8g of aluminum (III) chloride with 1g of acetic acid in ethanol under reflux for 2 hours. After 2 hours, 3ml of DI water was added and refluxed for an additional 2 hours. Finally, 8.75g of CTAB was dissolved in 25ml of ethanol and added to the aluminum solution and then brought up to 60°C and refluxed for another 3 hours.

The CoNR/Al\textsubscript{2}O\textsubscript{3} catalyst was synthesized by adding 9g of the aluminum solution dropwise to the coated CoNRs and stirred for 6 hours at room temperature. The stirred solution was then heated to 60°C under reflux and stirring. A separate solution of 2ml hydroxylamine was added to 20ml of methanol, then added to the cobalt/aluminum/CTAB solution and stirred for 3 additional hours. The resulting solution was vacuum filtered and washed with ethanol, then dried at 50°C under vacuum overnight. The dried catalyst was then calcined at 650°C for 4 hours.
Hydrothermal Synthesis

A typical catalyst composition was synthesized using 4.03 g ammonium molybdate tetrahydrate (Sigma-Aldrich, 81–83% MoO₃ basis) mixed with 0.88 g ammonium niobate (V) oxalate hydrate in 60 mL of deionized water (DI water) while heating to 50 °C to ensure complete solvation of the precursors. The vanadium precursor was prepared in a separate container consisting of 1.73 g of vanadium oxide sulfate in 15 mL of DI water at 50 °C. Dopants were added before mixing the base catalyst components via stock solutions of either ammonium tetrachloropalladate, titanium sulfate solution, nickel sulfate, cesium sulfate, telluric acid, and potassium sulfate, prepared via dissolving the precursor salts in DI water. After addition of the required amount of dopant, the molybdenum/niobium and vanadium solution were added to the dopant mixture and allowed to mix for 20 minutes under stirring. The mixed precursors were then transferred into PTFE liners and set in autoclaves to carry out the hydrothermal synthesis at 175 °C for 48 hours. Upon completion of the hydrothermal synthesis, the catalyst was washed with water and acetone to ensure only the precipitated product was recovered, after which the washed catalyst was set to dry at 120 °C for 2 hours followed by calcination at 400 °C for 4 hours in air using a 10 °C ramp rate for heating and cooling. Synthesis of the base catalyst was carried out following the same steps without the addition of dopants.

Boronitride based Catalysts Synthesis

Preparation of porous h-BN (pBN). First, 4 mmol of boric acid and 20 mmol of guanidine carbonate were dispersed into 40 ml methanol. The solution was stirred and heated on a hot plate until all of the methanol was evaporated. The obtained solid was
ground into powder and annealed at 1000 °C under an equivalent ratio of Ar/NH₃ for 2 h, resulting in the formation of pBN.

**Preparation of Ru/pBN.** 15 mg hexaammineruthenium (III) chloride ([Ru(NH₃)₆]Cl₃) was dispersed into 200 ml DI water and mixed with 1 g pBN. The above mixture was sonicated for 5 h followed by vacuum filtration with a filter membrane (pore size 0.025 μm) and drying at room temperature. The dried powder was annealed at 750 °C in a stream of 50%-Ar/50%-NH₃ for 1 h, resulting in the Ru/pBN catalysts. The Ru loading was tuned by varying the ([Ru(NH₃)₆]Cl₃ content. The other two contents were 30 mg and 45mg in Ru/pBN-1.13%F and Ru/pBN-1.76%F, respectively. The catalysts obtained by vacuum filtration drying are denoted as Ru/pBN-xF, x representing the weigh percent of Ru. For comparison, the same procedure was used to prepare Ru/pBN-xR dried by rotary evaporation instead of vacuum filtration.

*Nitrogen Doped Graphene Quantum Dots Synthesis*

Graphene quantum dots synthesis. The graphene oxide (GO, 300 mg) was dispersed in dimethylformamide (DMF, 60 ml) by sonicating in a bath sonicator for 1 hour. The dispersion was transferred to a PTFE lined autoclave and heat-treated at 200 °C for 10 h. The unreacted GO remained aggregated after reaction. The suspension was vacuum filtrated using a cellulose membrane with 25 nm pore size, resulting in a dispersion of NGQDs in DMF. For other NGQDs with different N contents, the synthesis procedure is the same, except of the use of different solvents (ammonia solution or DMF diluted by isopropanol/water, 1/1 by volume). The pristine graphene quantum dots (GQDs) were prepared in a similar way by using a mixture of isopropanol and water (1:1 by volume) as
the solvent. The N-doped reduced graphene oxide was prepared by doping graphene oxide in a tube furnace at 800 °C while flowing ammonia for 1 h.

NGQDs/Al$_2$O$_3$ catalyst preparation. The NGQDs were loaded onto the γ-Al$_2$O$_3$ (Sigma-Aldrich) support by impregnation method. 0.2 g of Al$_2$O$_3$ was impregnated by a certain volume of NGQDs. The mixture was magnetically stirred and heated at ~80 °C to evaporate the solvent. After drying, the samples were collected, denoted as NGQDs/γ-Al$_2$O$_3$.

2.4 Characterization of Catalysts

*Infrared Spectroscopy*

The principle of Infrared spectroscopy is the measurement of differences in dipole-dipole interactions. This can be exploited to probe various different materials in the gas, solid, or liquid phase. IR spectroscopy is particularly use in identifying characteristic vibrational bands of carbon species. In the context of this work, diffuse reflectance infrared Fourier transformed spectroscopy (DRIFTS) was utilized. DRIFTS allows one to observe solid samples under various gaseous environments, which is a powerful tool for catalytic studies. Catalysts can be observed under reaction conditions, to obtain information on reactive intermediates, or probe gas to obtain information on the surface configuration of the catalyst. CO adsorption uses CO as a probe molecule to discern the active site structure of a given catalysts. Due to CO’s strong adsorption towards most transition metals, it is ubiquitously used in literature to probe surface structure. The main configurations CO can take on the surface are atop, bridged, three-fold hollow and four-fold hollow, which correspond to the interaction between one CO molecule and one, two, three, or four surface
atoms; respectively. The differences in dipole-dipole interactions between CO and the catalytic surface results in the formation of distinct CO adsorption bands.

To probe the reaction mechanism via DRIFTS, the measurement must be carried out in situ under the relevant reaction conditions. Furthermore, the reactant must be discernable via the principles of IR spectroscopy and have sufficiently speciated peak positions such that meaningful information can be extracted. For CO$_2$ hydrogenation, DRIFTS yield strong evidence of the reaction mechanism, each of the elementary steps associated with CO$_2$ hydrogenation can be readily speciated in an IR spectrum. It is important to note that DRIFTS can only measure the most abundant reaction intermediate in a given reaction, as transition states occur on a femtosecond timescale and therefore cannot be observed experimentally using traditional IR spectroscopy. However, the benefits of doing time resolved IR spectroscopy is that both spectator species can be observed due to their growth while the catalytically relevant band will remain constant and that shifting in the peak position of the most abundant reactive intermediate may suggest restructuring of the catalyst surface.

_in situ_ IR experiments were conducted on a Bruker Equinox 55 benchtop equipped with a Praying Mantis _in situ_ (DRIFTS) cell to investigate the reactive species presented on the catalyst surface during CO$_2$ and CO hydrogenations. Before _in situ_ IR experiments, Co nanorods and nanoparticles were reduced at 450 °C with H2 for 5h, then were cooled down to 250 °C afterward. A background spectrum of the sample was taken with resolution of 4 cm$^{-1}$ under pure hydrogen. Once the temperature equilibrated the reactant mixture mixture of CO$_2$+ 4H$_2$ or CO + 2H$_2$ was introduced into the _in situ_ DRIFT cell and the reaction was monitored at 250°C at atmospheric pressure. Spectra was taken continuously
to monitor the surface species changed during reactions. For CO adsorption, the catalyst is pretreated in either hydrogen if the desired surface is the reduced metal or under inert if the desired surface is the oxide and a background is taken under inert gas. CO is admitted to the DRIFTS cell until the cell is saturated with CO, evidenced by stable gas phase CO bands, and then the surface is flushed with inert to remove excess physisorbed CO, resulting in the final CO adsorption spectra of the chemically adsorbed species.

**X-Ray Photoelectron Spectroscopy**

X-Ray Photoelectron Spectroscopy (XPS) is a technique which irradiates a material with high energy X-Rays to produce photoelectrons with a characteristic emission energy. This precise photoelectron emission energy has made XPS a very powerful tool in characterizing surfaces. Furthermore, XPS is a highly surface sensitive technique, while X-Rays are highly penetrating, often reaching micron into the material, photoelectrons have a very short mean free path before they are reabsorbed into the bulk. Generally, the mean free path for photoelectrons is a few nanometers deep[82], making XPS a highly surface sensitive technique. Due to the high energy of X-Rays, photoelectron are ejected from the core levels of the probed atoms, where the peak position, areas, and relative intensities, are exactly related to the chemical identity of the atom.

For this thesis, XPS was used most heavily to discern the chemical environment of cobalt single site catalysts after various reductive pretreatments. Therefore the Co 2p spectral region was of most interest. For cobalt species, specifically for cobalt cationic species, final state effects must be considered when fitting XPS spectra. This results in the formation of corresponding satellites peaks associated the primary cationic peaks where for cobalt the satellite peak for tetrahedral Co$^{2+}$ is 5-6 eV below the primary peak, while
for octahedral Co$^{3+}$ the satellite is 10-11 eV below the primary peak. Peak fitting for the 
XPS was carried via CasaXPS, where the peak position, FWHM, and area of the Co2p$_{1/2}$ 
peaks were all constrained relative to the Co2p$_{3/2}$ peaks. A $\Delta E$ of 15.6 eV was used for the 
separation of the Co2p$_{3/2}$ and Co2p$_{1/2}$ peaks and the relative ratio between the peak area of 
the 2p$_{3/2}$ and 2p$_{1/2}$ of 2:1 was used in accordance with physical laws of spin orbital splitting.

X-ray photoelectron spectroscopy (XPS) spectra were measured on Kratos AXIS Ultra 
DLD XPS system equipped with a monochromatic Al K$_\alpha$ (1486.6 eV) X-ray source 
operated at 15 keV and 120W. The pass energy was fixed at 40 eV for the detailed scans. 
The binding energy in the XPS spectra is calibrated with the bulk silica signal (Si 2p at 
102.15 eV from the supporting material).

**UV-vis Spectroscopy**

UV-vis spectroscopy is useful for determining the electronic properties of the 
valence states of the probed species by measuring the energy loss of a monochromatic 
source of UV-vis radiation. The absorption of UV-vis radiation is governed by Beer’s Law, 
shown in equation 2.10

$$I = I_0 e^{-\varepsilon l c}$$  

(2.10)

Where $I_0$ is the intensity of the light source, $I$ is the intensity after contacting the sample, $\varepsilon$ 
is the absorptivity of the species and $l$ is the optical path length and $c$ is the concentration 
of the species. For a solid material an integrating sphere must be utilized instead of a 
traditional cuvette, where the integrating sphere captures the totality of the reflected light 
from the solid to accurately measure the absorption.
In the context of this thesis, Diffuse reflectance UV-vis was collected on a Perkin-Elmer Lambda 35 UV-vis scanning spectrophotometer equipped with an integrating sphere using a wavelength range of 200-900 nm.

Raman Spectroscopy

Raman spectroscopy measures the difference in polarizability of a substance, specifically the molecular vibrations. For the work presented herein, Raman spectra were collected using a Horiba XploraPLUS microscope outfitted with a 638 nm laser operating at 0.3 mW power with a grating of 1200 gr/mm and a thermoelectric-cooled CCD detector. *in situ* Raman spectroscopy was done with a CCR100 Linkam cell.

X-Ray Absorption Spectroscopy

X-Ray Absorption Spectroscopy (XAFS) probed the core level electrons via high energy X-Ray radiation to probe the coordination environment, formal oxidation, and nearest neighbor distance of adjacent atoms. XAFS excites core level electrons from the K, L<sub>1</sub>, L<sub>2</sub>, and L<sub>3</sub> edges; where the K edge corresponds to the 1s initial state (principle quantum number, n=1) the L<sub>1</sub> edge corresponds to the 2s initial state (n=2) and the L<sub>2</sub>/L<sub>3</sub> edge corresponds to the 2p initial (n=2, l=1, up and down spin; respectively). The K edge is the most populated edge and generally required the most energy to excite, while the L edges are lower in energy. XAFS is split into to distinct regions which yield unique information, first is the near edge region, X-Ray Absorption Near Edge Spectroscopy (XANES), and the latter is the Extended X-Ray Absorption Fine Structure Spectroscopy (EXAFS). XANES is the region between $-30$ eV < (E-$E_0$) < 50 eV, where $E_0$ is the edge energy, while EXAFS is the extended region of 50 eV < (E-$E_0$) < 1000 eV. The information afforded by XANES is the formal oxidation state of the core atom while EXAFS yields the
coordination number and bond distance of the core atom. Combined these two techniques are incredibly powerful tools for the analysis of a material, and when paired with calculated fittings; are essential for the characterization of catalysts where short range ordering dominates the structure, such as single site catalysts.

In order to interpret EXAFS spectra, equation 2.11 must be satisfied for each specified scattering path:

\[ \chi(k) = \sum_j N_j S_0^2 f_j(k) e^{-\frac{2R_j}{\lambda(k)}} e^{-2k^2\sigma_j^2} \frac{1}{kR_j^2} \sin \left[ 2kR_j + \delta_j(k) \right] \]  

(2.11)

Where \( N \) is the coordination number, \( S_0 \) is the amplitude reduction term, \( R \) is the distance to the nearest neighbor scatter, \( \sigma \) is the Debye-Waller factor, \( \delta(k) \) is the scattering phase shift, \( \lambda \) is the mean free path, \( f_j(k) \) is the scattering amplitude, and \( \chi(k) \) is the fractional change in \( \mu \). \( S_0 \) varies from 0.7 < \( S_0 \) < 1.0 and is determined experimentally via a known standard, after which is fixed for the duration of the fits; where is the generally dependent on the beamline and edge energy, not the sample. EXAFS is dominated by single scattering paths, where a scattering is the result of elastic collisions between ejected X-Rays and their nearest neighbor atoms. Single scattering is the linear scatter between the core atom and its first nearest, second nearest or third nearest neighbor. Multiple scattering occurs, defined by angled scattering or multi atom collisions, but results in significantly lower contribution to the overall signal, where single scattering paths are generally accepted to be the main contribution to the EXAFS signal[83, 84]. For example, when fitting a known CoO standard one would use two single scattering paths of Co-O and Co-Co; and possibly a Co-O-Co path to yield a better fit of the data. Fitting of the EXAFS spectra uses 4 parameters for each scattering path, which are \( R \), \( N \), \( \sigma^2 \), and the edge energy \( \Delta E_0 \). \( R \) yields the bond distance for the specified path, \( N \) the coordination number, \( \sigma^2 \) the Debye-Waller Factor
(DWF), and $\Delta E_0$ is the difference in edge energy from the pre-processed data and the fitted data ($|\Delta E_0|<10$eV is acceptable). The sum of the fitted paths will result in the final fit of the data.

High Energy Resolution Fluorescence Detection (HERFD) XAFS was also implemented in this thesis to probe the adsorbed species on the surface of a PtAu/HOPG electrocatalyst. HERFD XAFS utilizes high energy synchrotron radiation to probe the XANES region, where XANES is much more sensitive to slight perturbation than EXAFS due to its dependence on multiple scattering. XANES is generally not modelled as much as EXAFS due to the computational difficulty of the fitting relative to EXAFS[83]. To fit HERFD data, an accurate molecular model must be constructed, and the spectra is usually presented in the form of a difference spectra, a $\Delta \mu$ plot, which takes the difference between the clean surface and the surface with the introduced adsorbents. Due to the high sensitivity of XANES to full multiple scattering differences in the edge height and position between the clean and adsorbed surface can be captured and consequently modeled, yielding precise experimental and theoretical insight into the working structure of the catalysts.

As it pertains to this thesis, Cobalt K-edge (7709.0 eV) X ray absorption spectroscopy (XAS) measurements were carried out at Argonne National Laboratory at the Advanced Photon Source using the insertion device beamline of the Materials Research Collaborative Access Team (MRCAT, 10-ID). Measurements were carried out in transmission mode using ionization chambers using 10% absorbance in the primary chamber (29% He, in N2) and 70% absorbance in the secondary chamber (32% Ar in N2). Cobalt metal foil and a third reference detector were placed after the secondary ionization chamber to measure a reference spectrum in tandem with each sample to verify energy
shifts. A custom-built pretreatment cell was used, which allowed for heating up to 700°C and pretreatment under 50 mL/min 3.5% H2 in He (Praxair). The sample could be transferred under a helium atmosphere to prevent oxidation. All XAFS measurements were performed at room temperature under a helium atmosphere and analyzed using the Athena/Artemis software package for XANES/EXAFS. The normalization of the XANES was acquired via a pre edge range of -150 to -30 eV and a post edge regime of 150 to 890 eV with an edge step between 1.0-1.2 for all samples. \( E_0 \) was located via the first derivative of the white line, which was approximately 7718 eV. The energy shift was calibrated via a reference Co foil (7709.0 eV) run in tandem with each spectra. CoO and Cobalt foil were used as the Co-O and Co-Co EXAFS references; respectively.

HERFD XANES was performed on PtAu/HOPG prepared via arc plasma deposition. The Pt and Au were simultaneously deposited in an approximate 1:1 ratio onto the clean HOPG surface to form the PtAu/HOPG complex. HERFD XANES Pt L3 edge measurements were made in Spring-8 (beamline BL36XU, 2019-01-17/21). Measurement were carried out *operando*, using a flow cell configuration with deaerated 0.1 M HClO4 as the flowing electrolyte, a reference electrode of Ag/AgCl and a Pt coil counter electrode. The working electrode was PtAu/HOPG connected to a copper electrical contact. The XANES measurements were carried out via back-illumination of the PtAu/HOPG sample. The clean Pt L3 edge was measured at 0.17 V (V vs Ag/AgCl) and was the basis for the difference spectra.

Pt L3 edge measurements were also carried out in the KEK Photon Factory using PtAu/HOPG and a different cell set up. The cell consisted of a reference hydrogen electrode (RHE), a Pt coil counter electrode and PtAu/HOPG as the working electrode with flowing
deaerated 0.1 M HClO$_4$ as the electrolyte. The noise from the flowing solution was mitigated by incorporating a cone inset to the cell and utilizing a Nafion film to act as an electrolyte bridge to the working electrode. Samples measured at PF were also back illuminated and fluorescence was detected using a Bent Crystal Laue Analyzer (BCLA) coupled with a 16-element solid state detector (SSD). In both SP8 and PF, the edge position was adjusted before data collection using Pt foil with a known edge position of 11564 eV as a reference. The clean Pt L3 was measured at 0.40 V (V vs RHE) and was used as the basis for the difference spectra. The oxygen adsorbents were investigated using the difference spectra method ($\Delta \mu$) method at various voltages.

All data analysis and difference spectra were analyzed using the XAFS analysis software Athena[14, 15]. XANES spectra were smoothed using a 3-point Boxcar average via Athena, and all difference spectra of the experimental data were smoothed using a 10-point Boxcar average method, via the built in Athena smoothing algorithm.
CHAPTER 3
SURFACE FACET CONTROL OF NANOSTRUCTURES\textsuperscript{1,2}


Recent studies on the development of active catalysts for CO$_2$ hydrogenation are mainly focused on adjusting catalyst properties, such as particle size, oxidation states, and composition.[85-89] For example, Co catalysts with average particle sizes of 10 nm showed 3 times higher turnover frequency (TOF) than those with an average particle size of 3 nm.[27, 90] Rational design of catalyst structures on the nanoscale shows great potential toward increasing the catalytic activity of CO$_2$ hydrogenation. The design of a catalyst based on a fundamental knowledge of the CO$_2$ hydrogenation reaction and first principles of surface science is important for cobalt based catalyst for CO$_2$ hydrogenation.[8] Many previous studies on the influence of catalyst structure on reactivity are typically based on bulk properties, which are not always consistent with those of the active surface.[12, 91] The atomic structure and composition within the first few atomic layers of a surface is primarily responsible for the catalytic properties. Tuning the catalyst bulk structure will therefore not always result in a more active and selective catalyst. For instance, it is generally agreed that reduced Co on SiO$_2$ is about 4 times more active than oxidized Co for CO$_2$ hydrogenation.[27, 86, 92-94] Conversely, metallic Co on TiO$_2$ was shown to have up to 5 times lower activity than oxidized Co on the same support.[86] The mechanism of decreased activity due to Co reduction for the TiO$_2$ supported catalyst is not clear due to limited information on the surface structures of Co interacting with either TiO$_2$ or SiO$_2$ support. This example illustrates that tuning catalyst bulk properties (such as oxide vs. metal) without considering the intricacies of the surface structure can be misleading in the design of active catalysts.

Herein, we demonstrate that the existence of different surface facets on Co$_3$O$_4$ catalysts controls the catalytic activity of reduced Co catalysts for CO$_2$ hydrogenation, even
when the catalysts exhibit very similar bulk properties, such as crystallographic phase, oxidation state, and chemical composition. Based on our recent work, the catalysts were synthesized by reducing faceted Co$_3$O$_4$ particles, which serve as precursor state for the active metallic catalysts. These Co$_3$O$_4$ particles were obtained by controlling the catalyst morphology via a coprecipitation method\[29\], and bulk and surface structures were characterized with experimental techniques, such as X-ray diffraction (XRD), Raman spectroscopy, and High-resolution transmission electron microscopy (HRTEM). Mechanistic understanding of the influence of the catalyst precursor surface faceting on catalytic performance was investigated with kinetic studies and \textit{in situ} infrared (IR) spectroscopy.

Additionally, in order to enhance the catalytic performance of the cobalt particles a modularized synthesis was developed in order to graft supporting oxides onto the particles, such that the active surface faceting is preserved. To demonstrate the effectiveness of this methodology, Co$_3$O$_4$ nanorods with preferential \{110\} facets on the surface were chosen due to their catalytic performance and their high aspect-ratios, which add another layer of complexity to the support grafting in the form of an extended metal support interface. Different oxide supports, including SiO$_2$, Al$_2$O$_3$, and TiO$_2$ were selected to show the versatility of this methodology. The resulting Co$_3$O$_4$/MO$_x$ (M=Si, Al, and Ti) catalysts were tested using CO$_2$ hydrogenation as a model reaction. Due to the strong chemical interaction between the Co$_3$O$_4$ nanorods and TiO$_2$, higher activity was achieved compared with relatively the inert supports, SiO$_2$ and Al$_2$O$_3$. The structure properties of the supported and unsupported catalysts were carefully characterized with a variety of experimental techniques, including X-ray diffraction (XRD), scanning transmission microscopy.
(STEM), and Raman spectroscopy. Catalyst properties and their relationship to catalytic activity in CO$_2$ hydrogenation are discussed to guide future design of active catalysts with controlled facets and controlled interfaces.

The relevant mechanism and structure of both the unsupported Cobalt nanostructures and the support catalysts were carefully characterized via a combination of XRD, HRTEM, STEM, Raman spectroscopy and in situ infrared spectroscopy. Ultimately, the relevant rate determining step was found for the cobalt nanostructures and a successful methodology was developed for supporting the cobalt nanostructures while preserving their selective surface faceting.

3.1 Surface Faceting on Cobalt Nanostructures for CO$_2$ Hydrogenation

*Catalytic Performance of Cobalt nanorods and nanoparticles*

Cobalt oxide catalysts with either nanorod or nanoparticle morphologies were synthesized and tested for CO$_2$ hydrogenation.[95] It is generally believed that the active site for CO$_2$ hydrogenation is metallic Co.[6, 11, 96-98] During the reaction tests, the feed composition of H$_2$ and CO$_2$ was kept at the stoichiometric ratio of 4:1. Figure 3.1 compares the catalytic activity for Co nanorods and nanoparticles. Co nanoparticles are used as a control group which is representative of a typical spherical cobalt catalyst, where the reaction rate between 220-400$^\circ$C of our Co nanoparticles ($0.11$-$5.16\times10^{-5}$ molCO$_2$·g$^{-1}$·s$^{-1}$, respectively) is comparable to that reported for other Co catalysts ($0.85$-$5.09\times10^{-5}$ molCO$_2$·g$^{-1}$·s$^{-1}$).[86] The Co nanorods show a reaction rate of $2.81\times10^{-5}$ molCO$_2$·g$^{-1}$·s$^{-1}$ at 220$^\circ$C, while the nanoparticles at the same temperature show a rate of $3.94\times10^{-6}$ molCO$_2$·g$^{-1}$·s$^{-1}$. In addition, the nanorods begin to catalyze CO$_2$ hydrogenation at temperatures about 80$^\circ$C lower than the Co nanoparticles. The selectivity to methane is maintained at 99±1%
on the Co nanorods for all reaction temperatures, while it gradually increases from 13±1% to 95±2% on the Co nanoparticles with CO formed as a major product below 300°C. The hydrocarbon product distribution on both nanorods and nanoparticles contains over 90% of methane for all reaction conditions, with the remainder being C₂-C₅. At 220 °C, the yield towards hydrocarbons is an order of magnitude greater than that on the nanoparticles. In fact, in the temperature range between 220 °C and 320 °C, the activity of the Co nanorods towards CO₂ hydrogenation is 3-17 times higher than that of the Co nanoparticles. The high activity and selectivity of Co nanorods was also maintained upon changing the ratio of H₂ : CO₂ from 4:1 to 2:1. Even for these sub-stoichiometric feed conditions, the Co nanorods maintained a steady selectivity of 98±2 % towards methane over the entire temperature range, while the selectivity to hydrocarbons on the nanoparticles increased from 27±5 % to 92±4 % with increasing temperature. Lean H₂ conditions should be expected to favor CO over hydrocarbon production (CO₂ + H₂ → CO + H₂O vs. CO₂ + 4H₂ → CH₄ + 2H₂O). Overall, not only do the cobalt nanorods show an order of magnitude greater reaction rate during CO₂ hydrogenation at identical operating conditions, the rods favor the complete reduction into methane while the nanoparticles only partially reduce the CO₂ into CO; this shows that the exposed faceting must play a fundamental role in altering not only the structure, but the reaction intermediates formed on the surface as well.
Figure 3.1. CO$_2$ conversion, hydrocarbon and CO selectivity, and hydrocarbon yield for Co nanorods and nanoparticles with a H$_2$ to CO$_2$ ratio of 4:1 at 10 bar pressure and 18000 hr$^{-1}$ flow

**Particle size, structure and morphology**

To study the influence of catalyst structure on catalytic performance, Co nanorods and Co nanoparticles were characterized with a variety of imaging and spectroscopic techniques. As shown in the TEM image in Figure 3.2, the Co nanorods have a diameter of 14.2 ± 4.4 nm and lengths between 200 and 300 nm, which is consistent with our previous work.[28, 95] The Co nanoparticles have a particle size distribution of 24.5 ± 9.8 nm. The turnover frequency for particle sizes above 10 nm is expected to be independent of size for Co catalysts for CO$_2$ hydrogenation.[27, 96, 99]
Figure 3.2. Transmission Electron Microscopy image of (a) cobalt nanorods and (b) cobalt nanoparticles after washing and calcining. Scale bar 100 nm on both images.

The crystal structures were determined by powder X-ray diffraction (XRD), as shown in Figure 3.3. The XRD peak positions and intensity ratios for both Co nanorods and nanoparticles are consistent with those of the Co$_3$O$_4$ spinel structure (PDF 41-1467). The grain size distribution via XRD for the nanorods and nanoparticles were 14.1 ± 2.4 nm and 28.5 ± 9.5 nm; respectively, which are within error of the measured size distribution via TEM. The grain size of the nanorods reflects the diameter of the nanorods measured via TEM, since during synthesis the nanorods grow preferentially along the [110] direction from the Co$_{x/2+y}$(OH)$_x$(CO$_3$)$_y$ precursor,[28, 29] forming continuous grains during its growth, whereas the nanoparticles grow uniformly along their radial axis resulting in grain sizes that are consistent with their actual particle size.
In a previous study we found that cobalt nanorods resist oxidation during Fischer-Tropsch synthesis with the addition of 10vol% H₂O to the feed, while cobalt nanoparticles were readily oxidized under the same conditions [95]. Given that the nanorods resisted oxidation, their improved catalytic activity towards CO₂ hydrogenation is most likely due to the preservation of the metallic cobalt phase during the reaction. Furthermore, bulk properties such as the particle size, crystal structure, and oxidation state of the prepared Co nanorods and nanoparticles are very similar. According to previous reports [27, 85-89] these similarities between nanorods and nanoparticles should lead to comparable activity and selectivity for CO₂ hydrogenation. This shows that the catalyst bulk properties do not
account for the observed differences in activity and selectivity differences, meaning a more detailed understanding of the catalytic surface is required.

*Exposed surface structure via HRTEM*

Aberration corrected-scanning transmission electron microscope (AC-STEM) equipped with a high angle annular dark field detector was used to characterize differences in surface properties between Co nanorods and nanoparticles. The AC-STEM images are shown in Figure 3.4. The $d$-spacing measured for the Co nanorods was $2.9 \pm 0.1 \text{ Å}$, which is consistent with the (220) plane of Co$_3$O$_4$ and results in the exposure of the {110} family of facets at the surface.[95] On the other hand, the $d$-spacing for the nanoparticles was measured to be $4.7 \pm 0.1 \text{ Å}$, which corresponds to {111} and {001} family of facets exposed at the surface. The {110} family is the only surface orientation that has both Co$^{2+}$ and Co$^{3+}$ present in the outermost surface layer, while predominantly Co$^{2+}$ is exposed on all the other facets.[29, 95]. As both nanostructures share the {001} family of surface facets the effective surface area of the {110} and {111} can be compared when taken as the percentage of the total surface area for the nanorods and nanoparticles, respectively. The general geometry for the nanorods is taken to be rod shaped with flat ends and sides, while the nanoparticles are octahedrons with truncated ends representing the {001} facets.[29] The relevant length scales from our TEM imaging was used to estimate the approximate percentage of surface facets; with an approximate diameter of 14 nm and a length of 200 nm for the nanorods and a diameter of 25 nm for the nanoparticles. The percentage of exposed {110} on the nanorods is approximately 39% while for the nanoparticles the percentage of exposed {111} is approximately 80%. Since the {001} family of surface facets does not possess the exposed Co$^{3+}$ cations, it is considered to be
less active than the \{110\} family of surface facets, however its contribution to the overall catalytic activity cannot be ruled out. Therefore, even though the Co nanorods and nanoparticles possess very similar bulk properties, the STEM images clearly show that they have different surface crystal facets and consequently expose different cations on the outmost, catalytically relevant surface. Direct imaging of the cobalt in the metallic state after a reduction could not be explored due to the highly oxophilic nature of cobalt. The use of environmental aberration correction transmission electron microscopy using a sufficiently high partial pressure of hydrogen to ensure reduction was not feasible. The presence of metallic cobalt as the catalytically relevant surface was verified via XPS, where the samples could be reduced in a pretreatment cell under the same pretreatment conditions used before the catalytic tests and then transferred under vacuum into the XPS measurement chamber, where the cobalt showed as completely reduced.

![STEM images of Co nanorods and nanoparticles](image)

**Figure 3.4.** Aberration corrected-scanning transmission electron microscope images of a) Co nanorods and b) nanoparticles. The insets show the corresponding Fast Fourier Transforms. Scale bar is 2 nm
in situ CO$_2$ hydrogenation DRIFTS spectroscopy

Differences in surface crystal facets on the Co nanorods and nanoparticles is expected to result in distinct catalytic activity, particularly for a structure sensitive reaction such as CO$_2$ hydrogenation.[27, 85-90] in situ IR spectroscopy was applied to study surface reactive species during CO$_2$ hydrogenation on both the Co nanorods and nanoparticles. Reaction temperatures and the reductive pretreatment were identical to those set in the plug-flow reactor. The in situ IR spectra under steady-state reaction conditions are shown in Figure 3.5. The formation of formyl (H-C=O*) species at 1700 cm$^{-1}$ was observed on both Co nanorods and nanoparticles. In contrast, formate species (HCOO*, bands at 1600 cm$^{-1}$ and 1415 cm$^{-1}$) were only formed on the Co nanoparticles. Formate has previously been reported as an inactive species for CO$_2$ hydrogenation,[19, 21, 100, 101] thus blocking catalytically active sites.
Figure 3.5. *in situ* IR of CO$_2$ hydrogenation on nanorods and nanoparticles at 250°C.

For PtCo based catalyst, the direct hydrogenation of CO$_2$ to form *HCOO is kinetically unfavorable (ΔE=−0.25 eV), while the formation of a *HOCO reactive intermediate (ΔE=−0.56 eV) is more energetically favorable.[19] The *HOCO intermediate can further dissociate into *CO and *OH, where the *CO undergoes another hydrogenation step to form *HCO and the adsorbed *OH is hydrogenated to form water.[19] Formate has been reported as a reactive intermediate for the production of methanol over Cu/ZnO,[22] however for methanation formate is generally considered a spectator species,[19, 21, 100, 101] which is consistent with our experimental findings. Furthermore, in the case of nickel based catalyst, CO$_2$ is also believed to undergo a dissociation step, however, the resulting adsorbed CO further dissociated to adsorbed C and O which are then hydrogenated to form
methane and water, respectively, where formate was also observed as a spectator species.[102] To probe the formation of the site blocking formate species on both catalysts, room temperature adsorption of CO$_2$ and CO was performed, as shown in Figure 3.6. Both catalyst formed bidentate- and unidentate-carbonates ($1650$, $1540$, $1293$, and $1032$ cm$^{-1}$),[103] but only the nanoparticles showed the formation of formate species. Bidentate- and unidentate-carbonates are typically less stable than formate,[104] which explains why only formate species can be observed during in situ IR reaction experiments conducted at 250 °C.

Figure 3.6. IR spectra of CO$_2$ and CO adsorption on nanorods and nanoparticles at room temperature. The formate species located at $1600$ and $1293$ cm$^{-1}$ are fitted with orange dot lines, and carbonate species ($1650$, $1540$, $1293$, and $1032$ cm$^{-1}$) are fitted with black dot curves.
The site-blocking role of formate species on the surface of the Co nanoparticles is also supported by CO$_2$-Temperature Programmed Desorption (TPD) results, shown in Figure 3.7. Both catalysts have a CO$_2$ desorption peak at 80 °C, while the nanoparticles show an additional CO$_2$ desorption peak at 175 °C. The lower temperature peak can be attributed to the desorption of the bidentate carbonate species, while the higher temperature peak on the Co nanoparticles can be assigned to the desorption of the formate species.[104, 105] This further validates that formate species are acting as a spectator to the reaction, limiting the total number of active sites for the reaction. To understand the nature of the active sites, the apparent activation energies for CO$_2$ hydrogenation on both nanorods and nanoparticles were calculated based on the Arrhenius equation. The resulting energies are nearly identical at 87.5 ± 4 and 81.6 ± 7 kJ/mol; respectively. Additionally, since the presence of sodium as a remainder from the synthesis procedure has been shown to promote hydrogenation reactions,[17, 106, 107] an X-Ray Photoelectron survey scan was performed before and after washing the catalyst and found no presence of the Na 1s peak at 1070 eV, ruling out the influence of sodium on the catalytic activity.
Figure 3.7. CO\textsubscript{2} TPD profiles on nanorods and nanoparticles, mass 44 is tracked in the mass spectrometer for CO\textsubscript{2}.

**Effective surface area and turnover frequency**

To further elucidate the catalytic surface, chemisorption and physisorption were employed to determine the number of active sites and the surface area of the catalyst; respectively. Table 3.1 shows the surface area and the chemisorbed CO uptake of both the Co nanorods and Co nanoparticles as well as the CO\textsubscript{2} turnover frequency (TOF) at 220\degree C. The nanorods had a surface area of 196 ± 14 m\textsuperscript{2}/g while the nanoparticles had a surface area of 155 ± 22 m\textsuperscript{2}/g. Furthermore, upon reduction under the same reaction pretreatment conditions, the fresh Co nanoparticles possess a comparable number of active sites as the Co nanorods. CO chemisorption on the nanorods yielded an uptake of (0.97 ± 0.08) x10\textsuperscript{-2} mmol\textsubscript{CO}/g\textsubscript{cat}, while the nanoparticles had an uptake of (1.09 ± 0.12) x10\textsuperscript{-2} mmol\textsubscript{CO}/g\textsubscript{cat}, showing the number of active sites on both catalysts are within error of each other; ruling out the possibility of the presence of more active sites on the nanorods being the cause for
the difference in catalytic activity. This is captured in the turnover frequency (TOF), where the rate of CO$_2$ (mol$_{CO2}$·g$^{-1}$·s$^{-1}$) conversion was normalized by the total number of active sites measured via CO chemisorption (mol$_{CO}$/g$_{cat}$). At a temperature of 220$^\circ$C, the nanorods possess an order of magnitude higher TOF than the nanoparticles, where the nanoparticles show a comparable TOF to that which is reported in the literature for spherical cobalt nanoparticles for CO$_2$ hydrogenation.[27] The difference between the two catalyst can be further exemplified if the TOF of methane as opposed to the TOF of CO$_2$ is considered, where the nanorods have a factor of 5 greater selectivity towards methane at 220$^\circ$C than the nanoparticles. These results coupled with the comparable activation energy of both the nanorods and nanoparticles further confirm that site-blocking by formate species under reaction condition is the cause of lower activity on nanoparticles instead of smaller surface area or lower number of active sites on fresh catalysts.

Table 3.1. Total surface area, amount of available surface sites, the CO$_2$ turnover frequency at 220$^\circ$C, and apparent activation energy for both catalyst

<table>
<thead>
<tr>
<th>Sample</th>
<th>Surface Area (m$^2$·g$_{cat}^{-1}$)</th>
<th>CO Uptake (mmol$<em>{CO}$/g$</em>{cat}$)</th>
<th>TOF at 220$^\circ$C (s$^{-1}$)</th>
<th>E$_a$ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CoNR</td>
<td>196 ± 14</td>
<td>(0.97 ± 0.08) x 10$^{-2}$</td>
<td>2.89</td>
<td>87 ± 4</td>
</tr>
<tr>
<td>CoNP</td>
<td>155 ± 22</td>
<td>(1.09 ± 0.12) x 10$^{-2}$</td>
<td>0.36</td>
<td>82 ± 7</td>
</tr>
</tbody>
</table>

**CO hydrogenation mechanism on nanorods and nanoparticles**

Aside from the higher catalytic activity, the Co nanorods also have substantially higher selectivity towards methane if compared to the nanoparticles (see Figure 3.1). The hydrogenation mechanism follows a two-step reactions scheme.[8, 30, 97] First, CO$_2$ is partially hydrogenated into CO, which is then further hydrogenated in a second step to
form methane. The second hydrogenation step \((\text{CO} + 3\text{H}_2 \rightarrow \text{CH}_4 + \text{H}_2\text{O})\) is widely reported as the rate-determining step for methane production,[8, 96] and thus should determine the selectivity to CO and methane in the overall \(\text{CO}_2\) hydrogenation process. To investigate the selectivity differences observed between the Co nanorods and nanoparticles, reactive intermediates were studied by using \textit{in situ} CO hydrogenation (second hydrogenation step) as a model reaction, shown in Figure 3.8. It is expected for reactive intermediates to quickly respond to changes in the gas phase environment, while the response of spectator species will be considerably slower.[108] The IR intensity of chemisorbed CO (bands above 1650 cm\(^{-1}\)) remains mostly constant during reaction, while that of carbonate bands (below 1650 cm\(^{-1}\), bidentate and unidentate) increases with time on-stream. Thus, the IR spectra confirm that chemisorbed CO is a reactive intermediate, while the carbonates are spectator species, which is consistent with the CO hydrogenation literature.[109] More interestingly, while both nanorods and nanoparticles have CO chemisorbed in hollow sites (band at 1760 cm\(^{-1}\)), the nanorods show an additional band corresponding to CO chemisorbed on a bridge site (1900 cm\(^{-1}\)). The presence of these extra sites on the Co nanorods is corroborated via CO-TPD where an extra CO desorption peak was detected around 115 °C. This CO desorption peak can be attributed to the desorption of bridge site CO,[110, 111] while the carbonate and hollow site chemisorbed CO species are desorbing in the form of \(\text{CO}_2\) at higher temperatures. Bridge site CO was reported to have higher hydrogenation activity compared with hollow site CO, and will in-turn promote methane production.[112-114] In summary, the \textit{in situ} IR spectra and TPD profiles show bridge-site CO intermediates with higher activity on the nanorods, which facilitates the production of methane.
Figure 3.8. *in situ* IR of CO hydrogenation on a) nanorods and b) nanoparticles at 250°C.

*Preferential crystallographic growth*

To understand differences in surface species present on the reduced Co nanorods and nanoparticles during CO$_2$ hydrogenation, the IR spectra of CO adsorption shown in Figure 3.6 were found to be comparable to those reported for CO adsorption on stepped {10-12} and flat {0001} surfaces, respectively.[113] CO prefers to adsorb and dissociate on both bridge and hollow sites on stepped Co surfaces, but prefers atop or hollow sites on flat Co surfaces.[113, 114] During our *in situ* IR experiments, the Co nanorods showed CO adsorbed on both bridge and hollow sites, while the nanoparticles showed only hollow site CO. Furthermore, the stepped surfaces have a lower activation energy of 160.9 kJ/mol for CO dissociation than the 220 kJ/mol required on the flat surface, leading to higher activity for CO hydrogenation.[113] This is consistent with our CO$_2$ hydrogenation results on the Co nanorods, which demonstrated higher activity for CO$_2$ hydrogenation than the Co nanoparticles. The stepped {10-12} and the flat {0001} Co planes can be expected to form epitaxially on the Co nanorods and nanoparticles surfaces during catalyst reduction due to the similarity between their lattice parameters. The lattice mismatch between facet groups
of Co₃O₄ {110} and Co {10-12} is less than 5%, and it is less than 2% between Co₃O₄ {001} and Co {0001} planes. A formation of Co {0001} planes on Co₃O₄ {110}, on the other side, will lead to a lattice mismatch of 39%, which represents a significant energy penalty for non-epitaxial growth of reduced Co. Furthermore, the formation of Co {111} planes on Co₃O₄{111} has been proven previously via environmental HRTEM during the H₂ reduction of model Co₃O₄ catalysts.[115] A similar reduction process was performed here for Co nanorods and nanoparticles before CO₂ hydrogenation. As both the nanorods and the nanoparticles share the {001} family of surface facets, the observed differences in the surface species on both catalyst is attributed to the different surface structures present on the reduced form of the {110} family of surface facets, while the reduced form of the {111} family of surface present on the nanoparticles resulted in the presence of both the reactive intermediate as well as the spectator species. The comparison of our results with literature suggests that the Co nanorods and nanoparticles have distinct active Co surfaces exposed during CO₂ hydrogenation, where the metallic Co surface that arises from the reduction of the {110}/{001} based nanorod ultimately leads to the suppression of the site blocking species and promotes the exclusive formation of the reactive intermediate. Ultimately, by mitigating spectator species via the tuning of the exposed surface facets of the cobalt oxide, we have developed a highly active catalyst; where the performance of the catalyst in this study are comparable to some of the state-of-the-art catalyst in literature,[19, 25, 27, 30, 116, 117]. However, it should be noted that due to the inherent difference in operating conditions (such as pressure and temperature) a direct comparison with literature is not feasible.
Since Co catalyst are very susceptible to oxidation and subsequently deactivate,[28, 29, 95] CO₂ hydrogenation activity was tested under reaction conditions for 50 hours. The results are shown in Figure 3.9 and no change in selectivity was observed. Additionally, the CO₂ conversion remained at a constant 70% throughout the entire testing period. This suggests the catalyst did not undergo deactivation, which could arise from either oxidation of the catalyst due to the water produced via the hydrogenation or by the formation of coke,[29, 30, 95] which would deposit onto the active sites and lower the activity and selectivity towards methane. The oxidation state of the catalyst was observed during CO₂ hydrogenation after a reduction at 450°C under hydrogen for the Co nanoparticles, shown in Figure 3.10, where metallic cobalt is Raman inactive.
Figure 3.9. Time on stream study for Cobalt nanorods at 230°C, 10bar, 4:1 ratio of H$_2$ to CO$_2$ and a flow rate of 18000 hr$^{-1}$.
Figure 3.10. *in situ* Raman spectra of the Co nanoparticles. 450°C H₂ for 3hr pretreatment, 4:1 H₂ to CO₂ inlet gas composition, operating temperature of 230°C.

There was no observed formation of the cobalt oxide phase at 680, 450 or 200 cm⁻¹, which would be attributed to the formation of either the spinel Co₃O₄, rocksalt CoO, or the CoOOH hydroxide structure.[118, 119] The shift in selectivity from predominantly CO to methane was believed to be due to the formation of a surface oxide, however no oxidation was observed. As no change in selectivity was observed for the cobalt nanorods the *in situ* Raman was not carried out on the Co nanorods. Deactivation via coke formation was also ruled by post reaction Raman spectroscopy, where the absence of D and G bands at 1340 and 1580 cm⁻¹, respectively, demonstrated that no carbon was deposited onto the catalyst, which can occur via CO disproportionation.[120]
3.2 Encapsulated Supporting Oxides on Facet Controlled Cobalt Nanorods

Supported Cobalt Catalyst Synthesis

Catalysts with preferential faceting have been shown to yield favorable catalytic properties, such as increased activity, a resistance to oxidation, and enhanced selectivity[29, 95]. This study is a continuation of our previous work on the effects of cobalt surface faceting for hydrogenation reactions[95]. Preferential exposure of {110}/{001} facets on the surface can be achieved through the promoting of growth kinetics along the [110] direction for $\text{Co}_{x/2+y}(\text{OH})_x(\text{CO}_3)_y$[29]. The advantage of the {110}/{001} faceting lies in the preferential surface exposure of both $\text{Co}^{3+}$ and $\text{Co}^{2+}$ cations. $\text{Co}^{2+}$ cations are stable centers due to their tetrahedral geometry resisting surface restructuring and reduction. Therefore, in general, they exhibit low catalytic activity[121]. In contrast, $\text{Co}^{3+}$ cations with octahedral coordination environment have a lower Gibbs free energy of reduction, as compared to $\text{Co}^{2+}$, and are therefore more readily reduced, as shown by their differences in reduction temperature. For example, previous studies in our group showed that the {110}/{001} faceted $\text{Co}_3\text{O}_4$ nanorods have 3-7 folds higher catalytic activity towards CO$_2$ hydrogenation compared with state-of-the-art Co catalysts in literature. [86]

However, unsupported metal catalysts have very limited practical applications due to low surface area, and mass and heat transfer limitations, and thus are generally supported on high surface area supports. In order to couple preferential surface faceting of nanostructures with the benefits of supporting the catalysts, a modular synthesis method was developed to graft support onto cobalt nanorods, illustrated in Figure 3.11. Following the synthesis of the cobalt nanorods, CTAB ligands were grafted onto the nanorods via electrostatic interaction. CTAB was chosen as a ligand due to its cationic center, which can
act as a binding site for anionic metal oxide precursors[122]. The electrostatic interaction between CTAB and oxide precursors has been widely used for the synthesis of mesoporous metal oxides, including SiO$_2$, Al$_2$O$_3$, and TiO$_2$.[123-125] The ionic binding of CTAB to the nanorods on one side and to the metal-oxide precursor on the other side promotes the formation of chemical interaction between the nanorods and metal oxides. In contrast, traditional wet impregnation methods consist of physically mixing faceted particles with a support, leading to minimal chemical interactions.[126, 127] The three different oxide supports that were chosen for this study were silica for its inert nature, alumina for its ideal thermal conductivity properties, and titania for its reducible nature. The resultant supported catalysts had weight percentages of cobalt of 54.6±1.5, 52.2±1.5, and 41.1±0.7, for CoNR/TiO$_2$, CoNR/Al$_2$O$_3$ and CoNR/SiO$_2$, respectively, as measured by Induced Coupled Plasma Spectroscopy (ICP).
Figure 3.11. Representation of overall synthesis procedure. Step 1 shows the synthesis of nanorod structures and step 2 illustrates the grafting of support onto the nanorods.

Surface Morphology and Size Distribution of CoNR/MOx

As shown by the TEM images in Figure 3.12, the original nanorod morphology was preserved after the support grafting. Additionally, the cobalt nanorods were encased within the support, which maximizes the interfacial area between the cobalt nanorods and the support. To further investigate the surface structure, STEM-HAADF was used to identify the distinct surface faceting of the CoNR/MOx systems. The STEM images along with their corresponding Fast Fourier Transforms (FFT) in Figure 3.12 reveal a $d$-spacing of $3.0 \pm 0.1\text{Å}$ that corresponds to the $\{110\}$ family in the Co$_3$O$_4$ spinel. Furthermore, the support seems to have grown amorphously around the nanorods, where the support surface has no $d$-spacing corresponding to any of the oxide crystal structures.
Figure 3.12. (a) TEM images with a 20 nm scale to show the morphology of nanorods retained, and (b) STEM with a 2 nm scale to show the lattice and inset of the corresponding FFT.

**Structural and Vibrational Properties of CoNR/MO<sub>x</sub>**

Figure 3.13. XRD of the CoNR/MO<sub>x</sub> catalysts

To verify the amorphous nature of the oxide supports seen in STEM images, the crystal structure of the supported CoNR was further investigated using XRD, as shown in
Figure 3.13. The supported catalysts only exhibited the diffraction patterns of the Co$_3$O$_4$ spinel structure, which confirms the findings in the STEM. Particle size distributions from XRD yielded a diameter distribution of 13-15nm diameter both before and after the grafting procedure, indicating that no additional aggregation or particle growth occurred during the support grafting. This is again consistent with the diameters measured in the TEM images. Also, it has been shown for both CO$_2$ and CO hydrogenation that for particle sizes below~10nm, the catalytic activity decreases and that for particles above 10 nm, activity becomes independent of particle size[128, 129].

Raman spectroscopy was used to elucidate the oxidative state of the CoNR/MO$_x$ catalyst. The Raman spectra in Figure 3.14 also coincide with the XRD and STEM findings. The bands at 190, 490 and 690cm$^{-1}$ correspond to the Co$_3$O$_4$ spinel structure[48]. Given that the catalysts have a nearly equivalent amount of cobalt to support, the lack of Raman bands corresponding to the supports can only be attributed to the amorphous growth of the oxides around the cobalt nanorods.
The growth of an amorphous outer shell is often observed in aqueous media, where water disrupts the ordered formation of the support via the precursor[122]. To explore this possibility, the support was grown following the same procedure but without the addition of the cobalt nanorods. This resulted in the crystalline growth of the supports, as determined by XRD and Raman spectroscopy. This finding suggest that the cobalt is interacting with the support, which destabilizes the outer support shell leading to amorphous growth. Similar phenomena of amorphous outer shell growth have been reported for Au/SiO₂[130] and for Au/TiO₂[131], both of which used TEOS and TBOT as their source of silica and titania, respectively. For those reported core-shell structure, outer shells as thick as 20nm displayed no apparent X-ray diffraction patterns or significant optical properties[122].

Figure 3.14. Raman spectra of CoNR/MOx catalyst
The shift of the 690cm\(^{-1}\) and the 490cm\(^{-1}\) band from Co\(_3\)O\(_4\) seen in the CoNR to 680cm\(^{-1}\) and 480cm\(^{-1}\) for both the CoNR/Al\(_2\)O\(_3\) and CoNR/TiO\(_2\) samples suggest the formation of small amounts of interfacial cobalt aluminate and cobalt titanate. The formation of cobalt aluminates and titanates complexes have been reported to shift the cobalt spinel to lower wavenumbers[132]. In the case of CoNR/SiO\(_2\), there is a shift of the Co\(_3\)O\(_4\) bands to 670cm\(^{-1}\) and 460cm\(^{-1}\), which can be attributed to the formation of small amounts of cobalt silicate species at the interface. As the amount of interfacial species is negligible relative to the bulk CoNR/MO\(_x\), these species should be undetectable in XRD, however their presence would strain the cobalt surface, resulting in a shift of the Raman bands. Raman bands as low as 190, 470, and 650cm\(^{-1}\) have been reported for Co/SiO\(_2\) catalyst[133], consistent with our findings. Given that the synthesis method involves the chemical grafting of silica precursors to charged CTAB ligands on the cobalt nanorods, the formation of Co-O-Si bonds at the interface is highly likely. Bulk cobalt silicate forms bands at 695 and 890cm\(^{-1}\)[133], which are not present in this spectrum ruling out the bulk formation of cobalt silicate. In summary, the shifting of the Co\(_3\)O\(_4\) Raman bands towards lower wavenumbers for all of the CoNR/MO\(_x\) samples and the lack of any XRD peaks or Raman bands associated with the supports suggest a chemical interaction between the Co\(_3\)O\(_4\) nanorods and supports, which ultimately leads to amorphous growth of the outer shell.
**CO₂ Hydrogenation over CoNR/MOₓ**

Figure 3.15. (left) CO₂ conversion and (right) methane yield on CoNR/MOₓ catalysts operating under stoichiometric conditions of 4:1 H₂:CO₂.

The catalytic activities of CoNR/MOₓ catalysts are compared in Figure 3.15. All of the catalysts were reduced at 450°C for 3 hours under pure H₂ to yield metallic cobalt, which has widely been reported as the active phase for CO₂ methanation[134, 135]. The catalytic activity can be divided into two regions of interest, a kinetically controlled region between 150-250°C and a mass/heat transfer controlled region above 300°C[136, 137]. In the kinetically controlled regime, CoNR/TiO₂ shows considerably higher catalytic activity than CoNR/Al₂O₃ and CoNR/SiO₂, e.g., at 230°C conversion is almost 5x higher for the Ti supported nanorods. This increase in activity is likely due to the strong metal support interactions between metallic cobalt and the titanium in the CoNR/TiO₂ catalyst. Titania is known to interact with metals[138] and has been specifically reported to promote the catalytic activity of cobalt for the CO₂ hydrogenation reaction[139]. Titania is well-known to favor the reverse water gas shift reaction, which results in the production of CO [8, 140]. On the other hand, metallic Co is known for its high activity towards CO
hydrogenation.[95, 141] Therefore, a synergistic effect between metallic cobalt and titania is proposed to be responsible for the activity increase, with TiO$_2$ converting CO$_2$ to CO through the reverse water gas shift reaction and cobalt catalyzing the CO hydrogenation to the final product CH$_4$. This hypothesis is consistent with the CO$_2$ hydrogenation results, where no significant amounts of CO were produced under any reaction conditions, meaning the observed increase in activity is not due to the titania directly catalyzing CO$_2$ hydrogenation. In contrast, the CoNR/Al$_2$O$_3$ and CoNR/SiO$_2$ catalysts behave very similarly to the pure CoNR, which in the kinetic regime would be expected since both SiO$_2$ and Al$_2$O$_3$ are relatively inert supports compared with TiO$_2$ in the 150-250°C range. The mass transfer limited regime above 300°C is dominated by mass and heat transfer properties of the catalysts, where higher thermal conductivity mitigates transfer limitations. In the case of the supports used in this study, Al$_2$O$_3$ has the greatest thermal conductivity and has been reported to enhance activity at higher temperatures[142, 143], which agrees well with our findings. It should be noted that in both the kinetic and mass transfer control regimes, the CoNR/SiO$_2$ behaved almost identical to the pure CoNR, which suggests that the grafting procedure did not reduce catalytic activity by covering active cobalt sites, since SiO$_2$ is inert within the operating conditions.
Reducibility of CoNR/MO\textsubscript{x} Catalysts

In order to better understand the increase in catalytic activity during the CO\textsubscript{2} hydrogenation, the reducibility of the CoNR catalyst was explored via hydrogen temperature programmed reduction (H\textsubscript{2}-TPR). The TPR profiles in Figure 3.16 illustrate the differences in the reducibility for the different CoNR/MO\textsubscript{x} systems. CoNR/TiO\textsubscript{2} yielded the lowest reduction temperatures, where the first peak at 290\textdegree C corresponds to the Co\textsuperscript{3+}→Co\textsuperscript{2+} transition and the second peak at 420\textdegree C corresponds to the Co\textsuperscript{2+}→Co\textsuperscript{0} transition. These temperatures are at lower temperature than the pure CoNR. The additional shoulder observed for the CoNR/TiO\textsubscript{2} at 550\textdegree C corresponds to bulk CoNR reduction. The
peak around 610°C can also be seen in the TPR of the pure titania support and corresponds to the reduction of the titania support. For Co/SiO$_2$, the reduction profile is closer to that of the pure the CoNRs. The additional strong peak at 630°C can be attributed to the reduction of interfacial cobalt silicate at a higher temperature[144-146]. Similar reduction profiles for Co/Al$_2$O$_3$ were previously reported with both reduction events occurring in the 400-750°C range and were attributed to a strong interaction between cobalt and aluminium oxide, possibly forming cobalt aluminates[147, 148]. These results indicate that there is a strong interaction between the Co$_3$O$_4$ nanorods and the oxide supports, where each of the reduction profiles showed the formation of an interfacial species.

*Lifetime Study and Post-Reaction Analysis on CoNR/SiO$_2$*

As can be seen in Fig. 3.17, a decrease in catalytic activity for the Al$_2$O$_3$ supported CoNR catalysts is observed at temperature above 450 °C. This can be attributed to the formation of coke. Post reaction Raman spectra revealed the formation of the D and G bands at 1300 and 1600cm$^{-1}$, respectively, corresponding to the formation of graphitic carbon on the surface. Coke formation is known to occur preferentially on acid sites, such as those found on Al$_2$O$_3$[149, 150] and TiO$_2$[151]. Therefore, CoNR/SiO$_2$ was chosen for a time-on-stream study, since coke formation is expected to be lower on that catalyst due to the lack of additional acid sites. Figure 7 shows a 72-hour study performed in the kinetically controlled regime (≤10% conversion) at 230°C. The catalytic conversion decreased from its initial value of 10% and reached a steady state value of about 7% after 25 hours on stream. The selectivity towards methane continuously decreased from about 94% to 76%. At the same time, the CO selectivity increased from about 6% to 24%. Similar trends in the decrease of both CO$_2$ conversion and methane selectivity have been reported for
Co/SiO$_2$ for CO$_2$ hydrogenation[152], where a decrease in conversion was accompanied by a continuous decrease in selectivity towards methane. Coke formation, as shown in the Raman spectra, is known to decrease catalytic activity by either blocking active sites or separating metal from the support[153]. The isolation of surface Co sites by coke deposited on the cobalt surface will shift the product selectivity from CH$_4$ to CO. According to the widely accepted CO$_2$ hydrogenation mechanism,[154] CH$_4$ formation needs more than two adjacent active Co sites for CO$_2$ dissociation and H$_2$ activation. On the other side, CO$_2$ can dissociate into CO* and O*, which only needs two adjacent sites to proceed. As time on stream increases, more coke is deposited and selectivity towards CO gradually increases. Oxidation of the Co$^0$ to cobalt oxides another possible mechanism for the deactivation of cobalt catalysts during hydrogenation reactions. However, this is unlikely on our Co$_3$O$_4$ nanorods catalysts. The Co$_3$O$_4$ nanorods have been shown in our previous studies to be able to actively reverse the oxidation and deactivation during CO hydrogenation[95]. Furthermore, if the Co$_3$O$_4$ nanorods did undergo oxidation, a continuous decrease of conversion and CH$_4$ selectivity should be observed due to the loss of active Co$^0$ centers, instead of the relatively constant conversion as shown in Fig. 7. Therefore, formation of
coke is proposed to be mainly responsible for the selectivity change during the lifetime tests on the CoNR/SiO$_2$ catalysts by isolating the Co$^0$ sites from one another.

![Graph showing CO$_2$ conversion, CH$_4$ selectivity, and CO selectivity over time.](image)

**Figure 3.17.** Time on stream study of CoNR/SiO$_2$ for CO$_2$ hydrogenation

### 3.3 Conclusions

We have demonstrated that tuning the catalyst surface structures on cobalt via control of nanoscale morphology is an efficient way to design active catalysts by suppressing the formation of site-blocking surface intermediates. This is accomplished by selectively exposing different crystallographic facets on the active catalyst surface, while maintaining similar bulk properties, including particle size, crystallographic structure, chemical composition, and oxidation state. CO$_2$ hydrogenation tests show that Co nanorods that are synthesized as Co$_3$O$_4$ precursors with exposed \{110\} surface facets have substantially improved catalytic activity and selectivity towards methane than
nanoparticles from Co$_3$O$_4$ precursors with exposed {111} and {001} facets. The superior activity of Co nanorods results from a suppression of site-blocking formate species. The greater methane selectivity on the nanorods is attributed to the more active bridge-site CO as the reactive intermediate for methane formation. The catalyst reported here also requires less energy for the large-scale conversion of CO$_2$ to hydrocarbons, making the process more efficient and sustainable.

Furthermore, we have developed a robust methodology for the synthesis of supported catalyst with preserved surface faceting of the nanomaterials. By using surface sensitive techniques, such as STEM-HAADF and vibrational spectroscopy we were able to verify that the cobalt preserved the preferential {110} faceting of the Co nanorods and that the main surface species was indeed Co$_3$O$_4$. To test if the catalytic activity of the original unsupported catalyst was preserved, CO$_2$ hydrogenation was used as a model surface sensitive reaction. It was found that not only did the supported cobalt catalyst preserve the original catalytic activity, but also that the activity was enhanced in both the kinetic control regime (for CoNR/TiO$_2$) and the mass transfer regime (for CoNR/Al$_2$O$_3$). The activity increase in the kinetically controlled regime is due to the chemical interactions between the Co$_3$O$_4$ and TiO$_2$, which is supported by TPR, XRD, and Raman results, while in the mass-transfer regime, the activity increase is based on mitigated transfer limitations. Additionally, the deactivation trend of CoNR/SiO$_2$ agreed well with literature, suggesting the method of deactivation was due to the coke formation. Ultimately, our grafting methodology can promote supporting of highly coordinated surfaces to both preserve the exposure of active facets and gain advantages that accompany metal oxide supported catalyst.
CHAPTER 4
SINGLE SITE CATALYST AND CARBON MATERIALS FOR CO$_2$
HYDROGENATION$^{1-3}$


This work focuses on utilizing cobalt single site catalyst to probe the ensemble effects of cobalt cations on CO₂ hydrogenation[155]. The catalytic surface was studied using X-Ray Photoelectron Spectroscopy (XPS), X-Ray Absorption Fine Structure Spectroscopy (XAFS), UV-vis Spectroscopy, and Raman Spectroscopy, yielding a detailed understanding of the catalyst structure and its ensemble properties. With this information on the active-site structure of the catalyst, we can gain insight into the CO₂ hydrogenation reaction mechanism and how it depends on the local coordination environment of cobalt. We found that small ensembles of cobalt cations, i.e. Co²⁺ (Tetrahedrons) coordinated with free metal atoms on the surface, reach an optimal ensemble size and coordination environment that facilitates the methanation of CO₂, rather than the production of CO via the reverse-water gas shift reaction when they are atomically isolated.

The second single site catalyst that was explored was the use of ruthenium, with the advantage of reducing cost considerably while preserving catalytic performance. Furthermore, reducing the size of Ru significantly increases the surface atoms available for catalysis.[41] The higher density of surface atoms not only improves the catalytic activity but also the selectivity towards a single target product.[156] As an example, single Ru atoms bound on layered double hydroxide show high CO₂ conversion (turnover frequency, \(5.0 \times 10^{-4} \text{s}^{-1}\)) and formic acid selectivity (99%) for CO₂ hydrogenation.[157]. Unlike the introduction of external ligands in carbon supports, the B and N atoms in hexagonal boron nitride (h-BN) can act as the intrinsic ligands. The defect engineering of h-BN can give rise to B, N vacancies leading to unsaturated N, B sites which are good intrinsic ligands for coordinating metal atoms. On the other hand, the structure of h-BN can be tuned to be a porous structure with high specific surface area, which is beneficial to load a high
concentration of metal atoms. In addition, h-BN possesses excellent thermal conductivity (390 W m\(^{-1}\) K\(^{-1}\))[158] at room temperature, significantly higher than other traditional oxide supports such as TiO\(_2\) (8.5 W m\(^{-1}\) K\(^{-1}\)),[159] SiO\(_2\) (1.4 W m\(^{-1}\) K\(^{-1}\)),[160] Al\(_2\)O\(_3\) (28-35 W m\(^{-1}\) K\(^{-1}\)) and ZnO (50 W m\(^{-1}\) K\(^{-1}\)),[161] which can facilitate heat transfer in the catalyst. Therefore, porous defective h-BN is a promising support for thermocatalysts, additionally, due to the ability of h-BN to act as stabilizer for single atoms[162, 163] via the introduction of defects into the monolayer structure.

So far, the study of catalysts for thermochemical CO\(_2\) hydrogenation has focused on metal-based materials involving single metals or alloys, and their carbide and oxide phases.[164] Tuning of their structural and electronic properties has not substantially advanced catalytic activity. A broader search of efficient catalysts beyond metals is therefore needed to expand the research horizon. Here, we demonstrate, how the structure of carbon nanomaterials can be modified to improve its thermo-catalytic activity for CO\(_2\) hydrogenation. We further identified that this activity is governed by the dimension and defect density of the carbon nanomaterials. Reducing the dimension of graphene down to graphene quantum dots (GQD, lateral size < 5nm) with maximal exposure of edges sites and further introduction of nitrogen (N) dopants at those sites greatly promotes the CO\(_2\) hydrogenation activity. The catalytic activity can be tuned with different nitrogen sources to finely adjust the N-C bonding configurations and N content in the NGQDs. The mechanistic influence of N species on the CO\(_2\) catalytic hydrogenation is further investigated with in situ IR spectroscopy and density functional theory (DFT) calculation. This study establishes a new direction for the development of powerful catalyst for
thermochemical CO$_2$ reduction and provides insights into the fundamental understanding of structure-catalytic activity relationship for carbon nanomaterials.

4.1 Influence of Ensemble Size on Single Site Cobalt Catalysts for CO$_2$ Hydrogenation

*Cobalt single site structure*

Single site cobalt catalysts were synthesized via strong electrostatic adsorption of a hexammine cobalt chloride precursor onto amorphous silica. The electrostatic interaction between the hexammine cobalt (III) cation and the deprotonated silica, which contains negatively charged O’ species, resulted in a strong interaction between the precursor and the support[79]. Furthermore, due to the electrostatic repulsion and the corresponding hydration sheath of the hexammine cobalt (III) complex, adjacent cobalt centers, such as those that arise from adjacent silanol groups, are minimized[80]; resulting in uniform single site cobalt centers. To probe to structure of the cobalt Raman Spectroscopy was utilized due to its sensitivity to the influence of coordination environment on the vibrational modes of interested species[118, 119], and was utilized here to discern the vibrational structure of the Co/SiO$_2$ SSC. For cobalt oxide, there are several possible oxide structures that can readily form, where the most thermodynamically stable species are: the Co$_3$O$_4$ spinel structure, the rocksalt CoO structure, or the hydroxyl CoOOH structure. These structures have distinct Raman features, where Co$_3$O$_4$ has bands at 187, 473, 515, and 680 cm$^{-1}$ corresponding to $F_{2g}$, $E_g$, $F_{2g}$, and $A_{1g}$ modes, respectively.[165, 166] While CoOOH also has a Co$^{3+}$ cationic species, it has a distinct Raman band at 591cm$^{-1}$.[118, 119] The notable distinction that can be made via Raman spectroscopy is the differentiation of the HCP crystalline CoO from amorphous Co-O vibrations, where HCP CoO has bands at 190, 480,
519, and 690 cm\(^{-1}\),[148] while amorphous Co-O only has a broad band centered at \(\sim ca\) 500cm\(^{-1}\).[33, 167] These distinctions become clear in the Raman of the Co/SiO\(_2\) SSC compared against various cobalt standards, shown in Figure 4.1. For the Co/SiO\(_2\) SSC catalyst, the Raman spectra of 2 wt% Co/SiO\(_2\) and pure Co\(_3\)O\(_4\) standard were used as references. The 2wt% Co/SiO\(_2\) IMP was prepared via wet impregnation and was confirmed via XRD to yield crystalline Co\(_3\)O\(_4\) shown in Figure 4.2, which also yielded the characteristic Co\(_3\)O\(_4\) Raman spectra. The Co/SiO\(_2\) SSC only showed the characteristic Co-O broad band at \(\sim 480 \text{ cm}^{-1}\) [34, 119] Furthermore, the Co/SiO\(_2\) IMP shows a characteristic peak for silica at 610cm\(^{-1}\), arising from the amorphous siloxane rings, which is disrupted upon the addition of the cationic cobalt species in the Co/SiO\(_2\) SSC spectrum, due to the deprotonation of the surface via the use of ammonium hydroxide in the synthesis.[33, 34]
Figure 4.1. Raman spectra of Co/SiO$_2$ SSC compared against a control nanoparticle Co/SiO$_2$ IMP and a reference Co$_3$O$_4$ standard.
The valence electronic structure of the Co catalysts was studied using diffuse reflectance UV-vis spectroscopy to discern the presence of either Co\(^{2+}\) tetrahedral (Td) species and Co\(^{2+}\) octahedral (Oc) that could be present in CoO, shown in Figure 4.3. UV-vis elucidates the differences in Co\(^{3+}\), Co\(^{2+}\) (Oc), and Co\(^{2+}\) (Td) cations, since tetrahedral Co\(^{2+}\) has a distinct paramagnetic moment with a triplet degeneracy caused by the unpaired \([\text{Ar}]3d^7\) electron and asymmetric tetrahedral (Td) symmetry. Contrarily, Co\(^{3+}\) has a single peak due to the paired \([\text{Ar}]3d^6\) orbital and no paramagnetic moment due to its octahedral (Oc) symmetry, similar to Co\(^{2+}\) (Oc). The formation of Co\(^{2+}\) (Td) is a typical feature of atomically dispersed cobalt catalysts, due to its higher thermodynamic stability compared with other cobalt cations\([34, 35, 48]\). However, Co\(^{3+}\) will be present for all aggregated Co...
oxides, as observed in the case of the control sample, 2wt% Co/SiO₂ IMP. Diffuse reflectance UV-vis, performed on the Co/SiO₂ SSC yielded the triplet Co²⁺ (Td) peaks at 530, 580 and 630 nm, while any catalyst that contained Co³⁺ showed a broad band centered at 350 nm corresponding to octahedral Co³⁺ (Oc) found in the Co₃O₄ spinel structure. Additionally, there is no presence of Co²⁺ (Oc) on the Co/SiO₂ SSC, which has a broad shoulder located at ca 750nm, as the absorption of the Co/SiO₂ SSC closely follows that of the support SiO₂ material after the triplet peaks. Furthermore, it should be noted that upon completion of the electrostatic adsorption of the precursor onto the silica the resulting catalyst contains Co in the Co³⁺ (Oc) state due to the incorporation of the octahedral hexaamine Co³⁺ cations, but upon calcining at 300 °C the cobalt is completely reduced to the Co²⁺ (Td) state, most notably illustrated by the shift from an orange hue to a deep blue hue of the catalytic material.[33, 79]
Atomically dispersed transition metals on a surface have been shown to form unique oxidation states that correlate directly to the coordination geometry and neighboring atoms[168], therefore, XPS was utilized to probe this surface sensitive phenomena. In the case of cobalt, the most stable state is the Co$^{2+}$ (Td) cation, which has a distinct 2$p_{3/2}$ XPS peak at 780.2eV[82]. The absence of any 2$p_{3/2}$ Co$^{3+}$ peaks which form at approximately 779.5eV with its corresponding satellite shifted by ~10-11eV, is indicative that the surface is dominated by isolated Co$^{2+}$ (Td). The main route to produce Co$^{3+}$ on the surface is the formation of the Co$_3$O$_4$ spinel structure, where two thirds of the atoms in the spinel
structure are Co$^{3+}$ and one third are Co$^{2+}$. The XPS of the Co/SiO$_2$ SSC is shown in Figure 4.4, where the cobalt only yielded a peak at 780.7 eV, consistent with the formation of Co$^{2+}$ (Td). The surface concentration of cobalt in the Co/SiO$_2$ SSC was 1.88 at.%, which is in excellent agreement with the ICP concentration of 1.82±0.08 wt.%Co, showing the cobalt is highly dispersed.

Figure 4.4. Co 2p of Co/SiO$_2$ SSC taken at room temperature

X-Ray Absorption Spectroscopy (XAS) is the most definitive means of determining the coordination environment for SSCs. The backscattering obtained from Extended X-Ray Absorption Fine Structure (EXAFS) is directly related to the nearest neighbor and 2nd nearest neighbor interactions, while the pre-edge energy obtained from X-Ray Absorption
Near Edge Spectroscopy (XANES) is indicative of the coordination environment. The XANES and EXAFS spectra for the Co/SiO$_2$ SSC catalyst are shown in Figure 4.5. The data were analyzed via the Athena/Artemis software package and fitted using primarily single scattering paths[84, 169]. The pre-edge energy of 7709.6eV is attributed to the +2 formal oxidation state of cobalt with a coordination environment of 4 from the Co$^{2+}$ (Td) cations. EXAFS showed that the Co$^{2+}$ (Td) has a distinct Co-O bond distance of 1.974±0.007Å, consistent with the formation of single site cobalt, and a coordination number (CN) of 3.87±0.22 that is consistent with the tetrahedral geometry of the Co$^{2+}$ species. The summary of the first shell fits are shown in Table 4.1. Additionally, Co-O-Co backscattering has a bond length of 2.5Å,[33, 34] where Co-O-Co scattering can arise from cobalt dimers, or small clusters that occur when two or more adjacent hydroxyl groups adsorb cobalt precursors during the synthesis. Since cobalt is directly adsorbed onto the silica support and forms a uniform monolayer due to the electrostatic adsorption and corresponding hydration sheath sterically hindering surface clustering beyond a monolayer, the formation of a Co-O-Si second shell, also at 2.5Å, has been reported for similar highly dispersed cobalt species[33, 34, 79]. Based on the possibility for the Co-Si scattering, a Co-Si single scattering path was utilized to fit the Co/SiO$_2$ SSC room temperature data, resulting in CN of 1.5 ± 0.5 and a bond length of 3.16 ± 0.01 Å, which is slightly shorter than reported Co-Si for mononuclear octahedral Co$^{2+}$ supported on silica which was found to be ca 3.22 Å[34, 170], where the shorter Co-Si bond distance is expected for a tetrahedrally coordinated cobalt species due to the induced strain on the bonds[34]. An illustrative fitting used throughout XAFS analysis is shown in Figure 4.6,
showing the real $R$ space and magnitude of $R$ space fitting, alongside the $k$ space window and $r$ space window.

Figure 4.5. (a) XANES of Co K edge of Co/SiO$_2$ SSC and Co/SiO$_2$ IMP (b) $k^2$ weighted EXAFS of Co/SiO$_2$ SSC with the corresponding fit; measured at room temperature under He.

Table 4.1. Co K edge first shell EXAFS fitting and XANES pre-edge features ($2.2 \leq k \leq 12.7$ $\Delta k=4.0$, $1.0 \leq R \leq 3.2$ $\Delta r=0.2$).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Pre-Edge (eV)</th>
<th>Formal Oxidation</th>
<th>CN</th>
<th>R (Å)</th>
<th>Scattering Path</th>
<th>$\Delta E_0$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co/SiO$_2$ SSC RT</td>
<td>7709.6</td>
<td>+2</td>
<td>3.9±0.2</td>
<td>1.97±0.01</td>
<td>Co-O</td>
<td>0.48±0.52</td>
</tr>
<tr>
<td>Co/SiO$_2$ SSC 500°C</td>
<td>7709.6</td>
<td>+2</td>
<td>3.5±0.3</td>
<td>1.96±0.02</td>
<td>Co-O</td>
<td>0.30±0.93</td>
</tr>
<tr>
<td>Co/SiO$_2$ SSC 600°C</td>
<td>7709.6</td>
<td>+2</td>
<td>3.8±0.3</td>
<td>1.97±0.01</td>
<td>Co-O</td>
<td>0.36±0.64</td>
</tr>
<tr>
<td>Co/SiO$_2$ SSC 700°C</td>
<td>7709.0</td>
<td>+0/+2</td>
<td>2.7±0.5</td>
<td>1.96±0.02</td>
<td>Co-O</td>
<td>-3.3±1.2</td>
</tr>
</tbody>
</table>

* Debye-Waller Factor constrained at $\sigma^2=0.0078\pm0.0006$, 0.0072±0.0005, and 0.0085±0.0007 for the Co-O, Co-Si, and Co-Co; respectively
Figure 4.6. $k^2$ weighted EXAFS of Co/SiO$_2$ SSC. (a) Magnitude of R space with corresponding window and fit (b) real R space and fit (c) k space and corresponding window

**CO$_2$ Hydrogenation on Co/SiO$_2$ SSC**

The catalytic activity of the Co/SiO$_2$ SSCs for CO$_2$ hydrogenation is shown in Figure 4.7. The catalytic activity of the Co/SiO$_2$ SSC was found to reach a steady state...
conversion of CO$_2$ of approximately 7% at 400°C, with a selectivity towards CO of > 95% with the remaining 5% selectivity favoring the production of methane. A similar finding was reported for small domains of ruthenium and nickel, where by making small clusters of highly dispersed metal on a support the main product of the CO$_2$ hydrogenation was CO.[26, 117] Cobalt single sites supported on silica have been shown to be highly stable under reducing conditions[33, 35, 79], where a stable Co$^{2+}$ catalytic center should promote the selectivity towards CO as metallic cobalt is generally required for the production of methane due to its ability to readily dissociate hydrogen[171, 172]. This finding is consistent with the fact the catalyst retains a constant activity and selectivity throughout the temperature ramp, where a change in the catalytic surface via reduction of Co$^{2+}$ to metallic cobalt would result in a noticeable shift towards the production of methane while on stream. Furthermore, the apparent activation energy for CO$_2$ hydrogenation over the as synthesized Co/SiO$_2$ SSC was 25.7 kJ/mol, shown in Figure 4.8, consistent with the activation energy observed for the reverse water gas shift reaction[173-175]. The stable selectivity towards CO is unique to the Co/SiO$_2$ SSC catalyst, whereas the Co/SiO$_2$ IMP catalyst run under identical[22, 24] conditions resulted in both higher catalytic activity and a selectivity towards methane that increases with temperature, indicating the reduction of the surface into metallic cobalt under higher temperatures. Furthermore, consistent with the increased selectivity towards methane came an associated increase in activation energy of the Co/SiO$_2$ IMP sample to 49.9 kJ/mol, indicative of an increase in methanation activity, where the activation energy of CO$_2$ methanation on cobalt is nominally 75-80 kJ/mol.[11, 27]
Figure 4.7. CO₂ Hydrogenation over as synthesized Co/SiO₂ SSC. Reaction Conditions: 6000 mL g⁻¹·hr⁻¹, 10bar, 4:1 H₂:CO₂ feed
Figure 4.8. Arrhenius plot for CO\textsubscript{2} hydrogenation on the Co/SiO\textsubscript{2} SSC without any pretreatment. Reaction conditions: 6000 mL·hr\textsuperscript{-1}·g\textsubscript{cat}\textsuperscript{-1}, 10 bar pressure, 18%CO\textsubscript{2}/72%H\textsubscript{2}/10%Ar mixture gas inlet.

Subnanometer clustering and nanoparticle growth

One of the expected challenges with carrying out the hydrogenation reaction using a stoichiometric feed of 4:1 H\textsubscript{2} to CO\textsubscript{2} is the fact that this feed composition is highly reducing. This can cause the eventual sintering and agglomeration of the catalyst. Highly dispersed single site cobalt on silica has been shown to resist aggregation in a hydrogen environment up to approximately 500 °C, beyond which irreversible sintering is observed.[33, 176] Hydrogen temperature programmed reduction was performed to probe the reducibility of the catalyst, shown in Figure 4.9. The Co/SiO\textsubscript{2} SSC was shown to resist reduction up to 600 °C where the onset reduction temperature begins, while the typical
reduction profile of a comparable loading of cobalt nanoparticles has two distinct reduction events, Co$_3$O$_4$→CoO at ~300°C and CoO→Co$^0$ transition at ~410 °C.[80, 177]

![Graph](image)

Figure 4.9. Hydrogen temperature programmed reduction of Co/SiO$_2$ SSC and a reference impregnated catalyst using 10% H$_2$/Ar and a ramp rate of 5°C/min

Given that atomically isolated cobalt preferentially undergoes the RWGS reaction, the thermal instability of the catalyst under reduction temperatures > 500 °C under hydrogen was used as a platform to develop a range of possible surface moieties, where the growth of clusters and eventually nanoparticles is primarily governed via the gradual mobilization of metallic cobalt adatoms on the surface via Ostwald ripening[178, 179], resulting in a mixture between stable Co$^{2+}$ (Td) species and metallic cobalt. Atomically isolated cobalt was preserved under mild reducing conditions (400-450 °C), while the
formation of small cobalt clusters at intermediate reducing conditions (500-650 °C) and finally the formation of cobalt nanoparticles at high reduction temperatures (700-800 °C) were observed and studied for CO₂ hydrogenation, shown in Figure 4.10. The catalysts showed a factor of two increase in conversion at 500 °C and a factor of three higher conversion at 600 °C relative to the conversion of the atomically isolated Co²⁺, with an associated increase in selectivity towards methane. The CO₂ conversion reaches a local maxima at 600 °C, where the conversion and selectivity towards methane both decrease upon further reduction at 650 °C. At this point, the formation of small nanoparticles on the order of 1-2 nm has been reported elsewhere[180]. Furthermore, the partial reduction of the surface in the 500-650 °C range can also be attributed to the innate differences in the anchored silanol groups, where surface silanol groups are generally agreed to be the anchoring sites of the catalytic active elements[79, 80]. Depending on the vicinity of surface silanol groups, several different species can be found, including the isolated, vicinal, and geminal silanols, where each species has a distinct binding energy to a metal complex due to the changes in the coordination environment of the silanol group[181, 182]. Due to the complexity of understanding the nature of the support[183, 184], the surface silanols were not identified in this study and are beyond the scope of this work.[117, 185]
Figure 4.10. Effect of reductive pretreatment temperature on CO$_2$ hydrogenation for Co/SiO$_2$ SSC

Upon reduction at 700 °C and 800 °C, the formation of ~5nm and ~30nm particles was observed via post reduction STEM imaging, shown in Figure 4.11, whereas no distinguishable particle formation was found for the 600 °C reduced samples due to the poor Z contrast between silica and cobalt at the angstrom scale. The increase in CO$_2$ conversion particles in the range of 5-10 nm has been observed for cobalt nanoparticles before, where an optimal CO$_2$ conversion is achieved at roughly 10 nm, after which the catalytic activity is minimally affected by particle size[27]; consistent with our findings for the case of the highly reduced samples, where a higher rate of reaction is observed in the
sample reduced at 800 °C as opposed to the smaller nanoparticles corresponding to the 700 °C reduction.

![Figure 4.11. STEM-HAADF image of Co/SiO₂ SSC after a (left) 700°C and (right) 800°C reduction under hydrogen for 3 hours](image)

The change in selectivity is due to the preferential formation of edge sites for small clusters and nanoparticles, whereas the particle size increases the relative ratio of terrace sites increase, which should favor the production of CO as opposed to methane due to edge sites having a greater affinity to re-adsorb *CO relative to terrace sites,[186] thus facilitating the complete reduction of CO₂. The stability of the reduced catalyst under reaction conditions was explored via a hysteresis analysis, where the CO₂ conversion as well as the selectivity to both products was equivalent during a ramp up as a ramp down for the temperature of interest (400 °C), shown in Figure 4.12, for the catalyst reduced at 600 °C for 3 hr.
Figure 4.12. Hysteresis study on Co/SiO$_2$ SSC after a 600°C pretreatment for 3 hours. Reaction Conditions: 6000 mL·hr$^{-1}$·g$_{cat}^{-1}$, 10 bar pressure, 18%CO$_2$/72%H$_2$/10%Ar mixture gas inlet. Ramp rate 5°C/min with a step size of 50°C and a 3-hour dwell on each temperature.

Surface and Structural properties of Co/SiO$_2$ SSC after varied reductions

To gain further insight into the catalyst surface after reduction, XPS outfitted with a pretreatment chamber was used to characterize the cobalt species present on the surface after different reductive pretreatments. The XPS spectra, shown in Figure 4.13, confirm that the species present on the catalyst surface consist of a mix of Co$^0$/Co$^{2+}$ for the pretreatment conditions of interest. For the 500 °C reductive pretreatment, the surface is almost entirely Co$^{2+}$, with only a small fraction of being reduced to Co$^0$; resulting in a ratio of Co$^0$/Co$^{2+}$ of 0.122. In the case of the 600 °C reduction, the Co$^0$/Co$^{2+}$ ratio
increases to 0.363, which is also the composition resulting in optimal methane yield. However, increasing the Co\textsuperscript{0}/(Co\textsuperscript{2+}+Co\textsuperscript{0}) ratio is not sufficient to promote higher catalytic activity, as the catalyst performs poorly after a reduction of 650 °C, even though this pretreatment should yield a higher Co\textsuperscript{0}/(Co\textsuperscript{2+}+Co\textsuperscript{0}) ratio than the pretreatment at 600 °C given all other parameters were held constant. A synergistic effect between Co\textsuperscript{2+} and Co\textsuperscript{0} is proposed to be the cause for the change in catalytic activity of the clustered atoms, where similar synergistic effects have been observed for catalyst consisting of a partially reduced a CoO/Co\textsuperscript{0} surface[86]. For the case of subnanometer clusters, the optimal ratio of Co\textsuperscript{0}/(Co\textsuperscript{2+}+Co\textsuperscript{0}) was found to be 0.363, where the metallic cobalt should facilitate the dissociation of hydrogen, which is energetically unfavorable on cationic cobalt species, specifically when silica is used as the supporting material[85, 86]. Moreover, as there is no observed shift in the binding energy of the Co\textsuperscript{2+} species at 780.6 eV under all reductions where Co\textsuperscript{2+} is present, the ensemble size of metal clusters on the surface is believed to be the cause for the difference in CO\textsubscript{2} conversion and methane selectivity. Under a 700 °C reduction the cobalt exists in a Co\textsuperscript{2+} (Td) geometry in addition to a metallic cobalt state, giving rise to a peak at 780.6 eV corresponding to Co\textsuperscript{2+} (Td) and a set of peaks at 778 eV and 776 eV, corresponding to metallic cobalt and very small metallic cobalt domains which are shifted to lower energy due to insufficient contact with the support, resulting in partial charging. The Co\textsuperscript{0}/(Co\textsuperscript{2+}+Co\textsuperscript{0}) ratio for the 700 °C reduction is approximately 0.776, where the surface is predominantly reduced, shown in Figure 4.13, along with the 800 °C reduction, where the entirety of the cobalt is metallic showing peaks that correspond to metallic cobalt (778 eV) and overcompensated metallic cobalt (774 eV) with insufficient contact with the support.
Figure 4.13. Co 2p XPS of the Co/SiO₂ SSC after (left) a 400°C, 500°C and 600°C and (right) a 700°C and 800°C reduction under pure hydrogen with a one hour dwell time at the specified temperatures.

The coordination environment of the Co/SiO₂ SSC was probed at various reduction temperatures via XAS, where the catalysts were reduced in 3.5% H₂/He at the specified temperatures and then placed under an inert helium environment for the XAS measurements, shown in Figure 4.14. As the reduction temperature increases from the base room temperature measurement, a shift towards the metallic state is observed. Specifically, at 600 °C the pre-edge position shifts towards 7709.0 eV from 7709.6 eV, indicating the presence of a metallic state, where the metallic pre-edge feature is further developed at 700 °C. Additionally, the XANES and the XPS agree for the 700 °C reduction, where the Co⁰/(Co²⁺+Co⁰) ratio for the 700 °C reduction is 0.776, showing there is still a considerable amount of cationic cobalt; where the XANES shows that the pre-edge and white line approach those of the Co foil, thus are consistent with the XPS measurements. To more closely mirror the conditions of the measurements the catalytic activity of the Co/SiO₂ SSC was also probed at 600 °C given a 1 hr reduction time, resulting in a CO₂ conversion of
~15% and a methane selectivity of ~15%, both lower than the 3 hr reduction time case. The stability of the catalyst under reducing environments has been observed before for similar single site cobalt catalyst supported on silica, where up to 550 °C, no reduction was observed via XAS[33, 79]. A linear combination fitting using the room temperature untreated Co/SiO₂ SSC sample and Co foil as standards was performed on the reduced single site samples. The extent of reduction for the 500 °C, 600 °C, and 700 °C samples were 5%, 10% and 38%, respectively. A lower extent of reduction observed via XAS is to be expected when compared to XPS, both due to the intrinsic surface sensitivity of XPS and due to the differences in reduction time between the two observations. Furthermore, the cobalt k pre-edge feature of the SSC remains at 7709.6 eV, consistent with a +2 formal oxidative state.

Figure 4.14. (left) XANES Co K edge spectrum for the Co/SiO₂ SSC samples under various reduction temperatures (Inset) Co pre-edge region (right) EXAFS for the Co/SiO₂ SSC samples. Reduction Conditions: 3.5%H₂/He inlet at 20 mL/min flow, 13mg of catalyst

The coordination environment and corresponding first shell fits for the reduced Co/SiO₂ SSC catalysts are summarized in Table 4.1. The catalysts treated at 500 °C and 600 °C show no considerable development of a Co-Co scattering at 2.1 Å in the uncorrected
FT. However, their Co-O coordination number decreases from 3.8 ± 0.2 from the untreated Co/SiO$_2$ SSC to 3.5 ± 0.3 and 3.8 ± 0.3 for 500°C and 600°C, respectively. The decrease in coordination number can be attributed to the partial reduction of the Co$^{2+}$ (Td) structure, while as the reduction temperature increases, the Co-O structure begins to form metallic cobalt. However, no Co-Co single scattering was observed for either 500 °C or 600 °C, where the shift in pre-edge for the 600 °C sample is possibly due to the innate sensitivity of XANES to multiple scattering events whereas EXAFS is mostly influenced by periodic single scattering[187]. For 700 °C, a considerable amount of metallic cobalt is observed in the EXAFS, forming both Co-O at 1.5 Å and metallic Co-Co at 2.1 Å in the uncorrected FT. The first shell fits for both Co-O and Co-Co were 1.96 Å and 2.48 Å, which is consistent with the Co-O for Co$^{2+}$ (Td) and metallic cobalt, respectively[33, 170, 188]. The coordination number for Co-O was reduced to 2.7 ± 0.5 and the Co-Co coordination number was 3.6 ± 0.6. This is consistent with metallic cobalt after factoring in the extent of reduction, where the cobalt was approximately 38% percent reduced giving rise to a true coordination number of 10.0 ± 1.3, in agreement the expected coordination number of N=12 for Co-Co[79]. This is consistent with both the XPS and the XANES, which both show that the 700 °C is partially reduced, containing both Co$^{2+}$ (Td) and Co$^0$. Furthermore, the contributions from the Co-Si scattering after the 700 °C reduction were negligible, where a decrease in both bond length and coordination number of the Co-Si scattering is expected after reduction; particularly if is there is considerable surface restructuring and agglomeration[34], where agglomeration was verified via post reduction STEM to occur after the 700 °C reduction.
While the catalytic performance during the transition from single sites to nanoparticles changes based on the cluster size, the deconvolution of interaction the effects between Co\(^{2+}\) and Co\(^0\) cannot be ruled out. Decoupling these effects has been explored via reducible supports such as CeO\(_2\) to sequester Ru adatoms on the surface before they aggregate[189], however, the use of reducible supports to create a distinct set of Co\(^{2+}\) and/or Co\(^0\) clusters would result in strong metal support interactions, where reducible supports are known to preferentially catalyze the Reverse Water Gas Shift Reaction[8, 140]. The use of pure cationic cobalt sub nanometer clusters supported on γ-Mo\(_2\)N has been recently explored as a promising reverse water gas shift reaction, where cobalt clusters were stabilized by the Co-Mo interactions[190]. However, the distinction between contributions between cationic species and metal species is addressed in this work, where the Co\(^{2+}\) cations remain stable due to their Co-O bonding on the silica while the metallic Co is mobile and forms clusters, where by increasing the extent of reduction the cluster size is also increased. Furthermore, increasing the total amount of metal on the surface did not result in higher methanation activity, as per typical behavior for Co/SiO\(_2\);[86] instead a local maxima is observed after a 600 °C reduction under hydrogen followed by a decrease in activity upon higher reduction temperature, showing optimal ensemble size for both the rate of CO\(_2\) reaction and selectivity towards methane..

4.2 Atomic Ru Immobilized on Porous h-BN for CO\(_2\) Methanation

In this project, we reported the synthesis of Ru atoms onto porous boronitride (pBN) via B-Ru and N-Ru coordination, outline in Figure 4.15. We first prepared pBN with abundant -OH functional groups at the edges or defects. After a simple vacuum filtration process of a mixed solution of Ru precursor and pBN, multiple nearby surface -
OH groups of pBN allow for the rapid fixation of [Ru(NH₃)₆]³⁺ molecules by electrostatic adsorption. After an annealing treatment, the single atomic Ru is formed through Ru-B and Ru-N bonding which well control the valence state of Ru. Interestingly, we find the [Ru(NH₃)₆]³⁺ molecule can effectively penetrate into the mesopores of pBN with the aid of vacuum filtration leading to the trapping of [Ru(NH₃)₆]³⁺ molecules at micropores,[191] whereas traditional evaporation method resulted in catalysts that showed approximately an order of magnitude lower catalytic activity. Furthermore, the resulting Ru/pBN samples obtained via filtration have a uniform distribution of Ru atoms on pBN and exhibit distinctly higher catalytic activity and selectivity towards CO₂ methanation than Ru nanoparticles.

![Diagram of Ru/pBN](image)

**Figure 4.15.** (a) Schematic illustration for fabricating Ru/pBN-xF assisted by vacuum filtration drying and (b) photograph of pBN and Ru/pBN-xF.

Generally, a porous structure with high specific surface area is beneficial to disperse more metal atoms, while an abundance of defect sites is helpful to immobilize single metal atoms. Therefore, we first prepared the pBN by a one-pot annealing method. Boric acid and guanidine carbonate were mixed followed by annealing at 1000 °C to prepare a defect engineered pBN (Figure 4.15a). The as-prepared pBN has the typical white colour of h-BN materials (Figure 4.15b). The TEM image of pBN shows abundant hierarchical pores (Figure 4.16a) which is confirmed via AFM image (Figure 4.16b). The AFM height profile shows a thickness of ~1.5 nm for pBN sheets corresponding to 2-3 layers. The BET
characterization reveals that the pore size ranges from 1 to 5 nm and the specific surface area of pBN is up to 623.7 m² g⁻¹. The pBN has a smaller crystalline size than commercial h-BN powder as indicated by the two broad (002) and (100) peaks in the XRD patterns (Figure 4.16c, bottom). The Raman spectra show that the E₂g peak of pBN blue shifted to 1372 cm⁻¹ compared to 1367 cm⁻¹ for commercial h-BN powder due to the shorter B-N bond length in an isolated monolayer (Figure 4.16c, top).[192] The full width at half maximum (FWHM) of 31 cm⁻¹ in E₂g peak for pBN is much broader than 10.8 cm⁻¹ for commercial h-BN indicating a smaller crystalline size as well.[193] The comparison in XRD pattern and Raman spectra indicate the structural defects of pBN. The location of the Ru is believed to exist within the defect sites of the pBN, however, the exact nature of the defects, i.e. edge sites versus planar defects, were not identified in this work.

The pBN possesses a rich density of -OH groups, verified via XPS and FT-IR characterizations of pBN. The [Ru(NH₃)₆]³⁺ molecules are immobilized via electrostatic interaction with surface -OH groups. In order to further disperse [Ru(NH₃)₆]³⁺ molecules into the mesopores/micropores of pBN, a vacuum filtration process was employed to overcome the capillary force in the mesopores.[194] After annealing the Ru precursor/pBN mixture in a stream of 50%-Ar/50%-NH₃ at 750 °C for 1 h, the -OH groups are reduced while Ru atoms are embedded into pBN by Ru-B and Ru-N coordination. Meanwhile, the structure of pBN support remains intact after the annealing treatment.[195] 15 mg of the Ru precursor were added to 1 g of pBN and the resulting Ru/pBN has a Ru content of 0.58 wt.% as determined by ICP-MS measurements. According to the weight percent, the Ru/pBN is named as Ru/pBN-0.58%F (F representing vacuum filtration process). The Ru/pBN-0.58%F has a brown color, unlike the typical white color of pBN (Figure 4.15b).
Following the same procedure, two additional Ru/pBN samples with higher loadings of 1.13 wt.% and 1.76 wt.% were prepared by increasing the Ru precursor content to 30 and 45 mg, respectively. In XRD patterns (Figure 4.16d), all of the three Ru/pBN-xF ($x = 0.58\%$, 1.13\%, and 1.76\%) samples have typical h-BN diffraction peaks of (002) and (100).[196] No obvious diffraction peaks for metallic Ru are observed in Ru/pBN-0.58\%F due to the Ru atomic dispersion on pBN. However, upon closer inspection, both Ru/pBN-1.13\%F and -1.76\%F still show two weak diffraction peaks at 38.2° and 44.5° corresponding to Ru$^{0}$ (100) and (101), respectively, indicating the existence of metallic Ru.[197]

The morphology of Ru was characterized by STEM. No Ru nanoparticles are found in the Ru/pBN-0.58\%F (Figure 4.16e). Instead, the Ru moiety with a subnanometer size of ~0.5 nm (slight aggregation of atomic Ru, Figure 1e)[198] exists as atomically dispersed (Figure 4.16f) and is uniformly distributed on the surface of pBN. The EDS spectrum shows Ru-L peak at ~2.6 keV confirming the presence of Ru (Figure 4.16g). As the Ru content increases, the Ru atoms further aggregate into nanoparticles (1 - 3 nm) in the other two samples (Ru/pBN-1.13\%F and -1.76\%F), as shown in the TEM images (Figure 4.17), consistent with the XRD results. As a comparison, using a traditional rotary evaporation method instead of the vacuum filtration method to synthesize samples with a similar Ru loadings was implemented to discern the effects of the penetrating effect of vacuum filtration. The Ru/pBN-0.56\%R (R denoting the rotary evaporation process) has a larger Ru nanoparticle size (~1.0 nm). Additionally, the larger Ru nanoparticles appear to be non-uniformly scattered over the surface of pBN. The larger size and non-uniform distribution of Ru nanoparticles are attributed to the inadequate contact between the Ru precursor and
pBN (Figure 4.18). Even larger Ru nanoparticles with a mean diameter of ~3 nm appear in the Ru/pBN-1.13%R (Figure 4.19). The vacuum filtration method shows considerable advantage over the general drying method due to the fact the vacuum filtration helps remove excess precursor that did not electrostatically adsorb on the surface, and permeate into mesopores/micropores whereas the general drying method proceeds to reduce the excess precursor, resulting in uncontrolled, non uniform particle growth. These differences in the metal dispersion of hexaamine precursors via electrostatic adsorption and traditional impregnation is consistent with other work, which resulted in larger, unregulated particle sizes via wet impregnation.[80] However, upon increasing the concentration of the precursor, the probability of forming nanoparticles on the surface against atomic dispersion in the mesopores increases, which ultimately results in the formation of nanoparticles as well.
Figure 4.16. (a) TEM image of pBN, 40 nm scale bar. (b) AFM image of pBN, 800 nm scale bar, inset is the height profile. (c) Raman spectra (top) and XRD patterns (bottom) of pBN and commercial h-BN powder. (d) XRD patterns of three Ru/pBN-xF samples with different Ru loadings. (e) HAADF-STEM images of Ru/pBN-0.58%F, 5 nm scale bar, (inset) has a 200 nm scale bar. (f) enlarged HAADF-STEM image, 0.5 nm scale bar, (g) EDS spectrum in selected area of Figure 1e (the cyan area).
Figure 4.17. TEM images of Ru/pBN-1.13%F and -1.76%F.

Figure 4.18. The Aberration-corrected HAADF-STEM images of Ru/pBN-0.56%R.
The coordination of B and N with Ru was characterized by XPS (Figure 4.20a-c). The stoichiometry ratio of B and N is 1.11 in the annealed pBN and the ratios are 1.26, 1.29 and 1.37 for Ru/pBN-0.58%F, -1.13%F and -1.76%F. In addition to other peaks assigned to B-N (C), B-N (BN₃) and B-O in the order of increasing B1s binding energy, an additional peak at 192.2 eV corresponding to B-Ru-O can be fitted in Figure 4.20a and b.[199] However, in the Ru/pBN-xR samples, besides the B-Ru-O peak, a peak appears at a higher energy of 193.0 eV assigned to B-RuOₓ (x > 1) indicating a higher valence of Ru (Figure 4.20b). In the N1s spectrum of Ru/pBN-0.58%F (Figure 4.20c), a N-Ru peak emerges at 397.4 eV; the other four fitting peaks at 397.7 eV, 398 eV, 398.4 eV and 398.9 eV are attributed to N-B-C, N-B-O, N-B (NB₃) and N-C/N-O, respectively.[193, 200] The Ru/pBN-0.56%R shows the same N1s fitting peaks but the binding energy increases by ~ 0.2 eV for the overall peak position because of high oxygen content (Figure 4.20c). On the
other hand, the weak Ru peaks can be detected in the Ru 3p spectrums by repeatedly XPS scanning though there are low Ru loadings.[201] The Ru peaks are located at between 461.2 eV (Ru⁰) and 463.3 eV (RuO₂) indicating the oxidation state of Ru⁵⁺ (0 < δ < 4). Compared to Ru/pBN-0.56%F, -1.13%F, the Ru peaks of Ru/pBN-0.56%R and -1.13%R showed high binding energies, closer to the 463.3 eV of RuO₂, which indicates the higher Ru valence state in Ru/pBN-xR than that in Ru/pBN-xF samples.[202, 203] The high Ru valence state in Ru/pBN-xR may be attributed to the O-enriched pBN support due to the high electron withdrawing property of O.[204, 205] X-ray absorption near-edge structure (XANES) spectra show that the Ru K-edge of Ru/pBN-0.58%F yields a white line in between Ru foil and RuO₂ (Figure 4.20d), indicating that the Ru has the positive charge of Ru⁵⁺ (0 < δ < 4) resulting from Ru-O/N/B bonds.[206] In the extended X-ray absorption fine structure (EXAFS) spectra, there is no Ru-Ru bonding in Ru/pBN-0.58%F (Figure 2e), indicating the lack of Ru⁰ and revealing isolated Ru atoms throughout the whole Ru/pBN-0.58%F.[207] The scattering event at ~1.6 Å in the uncorrected FT differs from the typical Ru-O peak in bulk RuO₂,[208] which can be attributed to the combined effect between Ru and N, B, O atoms of pBN support.[207, 208] First shell fitting of the EXAFS spectra yielded an apparent bond distance for Ru-O/N/B of 2.08 Å and a coordination number of 3.3, shown in Table 4.2.
Table 4.2. Ru K-Edge EXAFS fitting parameters

<table>
<thead>
<tr>
<th>Sample</th>
<th>Scattering Path</th>
<th>Coordination Number</th>
<th>Bond Length (Å⁻¹)</th>
<th>DWF (10⁻³Å²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ru/pBN-0.58%F</td>
<td>Ru-O/N/B</td>
<td>3.3</td>
<td>2.08</td>
<td>2.2</td>
</tr>
<tr>
<td>Ru Foil</td>
<td>Ru-Ru*</td>
<td>12</td>
<td>2.68</td>
<td>3.3</td>
</tr>
<tr>
<td>RuO₂</td>
<td>Ru-O</td>
<td>4</td>
<td>1.90</td>
<td>2.9</td>
</tr>
<tr>
<td></td>
<td>Ru-O</td>
<td>2</td>
<td>2.02</td>
<td>2.9</td>
</tr>
</tbody>
</table>

Error on coordination number was estimated as CN ±10%; Bond length ±1%; DWF ±10%.
* dictates fixed coordination number based on reference standard crystal structure

Where the absence of any Ru-Ru from RuO₂ scattering in the EXAFS indicates the lack of long range ordering, while the decreased amplitude of the Ru-O/B/N scattering is indicative of under coordinated single atoms, consistent with our findings. The lower state of Ru in Ru/pBN-xF is induced by more intimate contact between the Ru precursor and pBN through the filtration process. During the annealing process, the formed B, N coordination can restrict the aggregation of Ru atoms as shown in STEM images (Figure 4.16f). In addition, the stronger coordination prevents the oxidization of Ru. Based on the above analysis of valence state, we can simulate the structure of Ru in Ru/pBN-xF and Ru/pBN-xF samples as RuO and RuO₂ connected with nearby N and B atoms, respectively. As reported in other Ru catalysts, the B-Ru-B structure can stabilize Ru and improve catalytic activity.[209, 210]
Figure 4.20. (a) The high-resolution B1s spectra of pBN, Ru/pBN-xF and -xR samples. (b) The B1s spectrum of Ru/pBN-0.58%F and -0.56%R. (c) The N1s spectrum of Ru/pBN-0.58%F and -0.56%R. (d) The normalized Ru K-edge XANES spectra of Ru/pBN-0.58%F and references. (e) The Fourier transform magnitudes of the experimental Ru K-edge EXAFS spectra of Ru/pBN-0.58%F along with reference materials.

Ru-based catalysts are generally highly active for CO₂ hydrogenation, with an almost exclusive selectivity towards CH₄ in H₂/CO₂ (4:1) under 0.1-1.0 MPa.[8, 25, 211, 212] The catalysts were evaluated as synthesized to explore the effects of Ru catalyst size and state dependence. Catalytic contribution from the supporting pBN was ruled out. The blank pBN support yielded a CO₂ conversion of only 1.18% at 480 °C, with a complete selectivity towards CO, suggesting the occurrence of the reverse water gas shift (RWGS) reaction. The vacuum filtration method results in more active catalysts of which the initial catalytic activity was observed at 250 °C on all three catalysts loadings. The difference in conversion within the different Ru/pBN-xF catalysts can be attributed to the different Ru loadings (Figure 4.21a). The higher Ru loading contributes to a greater number of active
sites and thus higher conversion. A similar trend in the selectivity towards CH$_4$ observed in the Ru/pBN-xF suggests the presence of similar active sites (Figure 4.21b). The loading effect was also observed on Ru/Al$_2$O$_3$ (Ru loading ranging from 0.1 wt.% to 5 wt.%), where the presence of clusters at low Ru loadings (0.1 and 0.5 wt.% Ru/Al$_2$O$_3$) resulted in the preferential formation of CO while an increase in CH$_4$ selectivity was attributed to the sintering of the unstable ruthenium clusters.[198] However, in the case of the Ru/pBN-xF samples, the CH$_4$ product retained a high selectivity (93.5%) due to the B, N atoms coordinating with Ru atoms, thus mitigating the Ru aggregation and reducing the valence state. In the case of Ru/pBN-xR samples prepared via rotary evaporation, which have a comparable metal loading as the Ru/pBN-xF, the presence of larger particles as opposed to atomic dispersion results in both a lower catalytic activity as well as lower selectivity towards CH$_4$ in the low conversion regime (Figure 3c and Table 1), which suggest there is a synergistic effect between the Ru-O/B/N on the Ru/pBN-xF catalysts that promotes methanation, as atomic ruthenium supported on alumina has been shown to preferentially form CO.[198] An opposite trend has been reported when reducible supports are used to disperse Ru, such as CeO$_2$; where atoms/clusters showed the highest selectivity towards methane while Ru nanoparticles preferentially formed CO;[189, 213, 214] where the Ru/pBN catalysts are more in line with the behavior of Ru/CeO$_2$ than that of Ru/Al$_2$O$_3$. A comparison of the catalytic activity for various catalysts normalized by the total active metal loading, including those presented in this work. In the case of the Ru/pBN-xF catalysts, the Ru/pBN-0.58%F has the highest relative reaction rate compared to the higher loading Ru/pBN-1.13%F and Ru/pBN-1.76%F. Additionally, the Ru/pBN-0.58%F has a factor of 5 higher reaction rate than the Ru/pBN-0.56%R owing to the preferential
formation of atomic Ru on the filtrated samples as opposed to the Ru nanoparticles in the Ru/pBN-xR samples. The Ru/pBN-xF samples show promising catalytic activity when compared against catalysts reported in literature. However, it is important to note that a direct comparison with literature is not feasible due to the inherent differences in operating conditions found in each individual work (such as pressure and temperature); thus, consideration of relative reaction rates should be drawn to the comparison of the work outlined in this study; specifically the comparison between the Ru/pBN-xF and Ru/pBN-xR which represent the difference between traditional wet impregnated catalysts (Ru/pBN-xR) and the novel filtration synthesis (Ru/pBN-xF) outlined herein.
As single metal atoms tend to be unstable under reaction conditions,[40, 41] the stability of Ru/pBN-0.58%F was tested for CO₂ hydrogenation over the course of ~110 hours (Figure 4.22). Within the first the 12 hours the catalyst has a decrease in catalytic activity from approximately 28% CO₂ conversion to a steady state value of ~18% and a steady state selectivity toward CH₄ and CO of ~92% and ~8%, respectively. These values for conversion and selectivity are consistent within instrumental error of what we observed via the temperature ramp tests. The decrease in activity is attributed to the formation of
coke during the reaction, verified via post-reaction Raman spectroscopy on Ru/pBN-0.58%F, where the G band corresponding to graphene was at \( \sim 1600 \) cm\(^{-1} \) was observed, where the D band at \( \sim 1300 \) cm\(^{-1} \) was convoluted with the BN vibration and therefore not considered. Furthermore, the steady decrease in conversion coupled with the corresponding increase in CO selectivity further suggest coke formation as the method of deactivation, as CO\(_2\) and elemental carbon can react via the Boudouard reaction to produce CO.[215] To test for the possibility of ruthenium sintering, post reaction XRD was performed on Ru/pBN-0.58%F, -1.13%F and Ru/pBN-0.56%R, -1.13%R (Figure 4.23) to directly compare the effects of synthesis method on catalyst stability. All the catalysts with the exception of Ru/pBN-0.58%F show sintering, via the formation of the (110) peak of RuO\(_2\); where after exposure to ambient conditions the sintered Ru metal should preferably form the more stable RuO\(_2\) oxide. This suggest that Ru/pBN-0.58%F is either resistant to sintering and is keeping atomic dispersion or forms sub-nanometer clusters below the 1.54 nm detection limit of the XRD. Due to the difficulty of separating the catalyst from the quartz wool/sand used during reaction for heat dissipation and structural support, post reaction STEM imaging was not possible.
Figure 4.22. The catalytic stability of Ru/pBN-0.58%F for 110h. Reaction Conditions: 4:1 ratio of H₂:CO₂ with a 10% Ar internal standard, 10 bar pressure, 320 °C bed temperature, 18000 h⁻¹ space velocity.
Both TiO$_2$ and Al$_2$O$_3$ have been used as the supporting material for Ru in CO$_2$ hydrogenation.[25, 198] Compared to Al$_2$O$_3$, TiO$_2$ is a much more reducible support, which can have a significant metal support interaction with the Ru, creating new catalytic sites at the Ru-TiO$_2$ interface by migrating suboxide species onto the surface of Ru.[216] Although Ru/TiO$_2$ also shows high conversion and CH$_4$ selectivity at low temperature and pressure, the Ru loaded onto TiO$_2$ is in the form of nanoparticles with a size distribution between 1-5 nm.[25] which reduces the utilization rate of Ru. In this project, we applied defective pBN with abundant mesopores and B, N vacancies. The mesopores and B, N vacancies can restrict Ru size, and reduce the Ru state, respectively. Furthermore, h-BN is
acknowledged as an excellent thermal conductor and this thermal conductivity can reduce energy consumption during CO$_2$ hydrogenation.

Table 4.3. Summary of Catalytic Activity for Ru/pBN-xF and Ru/pBN-xR samples

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Temperature (°C)</th>
<th>CO$_2$ Conversion (%)</th>
<th>CH$_4$ Selectivity (%)</th>
<th>Reaction Rate (mol CO$<em>2$·g$</em>{Ru}$·s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ru/pBN-0.58%F</td>
<td>350</td>
<td>28.7</td>
<td>93.5</td>
<td>1.86x10$^{-3}$</td>
</tr>
<tr>
<td></td>
<td>400</td>
<td>35.6</td>
<td>94.5</td>
<td>2.36x10$^{-3}$</td>
</tr>
<tr>
<td>Ru/pBN-1.13%F</td>
<td>350</td>
<td>39.1</td>
<td>95.8</td>
<td>1.30x10$^{-3}$</td>
</tr>
<tr>
<td></td>
<td>400</td>
<td>61.6</td>
<td>96.5</td>
<td>2.05x10$^{-3}$</td>
</tr>
<tr>
<td>Ru/pBN-1.76%F</td>
<td>350</td>
<td>40.1</td>
<td>96.4</td>
<td>0.85x10$^{-3}$</td>
</tr>
<tr>
<td></td>
<td>400</td>
<td>81.1</td>
<td>98.8</td>
<td>1.73x10$^{-3}$</td>
</tr>
<tr>
<td>Ru/pBN-0.56%R</td>
<td>350</td>
<td>5.1</td>
<td>72.5</td>
<td>0.33x10$^{-3}$</td>
</tr>
<tr>
<td></td>
<td>400</td>
<td>17.8</td>
<td>84.4</td>
<td>1.16x10$^{-3}$</td>
</tr>
<tr>
<td>Ru/pBN-1.13%R</td>
<td>350</td>
<td>6.5</td>
<td>76.7</td>
<td>0.21x10$^{-3}$</td>
</tr>
<tr>
<td></td>
<td>400</td>
<td>44.0</td>
<td>92.7</td>
<td>1.46x10$^{-3}$</td>
</tr>
</tbody>
</table>

The reducibility of the Ru/pBN catalysts was also explored (Figure 4.21d). The reduction temperature of the Ru/pBN-xF ($x = 1.13\%$, 1.76%) is approximately 156 °C and that of Ru/pBN-1.13%R catalyst is approximately 136 °C. This is due to the presence of highly dispersed RuO$_x$ species, which is typically reduced between 50-150 °C.[217, 218] Furthermore, the higher reduction temperature of the Ru/pBN-xF species can also be attributed to a stronger metal support interaction effect, where XPS also showed electronic interactions between the Ru and B, N species. The greater particle size on the Ru/pBN-xR would inevitably result in a lower metal/support interface and the larger size leads to a thinner oxide layer on metallic Ru. The reduction temperature on these catalysts is possibly
a result of a passivating layer of RuOₓ forming over the metallic Ru post synthesis after exposure to ambient air.[219] The Ru state is achieved by reduction of [Ru(NH₃)₆]³⁺ followed by a mild oxidation proved to be the most active state in CO₂ hydrogenation,[220] which was demonstrated by the following DFT simulation. This is consistent with the XRD, where ordered metallic Ru particles are observed on the Ru/pBN-ₓF (ₓ = 1.13%, 1.76%) but no RuOₓ is observed. Passivating oxide layers are not typically thick enough to diffract; thus, cannot be observed in the XRD. The XPS spectra further corroborates this, where the surface sensitivity of XPS is sufficient to capture the effects of a passivating layer formed on the Ru/pBN-ₓR samples, shifting the binding energy closer to the Ru⁴⁺ state (463.3 eV). Due to the B, N coordination, the Ru passivating layer in Ru/pBN-ₓF has a lower state, where the average binding energy for the Ru/pBN-ₓF is ~ 462.7 eV whereas the average binding energy for the Ru/pBN-ₓR is ~ 463 eV. Furthermore, in the case of both the Ru/pBN-0.58%F and Ru/pBN-0.56%R, there is no observed reduction event, which suggests that the Ru is strongly bonded to the boron nitride by B-Ru and N-Ru.

As reported for other single atom catalysts,[156, 221, 222] the smaller size of catalyst can allow the distribution of more metal atoms to the reaction substrate, which can explain the enhanced catalytic activity of atomic-scale catalysts compared to that of nanoscale catalysts. This same mechanism is responsible for the catalytic enhancement observed in this work. Therefore, a simulation of the size effect was not carried out.

As demonstrated in Ni-based catalysts on different supports such as SiO₂, Al₂O₃, ZrO₂, and CeO₂, the different catalytic performance of Ni-based catalysts is partially attributed to the support effect.[212, 223] The support effect between pBN and Ru also plays an important role in tuning catalytic activity of Ru, for example, the O-enriched pBN
support can increase the valence state of Ru in Ru/pBN-\(\chi\)R samples. In order to explore the origin of the catalytic site and the high selectivity at the interface between Ru and pBN in the Ru/pBN catalyst, a density functional theory (DFT) simulation following the Eley-Rideal mechanism was carried out (See details in Supporting Information).[30, 224, 225] We simulated the structures of Ru/pBN-\(\chi\)F and Ru/pBN-\(\chi\)R samples both with the same Ru-B and Ru-N bonding but different oxidation states in RuO and RuO\(_2\), respectively. In order to determine the most stable structure of catalyst, we simulated RuO and RuO\(_2\) bonding to five different vacancy configurations: B vacancy, N vacancy, BN vacancy, B\(_3\)N vacancy and BN\(_3\) vacancy; as neither structure can be unequivocally ruled out from forming during the synthesis, multiple configurations were considered, shown in Figure 4.24. We found that RuO prefers most to dope into B vacancy with doping energy of -7.31 eV, consistent with other computational studies of single atoms supported on BN.[162] However, the doping energy at the BN vacancy is only slightly higher than the B vacancy (0.96 eV) as compared to the rest. The other N, BN\(_3\) and B\(_3\)N vacancies have much higher doping energy, being ~ 4.92 eV, 6.40 eV and 2.61 eV, respectively (See Figure 4a). Similarly, RuO\(_2\) also prefers to dope into B vacancy with doping energy of -6.19 eV, whereas doping at N, BN, BN\(_3\) and B\(_3\)N vacancies is higher in energy by ~ 4.19 eV, 1.32 eV, 5.88 eV and 4.77 eV B vacancy, respectively. Since the possibility for insertion of either RuO or RuO\(_2\) into the BN vacancy exist, and also because Ru prefers bonding to two B atoms (as confirmed by our XPS measurements).[199] we henceforth carried out all calculations on BN vacancies for both RuO and RuO\(_2\) (see Figure 4.25, top panel).
Figure 4.24. Relaxed structures of (A) RuO and (B) RuO$_2$ doping at B, N, BN, B$_3$N and BN$_3$ vacancies and side view at B vacancy. Note that RuO$_2$ at B site leads to rotation of O$_2$ parallel to the substrate, making it lower in energy. Color scheme, B (green), N (blue), O (red), H (white), C (yellow) and Ru (purple).

Based on the potential active sites, we simulated the adsorption of intermediates at not only the Ru (i.e. on the top side of RuO and RuO$_2$) site, but also the neighboring B and N atomic sites. The mechanism is shown in Figure 4.25 for CO$_2$ hydrogenation on both RuO and RuO$_2$ at 350°C. The maximum free energy change of the steps ($\Delta G_{\text{max}}$) is the least at the B site for RuO, whereas it is the Ru site for RuO$_2$. However, the $\Delta G_{\text{max}}$ is only 0.1 eV higher for adsorption on the remaining sites in the case of both RuO and RuO$_2$ structure. The reaction energy pathways for the hydrogenation of CO$_2$ into CH$_4$ at the B site for RuO and Ru site for RuO$_2$ are given in Figure 5. We find that the most endothermic step for the RuO site is the formation of *HOCO at ~1.17 eV. Whereas, in RuO$_2$ it is the formation of both *HOCO at ~1.61 eV and *H$_2$CO at ~1.44 eV, followed by *CH$_3$ at ~1.38 eV. Our results show that indeed the reaction pathway on the RuO$_2$ (1.61 eV) is higher in energy than that on RuO (1.17 eV) by approximately ~ 0.5 eV; hence, RuO, i.e., Ru/pBN-$x$F samples are more catalytically active in comparison with Ru/pBN-$x$R samples, in agreement with our experimental results. From Bader charge analysis, we find that RuO
dopes the adjacent B and N atoms with 0.75 e/atom (i.e. n-doped) and -0.61 e/atom (i.e. hole-doped), respectively. Whereas, doping of adjacent B atoms due to RuO₂ is reduced to 0.67 e/atom (i.e. n-doped), while that of N remains same, -0.61 e/atom (i.e. hole-doped). This change in doping of B atoms is related to the Ru oxidation state, where Ru loses -1.1 e/atom and -0.84 e/atom in RuO and RuO₂ (both hole doped), respectively. Whereas, O atom gains 0.67 e/atom in RuO, and in RuO₂ the O directly connected to Ru gains 0.37e/atom with next one gaining 0.51 e/atom. In total, RuO and RuO₂ negatively dope the h-BN lattice by 0.42e and 0.30 e, respectively. In terms of catalytic activity, we found that a large negative charge transfer to h-BN results in higher activity of RuO; hence by increasing the positive charge on Ru, one might further enhance the catalytic performance.

For catalysts with a strong affinity towards oxygen and carbon, such as Ru, it has recently been shown that the rate limiting step for atomically dispersed Ru supported on BN is also *COOH, while for single atom transition metals with a weaker affinity towards adsorbed *CO, the rate limiting step was found to be *CHO hydrogenation.[162] It is interesting to note that though CH₄ is energetically much less stable than CO₂ (Heats of formation of, CO₂ = - 4.07 eV and CH₄ = -0.77 eV); the total CO₂ methanation reaction is exothermic (ΔG (CH₄ + 2H₂O - 4H₂ - CO₂) = -1.1 eV at 350 °C see Figure 4), and is primarily due to higher combined stability of 2H₂O + CH₄ over 4H₂ + CO₂ (H₂ and H₂O not shown in Figure 5).
Figure 4.25. The reaction free energy diagram for CO$_2$ hydrogenation at 350 °C (623 K). Top panel shows the side view of RuO and RuO$_2$ at the BN vacancy. The middle panel is the top view of the RuO and RuO$_2$ structures, with the O atoms below Ru, and hence are hidden in the schematic. Bottom panel displays the free energy diagram of the reaction. Color scheme, B (green), N (blue), O (red), H (white), C (yellow) and Ru (purple).

4.3 CO$_2$ Hydrogenation over a Metal-Free Carbon-Based Catalyst

The NGQDs were synthesized through liquid phase exfoliation and shearing of graphene oxide (GO) precursor in the dimethylformamide (DMF) solvent at 200 °C in a PTFE lined autoclave.[226] DMF has a surface tension and ratio of polar/dispersion
component matching that of GO, guaranteeing efficient liquid-phase exfoliation of GO and favoring the formation of ultrathin sheets at a high yield.[227] Meanwhile, the cutting of exfoliated sheets takes place preferably along the boundary between the \( sp^2 \) domain and disordered \( sp^3 \) region with rich oxygen-containing groups. The \( sp^2 \) domains split from ultrathin GO sheets, which leads to the formation of graphitic NGQDs. As a result, these NGQDs contains predominantly mono- and bi-layers (0.5 to 1.0 nm), as shown in Figure 4.26a, while they possess lateral sizes of 2-3 nm, as determined by the high resolution transmission electron microscopy (HRTEM) images in Figure 4.26b. The N doping occurred simultaneously with the exfoliation, with DMF acting as a nitrogen source as it decomposed at elevated temperature and pressure. The NGQDs have an enhanced density of exposed edge sites compared to GO, which favors the formation of pyridinic N configuration (connecting to two C atoms in a hexagonal ring, illustrative structure shown in inset of Figure 4.26d) doping. The Raman spectrum of NGQDs demonstrates the characteristic D band at 1351 cm\(^{-1}\) and the G band at 1584 cm\(^{-1}\) (Figure 4.26c). The large ratio of D/G band intensities (~1.05) mainly originates from the N-doping defects and exposed edge sites. The N 1s core-level X-ray absorption near edge spectroscopy (XANES) reveals a strong peak at a photon energy of 399 eV and a weak peak at 401.2 eV, corresponding to 1s to \( \pi^* \) transitions of two different N substitutions (Figure 4.26d).[228] The peak at 399 eV can be assigned to pyridinic N with less electron-negative N-C bonds, while the peak at 401.2 eV is assigned to graphitic N (connecting to three C atoms in a hexagonal ring).[228, 229] There is a higher concentration of pyridinic N than graphitic N in the NGQDs, as indicated by the comparison of the \( \pi^* \) transition peak intensity. The peak for pyrrolic N (connecting to two C atoms in a pentagon ring) is not distinguishable from
that of pyridinic N in the XANES since its photon binding energy is very close to pyridinic N and it is at a low concentration.

Figure 4.26. Morphology and structure of N-doped graphene quantum dots. (a) AFM image. The inset shows the thickness profile of NGQDs along the red line. The scale bar is 50 nm. (b) HRTEM image of NGQDs. The inset shows a single NGQD containing hexagonal lattice. The scale bar is 1 nm. (c) Raman spectrum of NGQDs. (d) X-ray absorption near edge spectrum of N K-edge for NGQDs. The inset is a scheme of different N-C bonds, pyridinic (black), pyrrolic (blue), and graphitic N (pink).

To gain more information about N bonding and content of specific N motif, X-ray photoelectron spectroscopy (XPS) was performed on the NGQDs. The deconvolution of
the XPS N 1s for NGQDs quantitatively provides information on the content of specific N configurations. The total N content in the NGQDs is around 6.0 at.%, composed of predominant pyridinic N (binding energy 398.5 eV) with a content of ~3.9 at.%, pyrrolic N (400.0 eV, ~1.2 at.%), and graphitic N (401.2 eV, ~0.9 at.%).[230]

Figure 4.27. Thermochemical catalytic activity and selectivity towards CO$_2$ reduction over NGQDs/Al$_2$O$_3$. (a) Dependence of CO$_2$ conversion on temperature over NGQDs/Al$_2$O$_3$ with three different loadings (0.8 wt%, 1 wt%, and 3 wt%). Results for undoped samples are presented for comparison. (b) Dependence of CO and CH$_4$ selectivity on temperature over NGQDs/Al$_2$O$_3$ with three different loadings. (c) FTIR spectra of CO$_2$ adsorbed onto NGQDs/Al$_2$O$_3$ and GQDs/Al$_2$O$_3$ at room temperature. (d) Temperature programmed desorption of CO$_2$ from NGQDs/Al$_2$O$_3$ and GQDs/Al$_2$O$_3$. 
Three samples of NGQDs supported on Al$_2$O$_3$ (NGQDs/Al$_2$O$_3$) with different loadings (0.8, 1, and 3 wt.%) were prepared by an impregnation method (see experimental section in Supporting Information), with the catalyst content being estimated by thermogravimetric analysis. The activity and selectivity of NGQDs/Al$_2$O$_3$ towards hydrogenation of CO$_2$ were evaluated in the temperature range between 100 - 450 °C and under stoichiometric conditions of CO$_2$/H$_2$ (1:4) at 10 bar. The three NGQDs/Al$_2$O$_3$ samples exhibit similar catalytic behavior. The hydrogenation of CO$_2$ catalyzed by NGQDs/Al$_2$O$_3$ initiates around 170 °C (Figure 4.27a). The CO$_2$ conversion generally increases with the increase of temperature, and reaches values over 60% at 400 °C. The two main products that were observed were carbon monoxide (CO) and methane (CH$_4$). The predominant product is CO at lower temperatures, while CH$_4$ becomes the major product after the temperature increases to 380 °C (Figure 4.27b). The CO selectivity maintains around 60 - 65% in the temperature range of 170 - 255 °C. The CO selectivity rises to a maximum of 85% at a turning point at 300 °C. The initial selectivity of CH$_4$ is ~30% at 170 °C. It gradually decreases to 15% at 300 °C. With further increase of the temperature beyond 300 °C, the selectivity of CH$_4$ gradually increases to 55% at temperatures above 380 °C. A turning point in the CO$_2$ conversion and the CO/CH$_4$ selectivity at around 300 °C is observed for all three NGQD catalysts. A change in the rate-determining step (RDS) is proposed to be responsible for this turning point. As indicated by density functional theory (DFT) calculations, not shown, the RDS for the CO$_2$ hydrogenation switches from the hydrogenation of *CH$_2$OH to *CH$_2$ at 170 °C to the activation of CO$_2$ into COOH* at 300 °C. The formation of COOH* species, as predicted by the DFT calculations, is also observed experimentally via IR spectroscopy during CO$_2$
adsorption on the NGQDs (Figure 4.27c). The IR bands around 3480, 1540, and 1392 cm\(^{-1}\) are associated with the \(\nu_{\text{O-H}}, \nu_{\text{O-C-O}}, \) and \(\nu_{\text{C-OH}}\) vibrations of adsorbed \(\text{COOH}^*\) species.[231, 232] The rise of \(\text{COOH}^*\) species coincides with the decrease of \(\nu_{\text{C-H}}\) vibration at 2857 cm\(^{-1}\), which suggests that the protons from the C-H bond on the NGQDs are used to activate \(\text{CO}_2\) into \(\text{COOH}^*\) species. Other peaks observed in the IR spectra of \(\text{CO}_2\) absorbed on NGQDs can be assigned to the vibrations of various carbonate species, including lactones, bi-dentate, and uni-dentate carbonates.[233] Furthermore, the change in the RDS is consistent with the experimental observation that the \(\text{CH}_4\) selectivity increases at temperature higher than 300 °C. As the formation of \(\text{COOH}^*\) becomes the RDS at higher temperature, the formation of \(\text{CH}_4\) will be promoted as soon as \(\text{CO}_2\) is activated, because the rest of the hydrogenation elementary steps leading to \(\text{CH}_4\) occur much faster than the RDS. Therefore, the catalytic tests indicate that the catalytic selectivity and reaction kinetics of \(\text{CO}_2\) hydrogenation over NGQDs are susceptible to reaction temperature.

To understand the origin of the catalytic activity in NGQDs, a control experiment for \(\text{CO}_2\) hydrogenation was conducted on \(\text{Al}_2\text{O}_3\) supported, undoped GQDs (GQDs/\(\text{Al}_2\text{O}_3\)) under identical reaction conditions. The pristine GQDs were synthesized through the similar hydrothermal method as for NGQDs, except that the solvent was a IPA/H\(_2\)O (1:1 by volume) mixture. The pristine GQDs possess a morphology similar to NGQDs in terms of thickness, lateral size, and crystalline structure. However, the GQDs/\(\text{Al}_2\text{O}_3\) exhibit negligible activity towards the hydrogenation of \(\text{CO}_2\) at reaction temperatures of 100 – 400 °C. Only a very small amount of \(\text{CO}_2\) conversion below 2% was detected at 400 °C, and the product is exclusively CO. The sharp contrast between catalytic activity of NGQDs/\(\text{Al}_2\text{O}_3\) and GQDs/\(\text{Al}_2\text{O}_3\) strongly suggests a significant role of N doping for \(\text{CO}_2\)
hydrogenation. Based on CO$_2$-temperature programmed desorption (TPD) measurements, the NGQDs show great enhancement of CO$_2$ chemisorption over the GQDs because of the introduction of Lewis base sites via N doping. Such an increase of Lewis base sites by N-doping is consistent with literature reports that showed that doped N atoms are point defects, which can delocalize the π bonds of the graphene framework and lead to the formation of Lewis base sites.[234] The increase in the number of Lewis base sites and point defects is also consistent with our Raman spectra. The NGQDs have a much bigger ratio of D/G peak intensity compared to that of the pristine GQDs, an indicative feature of more defects in the NGQDs. The Lewis base sites can activate CO$_2$ and form the COOH*, which desorbs at around 300 °C, as seen from the TPD profile of the NGQDs sample.[235, 236] The formation of COOH* on NGQDs is consistent with the IR observations shown in Figure 2c. However, pristine GQDs lack the Lewis base sites. Therefore, they have a limited amount of COOH* groups, and the corresponding CO$_2$ desorption peak is far smaller. The desorption profile in the temperature range between 400 - 600 °C can be attributed to desorption of lactone groups.[235, 236] In addition to the decreased capability of CO$_2$ adsorption, GQDs are inert to activate the adsorbed CO$_2$ as indicated by the IR spectra where the peak intensity of the ν$_{C-H}$ vibration for GQDs remains constant compared to a sharp decrease for NGQDs after CO$_2$ adsorption. Based on the comparison between the catalytic performance of NGQDs and GQDs in the CO$_2$ hydrogenation, N-doping strongly promotes the catalytic activity through the introduction of active Lewis base sites.

To further explore the significance of N doping, a second control experiment was performed using N-doped graphene (NG) as the catalyst. The NG was synthesized by chemical vapor deposition of graphene followed by N doping using g-C$_3$N$_4$ as
precursor.[237] The NG is in the lateral size range of 10-100 µm, and therefore possesses far less density of edge C or N atoms compared with NGQDs. The NG/Al₂O₃ shows no activity towards CO₂ hydrogenation, although the NG contains a comparable amount of N.[237] These results suggest that another key aspect, the location of N at the edge, influences the catalytic activity for graphene based materials. We conclude that the N doping and enriched edge sites originating from reduced lateral size together contribute to the excellent catalytic activity of the NGQDs towards CO₂ hydrogenation, therefore the basal plane nitrogen defects are not sufficient.
Figure 4.28. Dependence of activity and selectivity on N content. (a) N 1s XPS of three NGQDs samples doped by different N precursor solvents, DMF, DMF diluted by IPA/H$_2$O, and NH$_4$OH. (b) Specific N content estimated from XPS. (c) CO$_2$ conversion of three NGQDs/Al$_2$O$_3$ samples. (d) CH$_4$ selectivity of three NGQDs/Al$_2$O$_3$ samples. The loading of NGQDs for three samples were kept the same at 1 wt.%. 

Furthermore, we synthesized NGQDs with different contents of N species by changing the N precursors or solvent (see synthesis details in supporting information). By diluting the DMF with IPA/H$_2$O (1:1), the total N content drops to 3.6 at.%, but pyridinic N is still the dominant N configuration with a content of 2.2 at.% (Figures 4.28a and b). The total N content is further reduced to 1.6 at.% and pyridinic N drops to 0.4 at.% when using ammonium hydroxide (NH$_4$OH) as the N doping solvent. The NGQDs synthesized in NH$_4$OH exhibit analogous thickness and lateral dimension to these in DMF solvent,
minimizing effects of morphological changes on catalytic performance. The activity and selectivity of NGQDs towards CO$_2$ hydrogenation strongly depends on the contents of different N configurations. The onset reaction temperature decreases while both CO$_2$ conversion and CH$_4$ selectivity at 400 °C increase with higher doping levels. Moreover, the trend of CO$_2$ conversion and CH$_4$ selectivity versus pyridinic N content clearly indicates a more linear relationship compared to the pyrrolic and graphitic N content, suggesting that pyridinic N is the most active N site, although the contribution from the other two N configurations cannot be completely ruled out.

Figure 4.29. TOF of CH$_4$ production for NGQDs samples synthesized with different N precursors. The loading is kept at 1wt% for all samples. The TOF is calculated by normalization to the number of total N sites.
We calculated the turnover frequencies (TOFs) of NGQDs/Al$_2$O$_3$ normalized to the number of total N defect sites, since the catalytic activity originates from the N-doping defects. The NGQDs with DMF as N precursor shows the highest TOF for CH$_4$ production. The TOF of CH$_4$ production for these NGQDs catalyst is calculated to be ~0.03 s$^{-1}$ at 177 °C, increases to 0.35 s$^{-1}$ at 257 °C and further to 1.50 s$^{-1}$ at 400 °C (Figure 4.29). This TOF is higher than the state-of-the-art metal-based CO$_2$ methanation catalysts, such as Co/SiO$_2$, Ru/TiO$_2$, Pd/SiO$_2$, Pd-Mg/SiO$_2$, and Ni/SiO$_2$, at the similar temperatures.[25, 238-240], TOF was calculated based on the total amount of N sites. For example, the catalysts has a 1wt.% loading of NGQDs/Al$_2$O$_3$. Each reaction used about 0.2 g NGQDs/Al$_2$O$_3$ catalyst, where the N concentration (e.g. N/(N+C)) in NGQDs is nominally 6 at.% based on XPS, where the remaining 94 at.% is assumed to be C, where we are neglecting oxygen content. Therefore, the following calculation of sites is as follows in Equation

**Total number of N sites**

\[
\text{Number of N sites} = \frac{N_{\text{concentration}}}{(N_{\text{concentration}} \times N_{\text{molecular weight}}) + (C_{\text{concentration}} \times C_{\text{molecular weight}})} \\
\times \text{catalysts loading} \times \text{catalysts amount}
\]

\[
= \frac{6\%}{(6\% \times 14 \frac{g}{mol} + 94\% \times 12 \frac{g}{mol})} \times 1\% \times 0.2g = 9.9 \times 10^{-6} mol_{N \text{sites}}
\]

This calculation of total number N sites is an under-estimate of the actual TOF of the system, since we believe the relevant active site to be primarily pyridinic N, however, we were not able to rigorously disprove the possibility of the other N sites, such as graphitic and pyrrolic, to possess catalytic activity.
4.4 Conclusions

We have demonstrated the catalytic performance of a wide range of catalytic cobalt surfaces, ranging from isolated atoms to subnanometer cluster of Co\(^0\)/(Co\(^{2+}\)+Co\(^0\)) to small nanoparticles (2-10 nm). Two distinct regimes were found with regard to the catalytic performance of the cobalt SSCs, one corresponding to the subnanometer clustered regime consisting of a distribution of Co\(^0\)/(Co\(^{2+}\)+Co\(^0\)) of 0.122 to 0.363 which yielded a local maxima in CO\(_2\) conversion under a reduction temperature of 600 °C; the other regime consisting of typical nanoparticle growth expected via Ostwald Ripening of cobalt at elevated reduction temperatures, reaching a characteristic maximum in CO\(_2\) conversion at a particle size of > 10nm. The superior activity of the cobalt surface consisting of a ratio of Co\(^0\)/(Co\(^{2+}\)+Co\(^0\)) of 0.363 is proposed to be due to the synergistic effects between the metallic cobalt and the Co\(^{2+}\), while as the surface was further reduced both the CO\(_2\) conversion and selectivity to methane decreased. Ultimately, these results can help bridge the gap between single atom catalysis and well-studied nanoparticle chemistry, offering insight into ensemble effects for transition metals in the subnanometer regime for surface sensitive reactions such as CO\(_2\) hydrogenation.

The defect-engineered pBN was used as support to synthesize atomic scale Ru catalyst to reduce the Ru loading and simultaneously maintain its high catalytic activity. The high specific surface area in pBN is beneficial to disperse Ru atoms. The B, N, atoms coordinate with the Ru precursor leading to the immobilization of Ru atoms and subsequent constraining of their size. This coordination also results in a reduced oxidation state of Ru. The vacuum filtration process mediates the permeation of the Ru precursor into mesopores/micropores and defects of pBN, which helps form uniformly dispersed Ru
moieties with sub-nanometer (slight aggregation of atomic Ru) to atomic length scales. These low valence Ru atoms on pBN exhibit enhanced activity and selectivity towards CH₄ during CO₂ hydrogenation compared to Ru nanoparticles with a high valence oxide surface. The DFT simulation supports that the low oxidation state of Ru is responsible for a significant enhancement of CH₄ selectivity. The methodology reported here is also feasible to prepare other atomically dispersed metal catalysts, which is of considerable interest for processes requiring the use noble metals.

Finally, we discovered a novel metal-free, carbon-based catalyst for CO₂ hydrogenation at moderate reaction temperatures, and we unraveled the underlying factors governing its catalytic activity. The pyridinic N doping at the edge sites of GQDs is responsible for the catalytic activity, with higher nitrogen contents leading to lower onset reaction temperature, higher CO₂ conversion, and improved selectivity toward CH₄ formation. The reaction mechanism was also found to be dependent on temperature, with impacts on the selectivity of the catalyst. A selectivity turning point was observed at ~300°C, resulting from the change of RDS at this temperature, as indicated by DFT calculations.[30] Moreover, the DFT modeling reveals the lower energy pathway to form CH₄ than CH₃OH, in agreement with the experimental results. Since the activity and selectivity are strongly dependent on the N density, the further increase of N content in NGQDs deserves more effort. The higher N density is expected to promote CO₂ conversion. In addition, the C−C coupling can be expected to yield high-order (e.g., C₂) products if there is more neighboring pyridinic N.
CHAPTER 5

MIXED METAL OXIDE CATALYSTS FOR ETHANE PARTIAL OXIDATION\textsuperscript{1,2}


Much of the literature dealing with M1/M2 catalysts is focused on addressing the effects of adding acid and redox elements in various ratios to elucidate their coupled effects on both ethane partial oxidation and their structural properties in an effort to gain insight into the origins of enhanced activity. To guide this work, a statistical Design of Experiments (DOE) was employed herein to screen a three-level four-factor ($3^4$) full factorial design space of distinct catalyst formulations based on doping a Mo$_8$V$_2$Nb$_1$ catalyst. A hydrothermal synthesis method was used to prepare the desired Mo-V-O mixed-oxide crystalline structure. The parameters explored include: transition metal redox element (Pd, Ni, and Ti) doped, acid/base element (K, Cs, and Te) doped, the ratio between the redox and acid/base element (0.005, 0.5, and 1.0), and the total dopant added relative to the niobium content of the base catalyst (0.005, 0.5, and 1.0). By systematically adjusting the acidity and reducibility of the catalyst across a range of elemental combinations, we can draw statistically significant conclusions on the coupled effects of doping Mo$_8$V$_2$Nb$_1$ mixed-oxide catalysts with elements of varied redox and acid functionality on the catalytic performance in ethane partial oxidation and the corresponding changes in crystalline structure.

This work also seeks to address the nature of the active phase on the M1/M2 catalysts using a composition of Mo$_8$V$_2$Nb$_1$R$_{0.005}$Te$_{0.995}$, where R = Ti or Pd, to probe the effect of redox dopant on catalytic performance. The structure was resolved via a comprehensive in-situ Raman spectroscopy study and supplemented with ex-situ X-Ray Diffraction (XRD) to monitor the vibrational and crystallographic structure of the catalysts under operating conditions. The results of this show that the M-O-V bond with a Raman shift located at ~944 cm$^{-1}$ was most influenced under operating conditions, suggesting this
is the active vibrational phase. Furthermore, the catalytic performance of these materials show the incorporation of Pd into the catalysts promotes the over-oxidation of ethane and Ti influences oxygen coordination, while the inclusion of Te results in phase segregation and increases selectivity to ethylene.

5.1 Statistically Guided Synthesis of MoV-Based Mixed-Oxide Catalysts for Ethane Partial Oxidation

_Synthesis of doped Mo$_8$V$_2$Nb$_1$O$_x$ catalysts_

The formation of a uniform solid solution of the Mo-V-O oxide has been widely reported lead to the preferential oxidation of alkanes to olefins and acids[59, 241, 242]. In contrast to conventional mixtures of molybdenum and vanadium based oxides, which give rise to multiple oxide phases due to phase segregation, the high dispersion of the vanadium in the Mo-V-O complex can be achieved via the formation of a solid solution[59, 62, 63, 65, 69]. Furthermore, the Mo-V-O complex allows for the incorporation of stabilization agents and promoters[73, 74, 77]. Niobium has been reported as a stabilizing agent in the Mo-V-O structure, helping keep the vanadium and molybdenum species stable throughout the reaction[53, 60-62] by facilitating their redox cycles. The solid solution is due to the formation of an Anderson-Type complex, which is formed upon mixing the molybdenum and niobium precursors to create a (NH$_4$)$_3$NbMo$_6$H$_6$O$_{24}$ complex[63, 69, 243]. The Anderson-Type complex then readily reacts with VOSO$_4$ to form the Mo-V-M-O structure, where M here is niobium, and forming a solid solution with no observable phase segregation of the individual oxide phases.
A composition of $\text{Mo}_8\text{V}_2\text{Nb}_1$ was chosen as the base catalyst due its high selectivity towards acetic acid and ethylene during EPO[56, 60]. Additionally, the excess molybdenum in the synthesis gel, where the Anderson-Type complex requires a stoichiometry of six to one $\text{Mo}:\text{Nb}$, serves to accommodate the addition of dopants into the base $\text{Mo}_8\text{V}_2\text{Nb}_1$ structure. The dopants for this work were chosen to probe the relationship between surface acidity and reducibility and EPO product distribution[2, 66, 244]. In this study, the reducible metals chosen included palladium, nickel, and titanium. Each of these dopants varies in terms of their reducibility with palladium being the most reducible and titanium being the least. Additionally, these metals have been shown to promote EPO to favor the production of ethylene or acetic acid, both being target products for this system.

Palladium is one of the most studied promoters for this system due to its ability to preferentially form acetic acid via an acetaldehyde intermediate[56, 61, 66, 245, 246]. Titanium has been chosen as a redox element due to its support interaction effects for EPO[62, 245], while nickel has been shown to preferentially form ethylene[75, 247-249] for various distinct catalytic systems. In a similar manner, the surface acidity was adjusted by introducing potassium, cesium, or tellurium to the catalyst precursor. These elements were chosen to cover a range of acidities, where potassium represents a typical alkali group metal of nominal acidity and cesium represents a much stronger acid. Tellurium was chosen due as the third acid/base component due to its overwhelming precedence in catalyzing EPO to promote greater catalytic activity and the more selective formation of acetic acid[58, 67, 70, 243, 250]. It is important to note that while tellurium can contribute catalytic activity via it’s redox cycling between the +4 and +6 state, its contribution to the overall reducibility of the catalyst is significantly lower than the chosen redox elements for
this study; warranting categorization as an acid/base element in this study and not a redox element.

To address mixed findings in the literature over the effect of the surface acidity and reducibility balance, we systematically varied the redox/acid element ratio between the acid elements and the redox elements to various degrees. Since the redox elements tend to affect catalytic activity largely by electronic effects caused by the electron orbital overlap from the $d$-shells of the transition metals, typically only small amounts of these elements are required to significantly change the catalytic activity. Conversely, acids affect catalytic activity by changing the surface acidity, where an effect on catalytic activity is generally only observed at higher doping levels.

*Design of Experiments Parameter Space*

To explore all possible combinations between redox elements and acid elements we created 81 distinct catalyst formulations by adding nine unique dopant pairs to the base Mo$_8$V$_2$Nb$_1$ catalyst and synthesizing catalysts including each dopant pair at nine distinct loadings. Dopant pairs included the following: PdK, PdCs, PdTe, NiK, NiCs, NiTe, TiK, TiCs, and TiTe. The balance between redox and acid functionality is tailored by varying the redox to acid (R/A) ratio and the total amount of dopant added is varied with the dopant to host (D/H) ratio, where each were treated as numerical variables ranging from 0.005, 0.5, and 1.0, as summarized in Table 5.1. The addition of dopants at different levels can yield varied effects, ranging from predominantly electronic interactions at low D/H ratios to phase segregation of the dopant species and possible formation of new active sites at high D/H ratios. The wide range of dopant/host ratios screened was intended to cover the range of these possible effects. Elemental ratios were relative to the niobium loading of the
base catalyst (Nb=1), where the sum of the both redox and acid species totals to either a dopant to host ratio (D/H ratio) of 0.005, 0.5, and 1.0. For illustration, a D/H and R/A ratio of 1.0 corresponds to a composition of Mo$_8$V$_2$Nb$_1$Ni$_{0.5}$Te$_{0.5}$.

Table 5.1. Parameter space for 3 level-4 factor full factorial design ($3^4$)

<table>
<thead>
<tr>
<th>Factor</th>
<th>Variable Type</th>
<th>Low</th>
<th>Center Point</th>
<th>High</th>
</tr>
</thead>
<tbody>
<tr>
<td>A: Redox element (R)</td>
<td>Categorical</td>
<td>Pd</td>
<td>Ni</td>
<td>Ti</td>
</tr>
<tr>
<td>B: Acid/base element (A)</td>
<td>Categorical</td>
<td>K</td>
<td>Cs</td>
<td>Te</td>
</tr>
<tr>
<td>C: Dopant to Host ratio (D/H)</td>
<td>Numerical</td>
<td>0.005</td>
<td>0.5</td>
<td>1.0</td>
</tr>
<tr>
<td>D: Redox to acid ratio (R/A)</td>
<td>Numerical</td>
<td>0.005</td>
<td>0.5</td>
<td>1.0</td>
</tr>
</tbody>
</table>

Catalyst Composition: Mo$_8$V$_2$Nb$_{(1-H)}$[R$_R$A$_A$]$_D$

**EDS Elemental Uptake Analysis**

The hydrothermal synthesis method employed here proceeds through the formation of an Anderson-Type heteromolybdate intermediate for which the possibility of incomplete element uptake exists [70, 71, 251]. Variation in elemental composition over the design space was accomplished by varying the R/A and the D/H ratio. EDS was used to both probe both intended and unintended variation in the loadings of catalyst components. Analysis of the EDS data was focused on perturbations to the base structure as evidenced by the measured vanadium and niobium contents. It should be noted that nominal loadings for the 81 catalysts were expected to fall in the following compositional range: Mo$_8$V$_2$Nb$_1$R$_{0.000025-0.5}$A$_{0.0025-1}$. Over the 81 samples studied, atomic loadings for the Mo$_8$V$_2$Nb$_1$ base composition were found to range from 1.28±0.1 to 3.33±0.84 for vanadium and 0.69±0.12 to 1.17±0.05 for niobium. While some of this variance can be ascribed to EDS
measurement error, certain relationships between the base catalyst uptake and the catalyst design variables were found to be statistically significant. For instance, uptake of both vanadium and niobium into the structure were negatively correlated with increased D/H ratio, meaning that, to some extent, the dopants displaced the V and Nb from the material. It should be noted that this effect was more pronounced in the case of Nb, with Nb uptake being almost 10% less when D/H was increased from 0.005 to 1. This effect was also much more significant when the elements being doped were primarily redox elements (i.e., high R/A ratio), as shown in Figure 5.1. This suggests that the redox elements were able to displace the niobium in part from the channels of the base structure.

Figure 5.1. Effect of dopant levels on Nb uptake in MoVNb based catalysts
Additionally, some sensitivity was found in terms of Nb and V uptake with respect to the specific redox and acid elements doped. The V uptake was found to be particularly sensitive to the doping of redox elements, being the lowest when Pd was doped, while the Nb uptake was sensitive to both redox and acid doping, with the lowest uptakes corresponding to Ti and Te doping. In general, the least amount of disturbance to the base structure was achieved when balanced levels of redox and acid elements were doped (R/A=1) and the greatest amount of disturbance was found at the highest doping levels (D/H=1). Additionally, an interaction between R/A ratio and D/H ratio was observed where increasing D/H ratio only caused significant changes to the base structure for high levels of redox element loading (R/A=1). This indicates that acid/base elements were more easily incorporated into the base structure than redox elements. Overall, it was found that increasing or decreasing D/H and R/A ratios yielded the intended variations in dopant loadings.

*Crystalline Structure of Doped Mo$_8$V$_2$Nb$_1$O$_x$ Catalysts*

The crystalline structure of the redox and acid/base element doped MoVNb catalysts were studied for all samples using powder X-ray Diffraction (XRD). The hydrothermally synthesized base MoVNb catalyst, shown in Figure 5.2, showed the Mo-V-O mixed-oxide phase hallmarked by sharp 22° and 45° (0 0 l) reflections and a broad 27° reflection. Based on literature[63-65, 71], this Mo-V-O structure is ascribed to a slab-like structure comprised of both ordered and disordered crystallographic directions. Additional peaks could be ascribed to MoO$_3$, Mo$_6$V$_9$O$_{40}$ and/or Mo$_3$Nb$_2$O$_{11}$[60, 72, 76, 252]. To understand the influence of the redox and acid/base dopants as well as their
relative and overall doping levels, differences between the hydrothermally prepared base MoVNb and doped MoVNb catalysts were studied.

![XRD pattern of hydrothermally prepared base MoVNbO_x catalyst](image)

Figure 5.2. XRD pattern of hydrothermally prepared base MoVNbO_x catalyst

The analysis of the XRD data focused on both the position and the Full Width Half-Max (FWHM) of the main 22° peak attributed to the M1 phase to calculate the d-spacing and grain size of the Mo-V oxide[64, 72, 252]. Additionally, crystal faceting of the primary slab-like Mo-V-O phase was analyzed by measuring the intensity ratio between the sharp 22° peak, showing the ordered crystallographic growth direction, and the disordered, amorphous peak at 27°. Previous work showed a correlation between the intensity of the 22° reflection and the specific activity for ethane ODH[64]. Additionally, it was found that
secondary phases were formed on top of the base Mo-V-O structure when doped with certain redox and acid/base elements at varying levels. The identity of these secondary phases are assorted Mo and V based oxides of different stoichiometry as well as, in a few cases, reflections from small particles of segregated oxides of redox/acid/base dopants. While exhaustive structural resolution of each design point was out of the scope of this study, the conditions under which secondary phase formation occurred were noted and relative intensities between the main reflection and the most intense peak arising from secondary phases were calculated to indicate the relative volume of the catalyst involved in secondary phase formation.

First, the d-spacing of the mixed oxide indicated by the peak location of the 22° reflection (d=4.01Å) was tracked for each sample as a possible gauge for dopant incorporation directly into the mixed oxide lattice[252, 253]. In such a situation an increase in d-spacing (evidenced by a peak shift to lower 2θ) would be expected, since most dopant elements have large radius compared with Mo, V and Nb. It was found, however, that the d-spacings of the 22° reflection for the doped samples only ranged from 3.98 to 4.02. This small range of d-spacings supports the conclusion that the various redox and acid/base dopants investigated were not actually incorporated directly into the mixed oxide lattice and most likely reside in the six and seven membered rings formed by the Mo-V-O structure, where these vacancies allow for the insertion of atoms [76].

The grain sizes calculated via Scherrer’s equation from the FWHM of 22° peak of the doped MoVNb samples were found to be sensitive to both the type of dopants and the levels studied. These parameters were investigated to understand how different doping levels could change the active surface area and/or redox properties of the catalysts; effects
which may be expected to accompany a change in Mo-V-O grain size. The grain size of the base MoVNb material, calculated using the broadening of the 22° peak according to Scherrer’s equation[254, 255], was 22 nm. Identical analysis of the doped MoVNb catalysts showed that grain sizes ranged from 12.4-35.0 nm, depending on the design levels employed. Statistical analysis of the relationship between doping elements and levels with grain size revealed that the most important factors for controlling grain size were the type of redox element and the D/H ratio, as well as the interaction between the two. It was found that doping with Ni increased grain size most significantly, while Ti yielded grain sizes which were smaller, and on average, identical to that of the base MoVNb oxide. In general, increasing dopant levels had the effect of decreasing grain sizes, but at the lowest level of D/H=0.005, no notable difference could be seen between the grain sizes when Pd, Ni, or Ti was doped. In an analogous manner, differences between grain sizes of Pd, Ni, and Ti doped materials were only apparent at R/A ratios of 0.5 or greater. These interactions simply indicate that the different behavior of redox elements with respect to grain size were not apparent under the conditions where the redox elements were doped in the smallest amounts (i.e., small D/H and R/A ratios). The observation of decreased grain sizes at higher dopant levels, as can be seen for the MoVNbNiCs family of catalysts at the R/A=0.5 level in Figure 5.3, leads to the question of whether one of the effects of the redox dopant is to impede the crystal growth of the primary mixed oxide phase.
The relative intensity of the ordered $22^\circ$ reflection scaled to the intensity of the disordered $27^\circ$ reflection was investigated as an indication of ordered preferential growth. For convenience, this will be referred to as the primary phase intensity ratio (PPIR). The base formulation of MoVNb was found to have a PPIR of 3.41. R/A and D/H ratios were found to affect the PPIR significantly, with increasing each having the effect of decreasing the PPIR. It was also found that the significance of the effect of changing the D/H ratio was most apparent at the low R/A level of 0.005. In practice, this means that the highest PPIR values, and the only values which were greater than the base catalyst PPIR, occurred for catalysts with both low overall dopant levels and high relative levels of acid/base dopant (D/H=R/A=0.005), as shown in Figure 5.4. Interestingly, the redox and acid/base elements
doped were found to have virtually no effect on this measurement, meaning that nearly identical trends held for all redox-acid/base pairs studied.

Figure 5.4. XRD primary phase intensity ratio variations with dopant level

The final structural descriptor studied via XRD analysis was the formation and relative volume of secondary phases. This variable is important in understanding trends in activity due to its direct relation to the abundance of the active Mo-V-O phase. This will be defined as the secondary phase intensity ratio (SPIR) as the XRD intensity ratio between the largest secondary phase peak and the largest Mo-V-O primary phase peak at 22°2θ. While the redox element doped, particularly when the element was Pd, affected the occurrence of secondary phases, it had no significant effect on the SPIR. The SPIR was
found to be mostly sensitive to the type of acid/base element doped as well as the R/A and D/H ratios. Specifically, it was found that doping with Cs at a R/A level of 0.005 yielded the highest SPIRs and this effect was increasingly apparent at higher D/H ratios. The effect of increased SPIR with decreased R/A ratio and increased D/H ratio held for other redox-acid/base pairings as well, but at a much smaller magnitude. The effect of secondary phase formation when Cs was doped is illustrated in Figure 5.6.

Figure 5.6. XRD secondary phase formation in selected samples (R/A=0.005 and D/H=0.5)
The catalytic evaluation of the catalyst compositions guided by the statistical design were carried in a temperature range of 120°C-460°C with a fixed ethane to oxygen ratio of 4:5. As the product distribution of the EPO reaction has been shown to be highly sensitive to residence time and temperature, a space velocity and temperature optimization was carried out for the base catalyst composition to maximize the production of acetic acid, shown in Figure 5.7. The base catalyst with a composition of Mo₈V₂Nb₁ has been previously reported to produce optimal acetic acid yield[2, 54, 61], which is consistent with our experimental findings. The optimal temperature and space velocity for acetic acid selectivity were found to be 450°C±10°C and 1200 hr⁻¹, respectively. These conditions were used in the analysis of the DOE, which is summarized in Figure 5.8, showing the selectivity towards each product. Due to the fact the product distribution is highly dependent on residence time, where a slight change in residence time shifts the product distribution to favor ethylene, the catalysts were compared at different conversions with all other relevant variables held constant.
Figure 5.7. Ethane partial oxidation over base Mo$_8$V$_2$Nb$_1$ catalyst. Reaction conditions: 1200 hr$^{-1}$, atmospheric pressure, 4:5:1 ratio of ethane : oxygen : helium

Figure 5.8. Ethane Partial Oxidation product distribution at 450°C, 1atm, and 1200 hr$^{-1}$
The product distribution at 450°C for all 81 doped Mo$_8$V$_2$Nb$_1$O$_x$ catalysts is shown in Figure 5.8. Design of experiments was used to elucidate statistically significant relationships between design levels and product distribution. The analysis of effects relevant to the catalytic activity is highlighted in Table 5.2, which shows the trends across the different redox and acid/base elements, the D/H ratio, and the R/A ratio. A main conclusion from this analysis is that each variable investigated; redox element, acid/base element, redox/acid ratio, and dopant/host ratio had significant effects on the ethane conversion and product distribution. Furthermore, the effects of external mass transfer limitations were explored by reproducing catalytic activity with varying catalyst mesh sizes, where the same catalyst composition with a mesh size <125 μm performed identical to the same composition with a mesh size of 500-400 μm in both the differential conversion regime and the high conversion regime.

Table 5.2. Summary of DOE Main Effects for Doped Mo$_8$V$_2$Nb$_1$ Catalysts

<table>
<thead>
<tr>
<th>Factor</th>
<th>Ethane Conversion</th>
<th>Ethene Selectivity</th>
<th>AA Selectivity</th>
<th>Secondary Phase</th>
<th>Grain Size</th>
</tr>
</thead>
<tbody>
<tr>
<td>Redox element</td>
<td>Ti &gt; Ni &gt;&gt; Pd</td>
<td>Ni &gt; Ti &gt;&gt; Pd</td>
<td>Ti &gt; Pd &gt; Ni</td>
<td>No effect</td>
<td>Ni &gt; Pd &gt; Ti</td>
</tr>
<tr>
<td>Acid/base element</td>
<td>Te &gt; K &gt; Cs</td>
<td>Te &gt; K &gt; Cs</td>
<td>K = Te &gt; Cs</td>
<td>Cs &gt; Te &gt; K</td>
<td>No effect</td>
</tr>
<tr>
<td>R/A ratio</td>
<td>No effect</td>
<td>0.005 optimal</td>
<td>0.005 optimal</td>
<td>Decreases</td>
<td>No effect</td>
</tr>
<tr>
<td>D/H ratio</td>
<td>1 optimal</td>
<td>0.5 optimal (0.005 for Pd)</td>
<td>0.005 optimal</td>
<td>Increases</td>
<td>Decreases</td>
</tr>
</tbody>
</table>
Effect of Doping Mo$_8$V$_2$Nb$_1$O$_x$ on EPO Product Distribution

The single most important variable investigated for optimizing ethylene selectivity was the redox element used, with a significant sensitivity to the acid element co-employed. Ethylene selectivity, on the one hand, can be increased considerably by doping with PdTe rather than PdCs, which was detrimental to ethylene formation. Conversely, product distribution was largely insensitive to the acid dopant when the redox element being doped was Ti. Overall, ethylene selectivity was maximized by doping with NiTe at a D/H level of 0.5 and a R/A level of 0.005. Acetic acid selectivity, on the other hand, was optimized by doping MoVNb with TiK or TiTe at low R/A and D/H levels (D/H=R/A=0.005) but showed a high level of sensitivity to interactions between the parameters investigated. The most important relationship found was between the redox element, the acid/base element, and the D/H ratio, as illustrated in Figure 5.9. AA selectivity was optimized at very low dopant levels (D/H=0.005) for PdK and NiTe dopant pairs, whereas a large dopant level (D/H=1) optimized AA selectivity for the TiTe dopant pair, with these compositions performing remarkably better than other redox-acid dopant pairs at equivalent D/H levels. It also should be noted that the optimum acid dopant pair for Ti was different at each D/H level studied.

Figure 5.9. Interaction between redox element, acid element, and D/H level for AA selectivity
A low R/A ratio of 0.005 was found to be favorable for both ethylene and acetic acid selectivity, indicating that in both cases an excess of acid/base dopant is needed relative to the redox dopant. This is consistent with literature, where the incorporation of acid/base elements at an atomic ratio of ~2:1 between V and the acid/base element has been shown to result in the increased formation of value added products in partial oxidation reactions[57, 59, 244]. Surface acidity is thought to play a large role in the product selectivity, where acid sites promote the formation and subsequent desorption of acetic acid while ethylene preferentially forms and desorbs on reducible sites[2, 256], such as those found on the redox elements. However, in this case, it was found that acid sites were also necessary for the formation of ethylene. The role of surface acidity also extends to other catalytic systems for the conversion of ethane into value added products, where in the oxidative dehydrogenation of ethane the inclusion of highly basic metals such as platinum lead to increased selectivity towards ethylene[49, 51]. It is well known that dopant effects can considerably affect catalytic activity when doping with transition metals due to the electronic interactions between the metals and the host oxide structure[51, 53, 56, 61, 66, 75].

Two distinct mechanisms are possible in the partial oxidation of ethane into ethylene and AA. The first possibility is the direct oxidation of ethane via a CH$_3$CH$_2$O* intermediate species followed by the subsequent oxidation to acetic acid[46, 55, 60, 257]; the second is the oxidation of an adsorbed ethylene species through a Wacker mechanism involving a surface X-O site which reacts with water to form a X-OHOH site capable of converting ethylene to AA[2, 66]. In our findings, an increase in AA formation was generally coupled with an immediate decrease in ethylene, suggesting that AA was forming
mainly through the oxidation of re-adsorbed ethylene via the Wacker mechanism. However, the possibility of parallel pathways cannot be ruled out entirely as the products were often co-produced. The competing mechanism for ethylene formation versus AA formation is shown in Figure 5.10, which shows that as the ethylene selectivity reaches a maxima as a function of D/H and R/A the AA selectivity reaches a minima for NiTe and TiTe based catalysts.

Figure 5.10. Ethane Partial Oxidation over (top) MoVbTiTE and (bottom) MoVbNiTe based catalysts. Reaction conditions: 450°C±10°C, 1200 hr⁻¹ space velocity, 1 atm pressure, 4:5:1 ratio of ethane : oxygen : helium

**Effect of Doped Mo₈V₂Nb₁ Structure on Catalytic Activity**

While a small R/A ratio being favorable for both acetic acid and ethylene formation can be attributed in part to an excess of surface acidity necessary relative to redox properties, it should be noted that small R/A levels were highly correlated with high primary phase intensity ratios (PPIR) introduced previously. In fact, at the low D/H and low R/A pairing, the PPIR was as much as four times greater than its value at other D/H and R/A combinations. This is consistent with observations of increased ethane oxidation
activity at higher intensity ratios reported previously[64]. It follows that in addition to creating favorable surface acid properties for reactivity, an excess of acid dopant could play a role in extending the aspect ratio of the slab-like structure of the primary active Mo-V-O phase indicated by the PPIR.

On the other hand, smaller D/H levels (D/H=0.005) were preferable for acetic acid formation while intermediate levels were optimum for ethylene formation (D/H=0.5). It should be noted that high D/H levels were associated with smaller Mo-V-O grain sizes measured with XRD and lower V and Nb uptake into the base catalysts evidenced by EDS. These results suggest that control over product distribution may be afforded through a combination of appropriate catalyst stoichiometry and tuning of grain size. It is clear, however, that a large displacement of V from the Mo-V-O structure is unfavorable for all value product yields, as this was observed to the greatest extent for high doping levels of Pd and Cs, which on average yielded the lowest selectivity towards both acetic acid and ethylene. This is consistent with the role of vanadia as a catalytically active center for alkane activation and olefin production [2, 258, 259].

In fact, the presence of Cs was detrimental to both ethylene and AA formation for all redox elements at all D/H and R/A levels, leading to the formation of almost exclusively total oxidation products. This is likely because Cs disrupts the structural integrity of the host, as evidenced by the formation of secondary phases visible in XRD. As the primary Mo-V-O phase, hallmarked by the characteristic 22° XRD peak, has been attributed to the preferential oxidation towards olefins and acids[64, 260], it is reasonable to assume that the destabilization of this phase and secondary phase formation induced by Cs would negatively affect activity through the loss of AA and ethylene selective sites or formation
of combustion sites. This type of structural disturbance induced by dopant addition to the base Mo-V-O structure is markedly different from that observed by others, where activity has been found to increase with increased dopant concentrations accompanied by higher defect densities and more polydisperse crystallites.[68]. Additionally, decreased activity can also be attributed to a disruption of the crystalline M1/M2 structure, which can hinder lattice oxygen mobility that results in a loss in selectivity towards acids and olefins from alkane oxidation [66, 242, 261]. The difference in observed structural effect is possibly due to the very large atomic radius of Cs in comparison to other dopants studied.

To address the finding that the doped MoVNb reached different levels of conversion at 450°C, the catalysts were compared according to their ethylene and acetic acid selectivity as a function of conversion, as shown in Figure 9. Catalysts are labeled by their standard orders according to the 3^4 full factorial design. The corresponding factorial design levels (dopants and loadings) for each design point are shown in Table 1 of the supporting info. To understand how changing the conversion level changed the selectivity of the most promising materials, the optimum catalysts were compared at different conversions achieved by ramping the catalyst bed temperature between 250-550°C. Optimum catalysts were defined as those samples which reached the highest AA or ethylene selectivity at the highest possible ethane conversions at 450°C. The ethylene and acetic acid selectivity of the selected catalysts at varied conversions are shown in Figure 5.11. In general, ethylene selectivity decreased with increased conversion, corresponding to higher bed temperatures, while acetic acid selectivity increased. For most catalysts, acetic acid selectivity was maximized at conversions > 80% while ethylene selectivity was maximized at conversions < 20%. While kinetic understanding of the system is convoluted
at high conversion, we chose to maximize the total yield of acetic acid by optimizing the system for high conversion and high acetic selectivity, shown in Figure 5.12.

Figure 5.11. Ethylene and acetic acid selectivity vs. conversion for all samples at 450°C

Figure 5.12. Ethylene and acetic acid selectivity vs. ethane conversion for optimum catalysts
5.2 Influence of dopant addition on catalytic performance and vibrational structure on mixed metal oxides for ethane oxidative dehydrogenation

Ethane Oxidative Dehydrogenation on doped Mo$_8$V$_2$Nb$_1$

The use of differential conversion allows for the elimination of mass transfer limitations and allows examination of the primary active site of the catalyst by minimizing the activity of less selective/active sites that function primarily at high temperatures. Therefore, utilizing differential catalytic testing allows for a one to one comparison of the primary active site and the effect of dopants on that site, shown in Figure 5.13. Additionally, the Weisz-Prater criterion was satisfied for the catalysts under differential conversion, where the criterion is as follows in equation 5.1:

$$\frac{r'_A \rho_c R_p^2}{D_e C_{AS}} \ll 1$$  \hspace{1cm} (5.1)

Where $r'_A$ is the measured reaction rate, $\rho_c$ is the pellet density, $R_p$ is the pellet radius, $D_e$ is the effective diffusivity, and $C_{AS}$ is the surface concentration. $D_e$ is given by equation 5.2

$$D_e = \frac{D_{C_2H_6-N_2} \phi_p \sigma}{\tau}$$  \hspace{1cm} (5.2)

Where $\phi_p$ is the pellet porosity, $\sigma$ is the constriction factor, and $\tau$ is the tortuosity and $D_{C_2H_6-N_2}$ is the diffusion coefficient. A close approximation of $\phi_p=0.4$, $\sigma=0.8$, and $\tau=3$ was used for the catalyst system[262]. The diffusion coefficient was taken to be $1.46 \times 10^{-6}$ m$^2$/s [263]. Under differential conditions the observed rate varied from $2.3 \times 10^{-3}$ mol/kg/s to $4.7 \times 10^{-3}$ mol/kg/s, $\rho_c$ was taken to be $4.69 \times 10^3$ kg/m$^3$, $R_p$ was $2.25 \times 10^{-4}$ m and $C_{AS}$ was taken to be equivalent to the bulk gas phase concentration of $14.86$ mol/C$_2$H$_6$/m$^3$. This resulted in a range of values for the LHS of the Weisz Prater criterion that varied between
0.026 to 0.0521, which is much less than 1; therefore, the criterion is satisfied and there is no mass transfer limitation.

Figure 5.13. Ethane ODH product distribution at differential conversion. Reaction Conditions: Ethane: O₂: He ratio of 2:1:3, 12000 hr⁻¹, 325 °C, 1 atm

While nearly all catalysts display a similar product distribution, the catalysts only doped with low amounts of Pd displays a much high propensity to form unselective combustion products. Interestingly, the addition of Te tempers this overoxidation, indicating an interaction between these species. This interaction can be explained by considering that perhaps Pd and Te selectively reside in the same site but doping of Te displaces Pd from these sites, influencing their chemistry and catalytic activity. This claim is further supported by examining the literature for ethane oxidation over supported Pd
catalysts. Even with substantially higher weight loadings of Pd than those used in this study, the rate of ethane oxidation over Pd is low at approximately 325°C [264]. However, if Pd was located at the same site in the six-membered ring that Te normally occupies, it may contribute to over-oxidation of activated ethane. Literature suggests that the V=O bond, in particular the V$^{5+}$=O bond [73], or M-O-V bond [73, 265, 266], located in the six-member ring may be responsible for the activation of ethane and additional active oxidation centers near this site contribute to over-oxidation of activated ethane [267]. Palladium adjacent to this active site is likely to react with the activated ethane intermediate more easily than an isolated Pd site reacting with un-activated ethane. Further, based on bond valence theory, Pd$^{2+}$ is able to fit within the five or six-membered rings of these catalysts [268]. However, as Te is present in such excess, it may be more likely to add to its preferential site when compared to Pd, potentially explaining differences seen with Pd and PdTe catalysts. When considering the other dopants, their activity and product distributions remain nearly identical and higher conversion conditions must be employed to discern how these dopants influence catalytic activity.

The performance of the doped MoVNb catalysts were probed under higher conversion than the previous differential test to probe the influence of dopant addition on selectivity towards ethylene, shown in Figure 5.14. Similar to the differential conversion regime, the addition of small amounts of Pd contribute to overoxidation of ethylene to CO and CO$_2$ as shown in the reduced ethylene selectivity. As conversion increases with temperature, the selectivity to ethylene increases likely due to increasing rate of ethylene activation and desorption from the surface of the catalyst reducing the relative effect channel Pd could have on activity. As previously documented in existing literature [267,
269], the addition of Te improves catalyst activity by increasing conversion and selectivity to ethylene. This effect is also seen with the PdTe catalyst as low ethylene selectivity is not observed regardless of conversion. The remaining catalysts show a similar trend with regards to ethylene selectivity. Notably, the most active catalysts for ethylene formation are the Te, PdTe, and TiTe, which all show comparable ethylene yield of approximately 35%. The ethylene yield for the base, Ti, and Pd doped catalyst are 23%, 26% and 19%; respectively. However, when examining the product selectivity to oxygenated non-combustion products, namely acetic acid, differences can be noted with both Pd and Ti redox dopants.
Figure 5.14. Ethylene selectivity as a function of ethane conversion

Figure 5.15. Acetic acid selectivity as a function of reaction temperature

The addition of Pd and Ti increase selectivity to acetic acid when compared to the base catalyst, shown in Figure 5.15, which shows no acetic acid production at low temperatures outside of differential conversion conditions shown previously. As palladium
is capable of dissociating oxygen readily [270], the presence of these species on the surface or near the primary active site of the catalyst could potentially be responsible for the formation of high levels of acetic acid. Interestingly, the addition of Ti, even with the presence of Te shows high acetic acid selectivity as well. In fact, in a previous study conducted by this laboratory at a different space velocity and gas composition, the catalyst with this level of Ti and Te doping had the highest overall yield for acetic acid out of all of the catalysts [271]. This effect is not yet well understood but may relate to either more rapid oxygen diffusion throughout the catalyst, resulting in a more facile regeneration of active species for oxygen insertion on the surface or through incorporation of extra oxygen throughout the catalyst after exposure to heightened temperatures.

*Reducibility of Mo$_8$V$_2$Nb$_1$ doped catalysts*

![Figure 5.16. Hydrogen Temperature Programmed Reduction for a) catalysts with one dopant and b) catalysts with two dopants](image)

Based on the reduction profiles depicted in Figure 5.16, the base catalyst had the highest onset reduction temperature of the main reduction event, similar to that seen
elsewhere in literature [272], while all the dopants lowered the temperature of the main reduction event. Furthermore, there is also a drastic lowering of the reduction temperature due to the addition of Pd. Interestingly, with the addition of Te to Pd containing samples, the bulk of the reduction occurs near the main reduction event for the rest of the catalysts. This can once again be potentially attributed to Pd and Te residing in the same site in the catalysts. The six-membered channels of this catalyst have previously been shown to be an oxygen reservoir and facilitating transfer of oxygen throughout the catalyst[273, 274]. If palladium resided in the top of these rings, hydrogen dissociated by palladium [275, 276] could find a labile supply of oxygen that would result in a significantly lowered reduction temperature as shown with the above TPR experiments. In the PdTe samples, a peak near 150°C is present, indicative of the reduction of PdO [277] in addition to a shift of the bulk reduction event to a lower temperature potentially due to hydrogen spillover from isolated Pd sites on the surface of the catalyst or in other rings providing hydrogen to labile oxygen in the six-membered ring channels. This is further supported by quantifying hydrogen uptake of the Pd and PdTe samples, hydrogen uptake for both catalysts is approximately 7.3 mmol H₂/g cat. If the addition of only Pd were contributing to excess reducibility of the catalyst, this number would be expected to deviate with the addition of Te. However, the similar uptakes indicate that the addition of Pd is only altering the temperature at which reduction occurs. The addition of Ti to the catalyst causes the formation of a spike at the high temperature end of the main reduction event for the catalyst. The additional peak in this region is at a similar reduction temperature to TiO₂ seen previously in literature [278, 279] and suggests that Ti is present in an oxidized state within the catalyst. This oxidized state could be due to Ti bonding with oxygen within the rings of the catalyst as anatase or
rutile TiO$_2$ is not observed via XRD or Raman spectroscopy even at high Ti dopings corresponding to Mo$_8$V$_2$Nb$_1$Ti$_0.5$. The addition of Te, with or without additional dopants, has the general effect of shifting the reduction event to lower temperature conclusive with its oxygen mobility effect noted previously in literature [280]. The formation of facile transport of oxygen from the bulk of the catalyst to the surface via infinite or semi-infinite Te chains would facilitate lower temperature reduction by providing oxidizing species at the surface of the catalysts.

*Crystallinity of Mo$_8$V$_2$Nb$_1$ doped catalysts*

Introduction of dopants into this catalyst system can cause the formation of various different species in addition to the base M1/M2 structure at high dopant concentrations; predominantly MoO$_x$ [271] as shown in Figure 5.17. Due to the low dopant concentration of the Ti and Pd addition, the production of secondary phases of the dopant oxides were not detected via XRD. However, the addition of high concentrations of Te does cause the formation of secondary phases, namely MoO$_x$, potentially due to distortion of the crystal structure of the M1/M2 catalyst or by causing crystallization of amorphous portions of the catalyst.
Figure 5.17. XRD of doped catalysts for (left) catalysts containing Te and for (right) catalysts without Te.

Sharp peaks at 22° and 45° as well as a broad amorphous peak at 27° are present in all spectra and correspond to the M1 phase of the catalyst [14]. Additional secondary phases present in catalysts containing Te correspond to MoO$_3$, indicating that high doping of this element contribute to substantial secondary phase formation as shown previously in literature [271, 281]. However, this phase is generally regarded as unselective and inactive for ethane partial oxidation and should not greatly influence the activity or performance of the catalyst [5]. For both Ti and Pd containing catalysts, there is no observed formation of independent dopant oxides, i.e. TiO$_2$ or PdO, which would signal the onset of phase segregation; however, for such low loading of dopant secondary phase formation is not expected. As the dopants are highly dispersed and in small quantities changes to the crystalline structure via XRD are expected to mainly influence the principle phases of the M1 catalyst. Specifically, the peaks at 22° and 27°, where the ratio of these two can be used as an indicator of structure, which will be referred to as the Primary-Phase Intensity Ratio.
The slablike (100) diffraction of the M1 phase at 22° is often an indicator of catalytic performance for M1/M2 catalysts since it indicates the preferential growth of the M1 phase, while the crystallinity referenced relative to the amorphous growth of the 27° peak is indicative of the degree of ordered crystallographic growth. The PPIR for the base Mo₈V₂Nb₁ formulation was found to be 3.44, consistent with our earlier work [271]. A decrease in the PPIR would suggest that the preferential crystallographic phase was suppressed while an increase suggest the promotion of crystalline growth. The PPIR for the catalysts are as follows for Te, Pd, Ti, PdTe, and TiTe: 2.7, 3.2, 4.2, 3.5, and 3.5; respectively. Upon addition of the Te, not only does the PPIR decrease but also a noticeably higher formation of secondary oxides occurs, where the formation of secondary MoO₃ phases may suppress the preferential growth of the (100) M1 structure. However, upon addition of PdTe and TiTe, the PPIR is brought back in line with the original base catalysts formulation, despite the occurrence of secondary oxide formation evidenced by the peaks at 28°, 34° and 39°. This suggest the addition of the redox elements is facilitating the ordered growth of the (100) M1 phase, even in the presence of Te; which by itself increases the amorphous properties of the mixed metal oxide. Tellurium also has an affinity to promote secondary MoO₃ phase formation, which may contribute to the amorphous character of the 27° peak. Interestingly, the inclusion of only Ti seems to increase the PPIR of the base catalyst considerably, from 3.4 to 4.2; which suggest that Ti is facilitating the growth of the ordered phase, even at low metal loadings.

_Vibrational Structure of Mo₈V₂Nb₁ doped catalysts_

To determine the influence of dopant addition on the crystal structure of the catalysts, Raman spectra were obtained for each catalyst under ambient conditions, shown
in Figure 5.18. Raman spectra were consistent with other literature for bulk synthesized MoVNb catalysts [258] with M-O-V peaks, where M is a metal atom (V or Mo), located at approximately 873 cm\(^{-1}\) and 932 cm\(^{-1}\), peaks corresponding to terminal V=O, Mo=O, and Te=O are generally not observed due to the lack of surface sensitivity of Raman spectroscopy, however they are prominent in the case of supported versions of these catalysts [282].

![Raman spectra of doped catalysts under ambient conditions for a) catalysts containing Te and for b) catalysts without Te](image)

Figure 5.18. Raman spectra of doped catalysts under ambient conditions for a) catalysts containing Te and for b) catalysts without Te

In reference to the base, undoped catalyst formulation the addition of dopants causes subtle changes in the structure of the catalysts as evidenced by changes in the Raman spectra. As shown in Figure 5.18, the addition of Te causes a blue-shift of the main band at \(-873\text{ cm}\(^{-1}\)\) as previously noted by Wachs [258] in this catalyst system due to Te addition and blue shifting has been noted in other catalysts systems due to induced lattice strain [268]. In addition, the development of a shoulder peak at approximately 850 cm\(^{-1}\) and \(-1000\text{ cm}\(^{-1}\)\), both of which correspond to the formation of MoO\(_3\) as indicated via XRD, is
observed for the Te containing catalysts. The formation of this phase which is unselective to ethane ODH does not cause a significant decrease in reaction performance and in fact, the addition of Te increases ethylene selectivity indicating that Te may not be causing destruction of the M1 phase but instead may be inducing the crystallization of the amorphous phase surrounding the M1 phase [283]. This is also supported by previous literature which suggests that Te helps stabilize the M1 phase during synthesis [284]. Similarly to Te, the addition of high amounts of Pd (Mo$_8$V$_2$Nb$_1$Pd$_{0.5}$) cause a similar blue-shift of the peak at $\sim$873 cm$^{-1}$, however the shift is not as severe and the doping does not cause the formation of distinct shouldering as with the case of Te. This is potentially due to the lower loading of Pd when compared to Te. As shown previously, Te$^{4+}$ is coordinated primarily with ring oxygen within the catalyst [269] and forms an oxygen reservoir within the six membered ring [269, 280]. This oxygen reservoir may induce an oxidation of V or Mo in the ring resulting in a strengthened M-O-V bond which corresponds to the blue shift of the band at $\sim$868 cm$^{-1}$ in the base catalyst. Pd may also have a similar effect, however as the blue shifting due to Pd introduction is much less than that of Te, Pd likely has a lesser contribution as it likely does not form an oxygen reservoir. Despite this, a similar effect on the spectra was seen for both dopants, potentially suggesting that Pd and Te may reside in the same site in these catalysts. In contrast, the addition of Ti, even at high loadings, does not display the same characteristic shifting as Pd or Te. While a shoulder is formed near the $\sim$873 cm$^{-1}$ band, it is in a different location and blue-shifting of the $\sim$873 cm$^{-1}$ band does not occur. Interestingly the band near 923 cm$^{-1}$ does display a blue shifting indicating that it may be adding to a different ring or site in the catalyst, unique to Ti.
In order to discern the effect of each gas component, in-situ Raman spectroscopy was performed with only inert, with only oxygen, and finally under working reaction conditions with a gas composition of 33.3% C\textsubscript{2}H\textsubscript{6}, 16.7% O\textsubscript{2}, and 50% inert. The inert only experiments were conducted to determine the effect of temperature on the catalysts as a previous study on vanadia reported peak shifting due to temperature effects [285]. Therefore, by determining shifting due to purely thermal effects, thermal shifting can be quantitatively accounted for in later analyses. Representative spectra for such an experiment are presented in Figure 5.19.

Figure 5.19. Raman spectra of Mo\textsubscript{8}V\textsubscript{2}Nb\textsubscript{1}Ti\textsubscript{0.005} heated under an inert environment
Ethane ODH in situ Raman Spectroscopy

Raman spectroscopy is a powerful vibrational spectroscopy technique that allows for the monitoring of changes in bond strength via the shifting of a Raman active band. Therefore, changes in the Raman shift of a vibrational mode are indicative of a change in the bond strength of that vibrational mode. When in-situ measurements are conducted, Raman spectroscopy allows for the determination of oxidation and reduction of catalytically relevant bands via the change in peak position (red shifting or blue shifting) as a function of temperature or gas composition which allows for the extraction of knowledge of how the catalyst behaves under actual operating conditions. From this, the effect of the addition of dopants on the behavior of the active site of the catalyst can be elucidated. The Raman active bonds for these catalysts correspond to the M-O-V vibration of the catalyst and changes in positioning of the band correspond to lengthening of shortening of the constituent M-O or O-V bond. A lengthening of either of these bonds would result in a decreased Raman shift, i.e. red-shifting, while an increased Raman shift would be due to a decrease in the bond length of either bond, resulting in a blue-shift. Figure 5.20 graphically represents this with the assumption that the O-V bond is impacted by the reaction conditions.
Figure 5.20. General effect of dopants on the Raman active site

Figure 5.21. *in situ* Raman spectra for (left) Mo$_8$V$_2$Nb$_1$ and (right) Mo$_8$V$_2$Nb$_1$Te$_{0.995}$ catalysts during Ethane ODH with a gas feed of 2:1:3 ethane : oxygen : argon
Figure 5.22. *in situ* Raman spectra for (left) Mo₈V₂Nb₁Ti₀.005 and (right) Mo₈V₂Nb₁Pd₀.005 catalysts during Ethane ODH with a gas feed of 2:1:3 ethane : oxygen : argon.

Figure 5.23. *in situ* Raman spectra for (left) Mo₈V₂Nb₁Pd₀.005Te₀.995 and (right) Mo₈V₂Nb₁Ti₀.005Te₀.995 catalysts during Ethane ODH with a gas feed of 2:1:3 ethane : oxygen : argon.
The *in situ* Raman spectra under reaction conditions are shown in Figures 5.21-5.23 for all of the catalysts compositions explored. Under elevated temperatures and gas compositions, several of the catalysts exhibited bulk MoOx peaks at roughly 820 and 990 cm$^{-1}$ [286], where the cross sectional area of MoO$_x$ for Raman scattering is significantly higher than the M1/M2 M-O-M bands; which has been reported for MoVTe based mixed metal oxides [286]. In order to quantify the peak shifting of the relevant Raman Bands attributed to the proposed active Mo-O-M (M= Mo or V) vibrational modes at ~930 cm$^{-1}$ and ~870 cm$^{-1}$, the spectra were fitted, where a representative spectrum fitting for the base
catalysts is shown in Figure 5.24 for the base Mo$_8$V$_2$Nb$_1$ catalyst under inert conditions. As the presence of MoO$_x$ oxides cannot be definitely ruled out the spectra were all fitted using four peaks, attributed to the two M-O-V bands located at ~873 cm$^{-1}$ and ~932 cm$^{-1}$, and two bands at ~820 cm$^{-1}$ and ~990 cm$^{-1}$ corresponding to MoO$_x$. During the reaction, the band located at ~932 cm$^{-1}$ was the most volatile band with regards to changing position while the band located at ~873 cm$^{-1}$ was fairly constant in position. This suggests that the band at ~932 cm$^{-1}$ may be responsible for oxygen transport within the catalyst and may correspond to a M-O-V stretch in the six membered ring of the catalyst while the other band at ~873 cm$^{-1}$ may be present in another ring of the catalyst or be in a portion of ring not responsible for oxygen transport. As Raman spectroscopy cannot resolve surface species without the use of surface enhanced techniques on bulk oxides, we cannot rule out the contributions of the terminal surface species in the reaction [250]. All shifting is calculated as the difference between the peak position at 525 °C minus the original position of the peak at 30 °C, corrected for thermal effects calculated with inert only experiments by making the same temperature correction under an inert environment. This methodology also corrects for the red or blue shifting of the band due solely to dopant incorporation potentially through structural effects and not changes induced due to the reaction environment. The summary of these results is presented in Table 5.3.
Table 5.3. Summary of thermally corrected *in situ* Ethane ODH Raman for Mo$_8$V$_2$Nb$_1$ Catalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Shifting of $\nu = 870$ cm$^{-1}$</th>
<th>Shifting of $\nu = 940$ cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo$_8$V$_2$Nb$_1$ (Base)</td>
<td>-3.1</td>
<td>-10.1</td>
</tr>
<tr>
<td>Mo$_8$V$_2$Nb$<em>1$Te$</em>{0.995}$</td>
<td>2.2</td>
<td>-5.2</td>
</tr>
<tr>
<td>Mo$_8$V$_2$Nb$<em>1$Ti$</em>{0.005}$</td>
<td>0.5</td>
<td>1.8</td>
</tr>
<tr>
<td>Mo$_8$V$_2$Nb$<em>1$Pd$</em>{0.005}$</td>
<td>-7</td>
<td>-9.6</td>
</tr>
<tr>
<td>Mo$_8$V$<em>2$Nb$<em>1$Pd$</em>{0.005}$Te$</em>{0.995}$</td>
<td>-3.9</td>
<td>-6.1</td>
</tr>
<tr>
<td>Mo$_8$V$<em>2$Nb$<em>1$Ti$</em>{0.005}$Te$</em>{0.995}$</td>
<td>5.3</td>
<td>-6.3</td>
</tr>
</tbody>
</table>

*Raman shifting calculated by correcting for thermal effect using an inert gas under identical conditions*

When compared to the base catalyst under reaction conditions, the addition of dopants can either increase or decrease the shift of the peak at ~940 cm$^{-1}$ (relative to the base catalyst) indicative of a decrease in degree of oxygen coordination to V (or the M species) or an increase in the oxygen coordination. The effect of dopant addition can be broken down into two general groups, Te containing catalysts and redox doped catalysts (Pd and Ti). For the case of Te containing catalysts, the shifting under reaction conditions is consistent across all the catalysts with a red shifting of 5-6 cm$^{-1}$. For MoV based oxides with the inclusion of Te, various mechanisms have been proposed for the reported increase in catalytic performance such as Te volatilization resulting in highly active O$^-$ radicals next to the Mo-O-V active site [71, 269] the surface enrichment of Te to form distinct active sites [68], or an increase in overall oxygen mobility/formation of an oxygen reservoir due to the inclusion of Te [280]. This is consistent with our results that show the vibrational mode of all the Te based catalysts, regardless of the secondary redox element, have a similar shifting; suggesting they all undergo a similar mechanism in the presence of Te.
Furthermore, relative to the base catalysts, the Te containing catalysts have a less pronounced shifting; where the base catalysts has a 10 cm\(^{-1}\) red shift while the Te doped samples show a \textit{ca} 6 cm\(^{-1}\) red shift; which may be due to the effect of Te serving as a labile oxygen reservoir that stabilizes the M1/M2 structure under reaction [280].

For the Pd and Ti based catalysts, there is a shifting of the 940 cm\(^{-1}\) band of -9.6 cm\(^{-1}\) and 1.8 cm\(^{-1}\); respectively. The blue shifting of the Ti may be due to the increase in lattice oxygen availability due to the Ti, which is consistent with the formation of an additional reduction event shown in the H\(_2\) TPR for the MoVNbTi catalyst, suggesting the Ti is likely either inhibiting oxidation of ethane or allows for faster transport of oxygen to and from the bulk of the catalyst. The red shifting of the Pd doped catalyst is most likely due to the increased reducibility, where the 940 cm\(^{-1}\) band remains constant relative to the base MoVNb, however, the otherwise stable 870 cm\(^{-1}\) also considerably red shifts; which may be caused by the reduction of a separate site on the M1/M2 catalyst. Furthermore, as the Pd doped catalysts shows the highest rate of combustion (CO\(_x\) formation) at all ethane conversion amounts we are attributing the promotion of the 870 cm\(^{-1}\) to the formation of secondary active sites which may be active for combustion as opposed to the partial oxidation towards ethylene. Additionally, Pd is well known to dissociate oxygen [270], which can result in highly active adsorbed oxygen which can promote combustion products, while ethylene formation generally occurs via a Mars-van-Krevelen mechanism which requires gas diffusion from the bulk oxide [242, 287]. However, due to the complex nature of the active site for this reaction over M1/M2 structures [3], the precise nature of the reaction mechanism over Pd doped catalysts was not explored.
A summary of the complete peak shifting for both the *in situ* Raman collected under an inert atmosphere and under reaction conditions is shown in Table 5.4. Under inert conditions, the shifting of the 870 cm\(^{-1}\) bands remains relatively constant at \(\sim 1\) cm\(^{-1}\) while the 940 cm\(^{-1}\) remains at *ca* 8 cm\(^{-1}\), with the exception of the Te doped catalysts, which shows a shift of *ca* 4 cm\(^{-1}\) of the 940 cm\(^{-1}\) band. Te is known to have high oxygen mobility in the MoV Nb systems, even under elevated temperatures under inert gas; which may contribute to the slight difference in the shifting of the 940 cm\(^{-1}\) band. More interestingly, the bands under reaction conditions show a clear trend that the 940 cm\(^{-1}\) is most influenced; whereas the 870 cm\(^{-1}\) band does not change relative to the inert gas measurements. We propose that the 940 cm\(^{-1}\) band is the catalytically relevant bands, whereas the 870 cm\(^{-1}\) band is influenced primarily through structural effects; which justify the lack of apparent change between the inert and reaction measurements while the 940 cm\(^{-1}\) band shifts considerably from inert to reaction. The outlier to this is the Pd doped catalysts, which possesses a large shifting of the 870 band under reaction; which may be attributed to the excess reduction of the MoV Nb base, where the H\(_2\) TPR shows that the inclusion of just Pd considerably decreases the reduction temperature of the catalyst.
Table 5.4. Summary of Raman band shifting under inert and reaction conditions for M-O-V bands

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Inert Atmosphere Shifting</th>
<th>Ethane ODH Shifting</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\nu = 870 \text{ cm}^{-1}$</td>
<td>$\nu = 940 \text{ cm}^{-1}$</td>
</tr>
<tr>
<td>Mo$_8$V$_2$Nb$_1$ (Base)</td>
<td>0.1</td>
<td>-6.1</td>
</tr>
<tr>
<td>Mo$_8$V$_2$Nb$<em>1$Te$</em>{0.995}$</td>
<td>-1</td>
<td>-4.3</td>
</tr>
<tr>
<td>Mo$_8$V$_2$Nb$<em>1$Ti$</em>{0.005}$</td>
<td>-0.9</td>
<td>-8.6</td>
</tr>
<tr>
<td>Mo$_8$V$_2$Nb$<em>1$Pd$</em>{0.005}$</td>
<td>-0.3</td>
<td>-9.6</td>
</tr>
<tr>
<td>Mo$_8$V$<em>2$Nb$<em>1$Pd$</em>{0.005}$Te$</em>{0.995}$</td>
<td>3.1</td>
<td>-8.6</td>
</tr>
<tr>
<td>Mo$_8$V$<em>2$Nb$<em>1$Ti$</em>{0.005}$Te$</em>{0.995}$</td>
<td>-7.2</td>
<td>-8.4</td>
</tr>
</tbody>
</table>

**in situ Raman Spectroscopy under pure oxygen**

Further evidence for this role comes from examining the catalyst under oxidizing conditions. For the base catalyst, Ti doped catalyst, and Pd doped catalyst discussed previously, the catalyst can be exposed to pure oxygen at 525°C and cooled down to room temperature without the development of any secondary phases. However, when the doping of Ti is increased, a secondary phase, MoO$_x$, is formed as shown in Figure 5.25. The same effect is not observed for an identical increase in Pd doping, further supporting the oxidizing effect of Ti addition.
Figure 5.25. Raman spectra of Mo₈V₂Nb₁Tiₓ under a pure oxygen environment

Structure/Activity Relationship of doped Mo₈V₂Nb₁ catalysts

By combining evidence obtained through each of the techniques discussed previously (TPR, in-situ and ex-situ Raman Spectroscopy) the role of select dopants and how they impact the complex chemistry of these catalysts can be better understood. The incorporation of Pd within the catalyst increases the reducibility of the catalyst by likely occupying a site adjacent to one of the ethane activation centers of the catalyst. This proximity would allow active dissociated oxygen species access to react with the activated ethane, resulting in excess non-selective over oxidation of ethane to CO₂ which was seen exclusively for the Pd only catalyst. As this proposed site is the same as the known site for Te, the incorporation of both these dopants simultaneously results in the displacement of Pd as Te is added in significantly higher quantities and could potentially have a higher affinity for this site. The addition of Ti and Te influences the degree of oxygen coordination or oxygen mobility of one of the active species within the catalyst (M-O-V) and influences the product distribution of the reaction to favor more selective oxygenated compounds,
namely acetic acid. Further evidence for this is provided by examining *in-situ* Raman spectroscopy of catalysts with high Ti dopings, as these catalysts exhibit over-oxidation of the catalyst to form MoO$_x$ at high temperatures under oxygen.

5.3 Conclusions

In our studies, the optimal catalyst compositions for ethane partial oxidation to both acetic acid and ethylene with regards to the addition of redox and acid dopants to a base Mo$_8$V$_2$Nb$_1$ catalyst were identified. A DOE methodology was implemented to gain statistically significant insights on the impact of tuning the balance between the acidity and redox behavior of the catalyst via the addition of the selected dopants and to identify useful trends to aid the design of mixed metal oxide EPO catalysts in the future. Analysis was carried out to correlate the redox-element loading (Pd, Ni, or Ti) and acid-element loading (K, Cs, or Te) with the catalytic performance and structural integrity of the materials. It was found that across all catalyst compositions explored, an excess of surface acidity relative to the redox element (R/A ratio of 0.005) benefited both ethylene and acetic acid formation. Additionally, investigation of the total dopant level (D/H ratio) led to the finding that doping high levels of Ti optimized the selectivity for both AA and ethylene, while doping high levels of Ni and Pd led to the formation of combustion products. Overall, AA production was favored with TiTe doping while ethylene production was favored with NiTe doping. Additionally, it was found that Cs-doped catalysts ubiquitously favored ethane combustion. The effects of dopant composition on the catalyst structure were elucidated, where the extent of phase segregation and incorporation of dopants into the base catalyst was most sensitive to the acid/base element doped, and the incorporation of cesium was found to trigger the formation of multiple secondary phases. Overall, tuning
the balance between redox and acid elements doped into Mo$_8$V$_2$Nb$_1$ catalysts resulted in not only changes to the surface acidity and redox properties, but also induced a change in the bulk catalyst structure, the coupled effects of which were found to ultimately determine the materials' catalytic properties.

The doping of Mo$_8$V$_2$Nb$_1$ catalysts with redox (Pd and Ti) and acid (Te) elements was investigated to gain a deeper understanding of how these dopants influence the complex chemistry of these catalysts. The addition of Pd contributed to the enhanced reducibility of the catalyst, potentially through being located in the six membered-ring of the catalyst adjacent to the active site for ethane activation. This proximity to the active site allows it to interact with activated ethane as well as sit at the top of a channel of labile oxygen. However, Te resides in this site and may displace Pd causing it to potentially reside in another ring or on the surface of the catalyst. Although out of the scope of this study, detailed electron microscopy could shed further light on the location of Pd in the catalyst. The addition of Ti increases the coordination (with oxygen) of one of the species in the M-O-V band as evidenced by *in-situ* Raman spectroscopy. This extra oxygen may be responsible for the enhanced selectivity to oxygenated species, namely acetic acid, seen for Ti containing catalysts seen in this study. As noted elsewhere in the literature, this effect is similar to that of Te, as Te can function as an oxygen reservoir and increase oxygen mobility throughout the catalyst. The experimental methodologies utilized in this work could be extended to other dopant materials to gain a more fundamental understanding of how they influence catalytic performance as well.
CHAPTER 6
ELUCIDATING OXYGEN ADSORBENTS ON PT-AU ELECTROCATALYSTS VIA XAFS

As the need for more efficient fuel cells is arising as the automotive market expands toward hydrogen fuel sources, the need for cost effective fuel cells is gaining considerable attention. Current fuel cell catalyst consists of platinum-based catalysts supported on carbon that allow for the efficient generation of electricity via the redox cycle of H₂ and O₂[288-290]. However, since catalysts are known to deactivate over time, particularly in the case for fuel cells where acidification can cause a loss in the total platinum loading, an industry adopted solution is to increase the platinum loading upwards of 45wt% Pt[289, 291]. This usually results in Pt nanoparticles on the order of 3-5 nm, which have limited atomic efficiency, as only the outermost surface atoms participate in the catalytic reaction given the surface to volume ratio of spherical particles scales by r⁻¹. Another viable alternative to increase catalytic activity of fuel cell catalysts while simultaneously reducing total cost is to replace a fraction of the Pt with Au[292-296] or other metals and metal oxides to either stabilize the Pt particles or to promote a synergistic bimetallic interaction that increases catalytic performance[291, 297-300].

In this study, we explored a PtAu bimetallic complex supported on highly oriented pyrolytic graphite (PtAu/HOPG) utilizing one monolayer (ML) coverage of PtAu. Due to the negligible X-ray absorptivity of HOPG, we can study the PtAu catalyst via back illumination of the electrode; providing a detailed understanding of the catalyst under operating conditions. Furthermore, by employing X-Ray Absorption Spectroscopy (XAFS) we can discern not only the coordination environment of PtAu, but also the surface structures via the difference spectra method, which can rule out the contributions from the bulk structure to give us insight into the adsorbed species, specifically oxygen and its derivatives.
6.1 HERFD-XAFS and Electrochemical Measurements on PtAu/HOPG Electrocatalysts

The HERFD XANES spectra collected at SP8 for the PtAu/HOPG catalyst is shown in Figure 6.1a. The most obvious difference between the spectra can be observed between 0.77 V (V vs Ag/AgCl) and all other voltages. The influence of oxygen adsorbates on XANES is expected to be approximately 1 or 2% of the actual white line intensity for all voltages below the point of oxygen evolution[291, 301], consistent with this finding. To closely examine the spectra, we utilized the difference spectra method, which uses a reference point where the material is well known (0.17 V vs Ag/AgCl) to elucidate the influence of adsorbates. At 0.17 V (V vs Ag/AgCl) the platinum catalyst should be entirely metallic without any adsorbents, which effectively eliminates the contribution from the bulk and/or clean surface from the difference spectra[302]. The difference spectra of the PtAu/HOPG, shown in Figure 1b, under the specified voltages shows that the only discernable oxygen species is observed at 0.77 V (V vs Ag/AgCl), which should be the formation of n ≥ 2 adsorbed oxygen. The contributions from the 0.57 V (V vs Ag/AgCl) cannot be distinguished from the baseline noise of the sample, given the peak for 0.57 V appears below the Pt edge (E₀=11566.1 eV).
Figure 6.1. (a) *in situ* HERFD Pt L$_3$ edge of PtAu/HOPG measured at Spring-8 and (b) its corresponding difference spectra using 0.17 V (V vs Ag/AgCl) as the reference. Cell parameters: WE: PtAu/HOPG, CE: Pt coil, RefE: Ag/AgCl, flowing deaerated 0.1 M HClO$_4$

Furthermore, the corresponding cyclic voltammogram for the PtAu/HOPG catalyst in 0.1 M HClO$_4$ is shown in Figure 6.2. The initial oxidation events can be observed in the first cycle at 0.37 V, 0.47 V, and 0.57 V (V vs Ag/AgCl). Upon the completion of the initial cycle the spectra no longer exhibits characteristic Pt oxidation event, which is consistent with reported systems that utilized PtAu metal complexes on glassy carbon electrodes, where increasing the Pt content resulted in more apparent redox properties[294].
The XANES spectra collected at KEK PF was concerned with determining the potential dependence of the Pt L₃ edge on the PtAu/HOPG catalyst under a flowing cell setup using a cone type cell with a Nafion membrane. The XANES spectra for these studies are shown in Figure 6.3a, where the white line intensity remains relatively stable until the potential exceeds 1.20 V (V vs RHE). The sharp increase in the white line intensity for 1.20 V (V vs RHE) can be attributed to multiple factors, such as the formation of subsurface oxygen or the development of Pt oxide surface layer [291, 295, 301]. For catalyst on the order of 3-5 nm, the possibility of surface oxide formation is more likely; which is typically followed by Pt dissolution due to the acidification of the solution at high voltage.
By incorporating Au, not only is the intrinsic activity increased, but also the Pt gains a resistant to dissolution and oxide formation due to the bimetallic interactions between Pt and Au [292, 294], as well as their ability to form an alloyed structure [303]. Furthermore, based on the differences between the Pt foil spectra and the PtAu/HOPG, there is possibly charge transfer occurring between the Pt and Au to result in a significant decrease in the Pt L₃ edge intensity relative to the pure foil. The difference spectra of for these experiments are shown in Figure 6.3b, where the reference point of 0.40 V (V vs RHE) was used to create the spectra (E₀=11563.1 eV). Therefore, the contribution from the 1.20 V (V vs RHE) is most apparent, with a maximum approximately 4 eV above the white line. The sharp increase in the white line is most likely due to the formation of sub surface oxygen forming in the PtAu/HOPG catalyst, which has been shown in significantly increase the white line intensity, particularly for higher voltages (>1.0 V vs RHE) where oxygen evolution is also expected to occur. However, the formation of a surface oxide cannot be unequivocally ruled out based on these findings alone and would require further experiments or modeling.
Figure 6.3 (a) in situ BI-XAFS on PtAu/HOPG at KEK Photon Factory and (b) corresponding difference spectra using 0.40 V (V vs RHE) as the reference. Cell parameters: WE: PtAu/HOPG, CE: Pt coil, RefE: RHE, flowing deaerated 0.1 M HClO$_4$, Nafion membrane, Cone-type cell configuration.

The electrochemical activity of the PtAu/HOPG, shown in Figure 6.4, was similar to the activity measured at SP-8; showing reproducibility between the two cells. The CV taken at PF shows a similar three oxidation events as did the CV at SP8, particularly at 0.7 V, 0.8 V and 0.9 V (V vs RHE). It is important to note the fundamental differences between the cells used at SP8 and PF; at SP8 a free flowing electrolyte solution was used while at PF, a cone cell was used which the required the use of a Nafion membrane to act as an electrolyte bridge; introducing considerable mass transfer limitations to the measurements taken at PF.
6.2 FEFF8 Pt (111) Oxygen Adsorption Models

To gain further understanding of the XANES spectra, FEFF8 modeling was used to determine the theoretical difference spectra for various adsorbents on a Pt 111 slab model corresponding to ~2.1 nm particles with a 0.5 nm height (147 atom cluster, with 91 exposed surface atoms). A representative surface consisting of the different types of oxygen adsorbents positioned on the surface are shown in Figure 6.5, where only the top 49 atoms were used in the modeling, as the bottom 49 are lying on top of the HOPG. The adsorption on the sides of the Pt particle were not considered in the simulation (21 total sites), however, the edge sites of the top layer were considered. The side facing bottom...
layer should not be considered as viable adsorption sites since those should be sterically hindered by the HOPG support (21 total sites).

Figure 6.5. Model representation of Pt (111) surface used in FEFF8 simulations, with atop -OH, -O hcp, -O fcc, and -O bridged shown (Pt-grey, O-red, H-white)

FEFF8 analysis was performed using the centermost Pt atom (center of middle layer) as the central absorbing atom. The full multiple scattering radius of 6.3 Å in the FMS FEFF8 card should model approximately 100 atoms in total, including the surface adsorbents. In the case for the middle layer absorbing Pt atom, our results show approximately a 1 eV shift between -OH atop and the remaining -O adsorbents are consistent with those reported for similar FEFF8 calculations using a six atom representative Pt (111) configuration, which reported minimal differences in the Δμ spectra based on different n fold oxygen adsorbents[301, 304]. However, the differences in the Δμ spectra become considerable when subsurface oxygen begins to form as opposed to surface adsorbed oxygen, which often occurs after oxygen evolution has initiated at a sufficient high voltage (>1.0 V vs RHE) [288, 291]. The complete summary of the parameters used and the corresponding influence on both the Fermi level and the charge transfer are
summarized in Table 6.1. Furthermore, based on the FEFF8 density of states analysis the charge transfer is primarily focused in the Pt d-orbital. However, in the case of atop -OH, there is a 0.018 eV contribution from the p-orbital, where the total change in the s-orbital was negligible for all cases. To determine the effects of size on the charge transfer of the Pt (111) central atom, a 5\times5 \times5 and 8\times8 \times8 slab was used to simulate bulk Pt. This resulted in the lack of any charge transfer and a constant Fermi level of -7.104 eV, showing that particle size no longer plays a role beyond a certain threshold.

Figure 6.6. (a) XANES FEFF8 simulation of Pt (111) with various oxygen adsorbents and (b) the corresponding difference spectra using the clean Pt (111) surface as the reference
Table 6.1. Summary of relevant FEFF8 model parameters and density of states for the middle Pt (111) layer

<table>
<thead>
<tr>
<th>Surface</th>
<th>Pt-X Bond</th>
<th># of adsorbents</th>
<th>Fermi Level (eV)</th>
<th>Charge Transfer (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt (111) Clean</td>
<td>Pt-Pt 2.77 Å</td>
<td>N/A</td>
<td>-6.743</td>
<td>0.120</td>
</tr>
<tr>
<td>Pt (111) OH atop</td>
<td>Pt-O 2.0 Å</td>
<td>49</td>
<td>-6.862</td>
<td>0.229</td>
</tr>
<tr>
<td></td>
<td>O-H 0.98 Å</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pt (111) O fcc</td>
<td>Pt-O 1.98 Å</td>
<td>36</td>
<td>-6.739</td>
<td>0.154</td>
</tr>
<tr>
<td>Pt (111) O hcp</td>
<td>Pt-O 1.98 Å</td>
<td>36</td>
<td>-6.761</td>
<td>0.143</td>
</tr>
<tr>
<td>Pt (111) O bridged</td>
<td>Pt-O 1.98 Å</td>
<td>42</td>
<td>-6.889</td>
<td>0.172</td>
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<tr>
<td>Pt (111) 5x5x5 Slab</td>
<td>Pt-Pt 2.77 Å</td>
<td>N/A</td>
<td>-7.103</td>
<td>0.000</td>
</tr>
<tr>
<td>Pt (111) 8x8x8 Slab</td>
<td>Pt-Pt 2.77 Å</td>
<td>N/A</td>
<td>-7.103</td>
<td>0.000</td>
</tr>
</tbody>
</table>

6.3 Conclusions

Based on the experimental and theoretical data acquired for the Pt L₃ edge we can conclude that PtAu undergoes similar oxygen adsorbents as traditional Pt/C catalyst. However, the influence is much less pronounced in the case for the PtAu/HOPG catalysts, which may be due to either the bimetallic/alloy interactions between Pt and Au. Evidence of a bimetallic interaction was observed in the 2019-05-17 SP-8 EXAFS beamtime via simultaneous blueshifting of the Pt L₃ edge and redshifting of the Au L₃ edge, however this was not discussed in detail in this report as there was not enough time to analyze/interpret
the data during my stay. The FEFF8 simulations show that there was nominally a 0.7 eV difference between the atop OH adsorbents and all other n>2 oxygen adsorbents, with the greatest charge transfer occurring between Pt (111) and atop OH.

Recommendations for future work for this project would be to do a particle size analysis (can be done via EXAFS coordination number fittings and STM) and an elemental mapping to discern if the Pt and Au are segregated/alloyed or in close proximity, which is a requirement for a bimetallic interaction to occur. Furthermore, as one of the novelties of this work is the utilization of arc plasma deposition to form a 1ML PtAu/HOPG complex, it would considerably strengthen the argument of improved catalytic/structural integrity of the PtAu catalyst if a Pt/HOPG reference synthesized via the same arc plasma deposition method were contrasted with the current PtAu/HOPG catalyst. Furthermore, the FEFF8 modeling can be further improved to incorporate an actual PtAu configuration instead of a Pt (111) model surface. Additionally, the incorporation of several layers of HOPG below the Pt(111) can also be incorporated to see if there is any significant scattering contribution from the Pt-C interactions, which will more closely model the PtAu/HOPG system.
CHAPTER 7
CONCLUSIONS & FUTURE WORK

The body of this work was centrally focused on resolving the structure/activity relationship for various catalytic compositions and reactive systems. Three examples of resolving the structure/activity relationship were given: surface facet-controlled nanostructures for CO$_2$ hydrogenation, single site catalysts for CO$_2$ hydrogenation and mixed metal oxide catalysts for ethane partial oxidation. In addition, a fourth case study explored was the oxygen adsorbents found on the surface of PtAu based electrocatalysts.

For the cobalt nanostructures, which were exploring the differences between selective surface faceting of particles, a clear conclusion was reached that the promotion of the active surface facets, the \{110\}/\{111\} facet, resulted in the suppression of spectator species. This claim is address in full detail in Chapter 3 of this thesis, where both the CO$_2$ hydrogenation reaction and the subsequent CO hydrogenation reaction were monitored via \textit{in situ} DRIFTS, which revealed the active cobalt nanorods suppressed spectator formate species and promoted the selective exposure of bridged sites, evidenced in the CO hydrogenation. In the second half of Chapter 3, a more practical approach was taken to catalysts design. In this design, we developed a modular synthesis that allowed us to encapsulate the cobalt nanorods in a supporting material, which ultimately increased the catalytic performance of the material. In this section, TiO$_2$ was found to increase the catalytic activity in the low temperature, low conversion regime, which we ascribed to the metal support interactions evidenced by the reduction profile of CoNR/TiO$_2$. Additionally,
Al₂O₃ was found to increase the catalytic performance of the catalysts in the high temperature high conversion regime, which we attributed to the increased heat transfer properties of Al₂O₃ relative to all of the other materials, therefore it assisted in the heat/mass transfer of the material.

The future work that can be adopted for the contents of Chapter 3 is the development of a similar methodology adopted herein for the Fischer Tropsch reaction. Specifically, by carefully controlling the feedstock in both dry and hydrated feed conditions the self-regenerating properties of the catalysts can be discerned. This would be a primarily spectroscopic approach, as the catalytic performance of the cobalt nanostructures was already explored in an earlier work from our group. Furthermore, the precise nature of the catalyst structure under reaction conditions is of question, where a high quality in situ STEM-HAADF can be utilized in collaboration with a highly trained microscopist to observe the exposed surface faceting of the catalysts after both a reduction under hydrogen and under relevant reaction conditions. This can be done in the powder phase for the actual catalytic material or as a model case using single crystal studies. The single crystal option is most feasible, which we would use a {110} Co₃O₄ single crystal and the corresponding {11-20} which is expected to form from the {110} oxide facet as a control group. This comparison can yield powerful information on the catalyst restructuring system in addition to high quality spectroscopy that is readily afforded to UHV systems, such as LEED, PM-IRRAS, and XPS/Auger.

For the single site catalysts work detailed in Chapter 4, the central conclusion is that cobalt catalysts perform best for CO₂ hydrogenation in subnanometer clusters while ruthenium is most active in the atomic/clustered regime as well. Furthermore, graphene
catalysts were explored and found that specific nitrogen defect sites result in high catalytic activity. For the cobalt single site catalysts, a surface composition of approximately 36% metal was found to be most active for methanation, with the balance metal being in the cationic Co$^{2+}$ state. This showed that cobalt cations supported on silica do not have the ability to readily dissociate hydrogen, which resulted in the exclusive formation of CO over the pristine Co$^{2+}$ single sites. Upon increasing the metal content the methanation reaction rate increased by over an order of magnitude. An contrary situation was found to be true for Ru/pBN, which had the highest methanation ability in the atomic and/or subnanometer cluster. Typically, Ru also behaves similar to cobalt in that it requires an ensemble to dissociate hydrogen, however, in the case of pBN, the abundant defect sites result in what is similar to a strong metal support interaction with ceria. In this case the CO$_2$ can adsorb onto adjacent sites next to the Ru centers and the atomic Ru can readily dissociate the hydrogen required for methanation. This was observed on the Ru/pBN-0.58%Ru, which formed almost exclusively methane and very little CO, suggesting that defect rich pBN has a strong synergistic effect with atomic ruthenium. The last case explored in Chapter 4 was the use of graphene quantum dots for CO$_2$ hydrogenation. In this study, we found a completely metal free catalyst for CO$_2$ hydrogenation. The active site for this system was proposed to the formation of edge site pyridinic nitrogen defect sites, where the other defect nitrogen species were graphitic N and pyrrolic N. Through IR and XPS studies, we were able to find that the incorporation of N defects in the graphene quantum dots resulted in the frustration of adjacent C-H vibrations while under a CO$_2$ atmosphere, which we attributed to be the active site.
The future work that can be adopted for Chapter 4 is primarily spectroscopic work to discern the mechanism of the single site catalysts. Specifically, for the cobalt single site catalysts, several *in situ* DRIFTS studies can be utilized. This thesis describes a detailed characterization of the cobalt after various reduction pretreatments and their affect on catalytic performance; therefore, the evolution of this work would be to spectroscopically discern the active site a reactive intermediate. This would involve using CO adsorption to discern the nature of the metal clusters and the sites that develop after the reducing pretreatments as well as CO$_2$ hydrogenation after the various pretreatments to ascribe a reactive intermediate to the catalytic performance outline herein. To probe the cationic single site catalyst structure, low temperature CO adsorption (under liquid nitrogen) should be adopted to discern if the single sites cobalt’s species are monomers or dimers/oligomers of cationic cobalt. This careful spectroscopic study can easily be expanded upon for a promising study. A similar study can be adopted for the Ru/pBN and nitrogen doped graphene quantum dots for CO$_2$ hydrogenation, however, these studies are much more insulated due to the contribution of DFT used to supplement the argument in these cases.

Mixed metal oxide catalysts for ethane partial oxidation was the focus of Chapter 5, which was concerned with elucidating the effects of dopant addition on both catalytic performance and vibration structure under reaction conditions. This work established a set of heuristics for dopant incorporation into a host Mo$_8$V$_2$Nb$_1$ structure via the use of Design of Experiments (DOE) which found several trends with total dopant loading and the relative ratios of the dopant species, specifically the redox to acid ratio. Additionally, the findings of this original study lead to the adoption of detailed in situ Raman spectroscopy to discern the active vibrational structure of the M1/M2 catalysts, which is contested in
current literature. The results of the DOE showed that ethylene yield could be maximized utilizing a PdTe doped composition while acetic acid production is maximized using a TiTe doped composition. Furthermore, the relationship between dopant incorporation and crystalline structure was established within the DOE parameter space, where the secondary phase formation, particularly in the presence of Cs as dopant, ubiquitously decreased the catalytic activity and increased combustion products, while the optimal D/H and R/A ratio was found to be 0.005 for both parameters with regards to both ethylene selectivity and acetic acid selectivity. In the latter half of Chapter 5, a detailed vibrational study was established, where the active vibrational band was found to be the ν=940 cm⁻¹ band, while the ν=870 cm⁻¹ band was suggested to be primarily structurally dependent. This was claim is founded by taking the difference between an identical temperature profile under inert gas and then under reaction, these resulting differences allows us to discern the reactive vibrational band relative to the proposed structural band. This was corroborated with catalytic measurements under differential conditions in the absence of mass transfer limitations, evidenced by the Weisz-Prater Criterion.

The future work that can be adopted for the findings of Chapter 5 are limited relative to the other chapters of this thesis. Herein, we established a catalytic system and set out to discern the catalytic performance of various dopants and then a mechanistic approach via in situ Raman spectroscopy. A possible avenue of research would be to explore the structure of the M1/M2 with two dopants to elucidate the actual location of the dopant in the complex M1 lattice. This would require judicious amounts of electron microscopy coupled with very careful probe reactions involving molecules with a radius greater than that of the pores to discern if the active resides on the external surface or the
pores. An additional study that can be explored is the oxygen isotope exchange reactive test, to probe the nature of the oxygen in the reaction, this can help clarify the Raman vibrational spectra and yield information when ethane ODH is carried out with $^{18}\text{O}_2$. The inclusion of isotopic oxygen should enter the lattice and proceed via the Mars-Van Krevelen mechanism. However, if sufficient redox species exist on the surface there should be highly reactive adsorbed oxygen, which would result in the formation of combustion products with oxygen labeling; therefore allowing one to carefully tune the redox properties utilizing this feedback to tune the reducibility of the catalyst to dampen overoxidation. Finally, \textit{in situ} XRD can be used to discern the crystallographic structure under reaction conditions.

The final chapter of this work was concerned with the use of PtAu/HOPG electrocatalysts as a model system to discern oxygen adsorbent during OER. The findings of this work suggested that the oxygen species under a PtAu alloy can be mitigated, evidences by the combination of both FEFF modeling results and experimental HERFD-XAFS. By using high energy X-Ray absorption, we were able to find that at moderate potentials of 0.77V (V vs Ag/AgCl) there is a clear formation of atop -OH on the PtAu/HOPG electrocatalysts. FEFF8.2 modeling also suggested that the atop -OH bonding has the most influence on the edge height, where bridged and 3- and 4-fold oxygen yielded a lesser difference in the edge position as well as the edge height.

Future work that can be done for this project is the development of a more sophisticated FEFF8.2 model. In this study, a basis set of Pt was used for the modelling results, where a PtAu alloy in a 1:1 of Pt : Au would be required to properly model the system. Furthermore, the shape of the modeled particles can be tuned to reflect different
possible conformations of the particles on the surface, such as cluster size (in atoms), surface facet exposure, and different possible oxygen configurations such as sub surface or surface layer oxidized platinum.
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