Development of Novel Catalysts for Air Pollution Control

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DEVELOPMENT OF NOVEL CATALYSTS FOR AIR POLLUTION CONTROL

by

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Dedication

I would like to dedicate this work to my parents Youliang Wang and Fang Li, for their enlightened education and guidance in my life.
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Abstract

The development of economy strongly related with increased consumption of fossil fuels, which causes severe air pollution issue. With more and more strict environmental regulations implemented all over the world, robust and efficient emission control technologies need to be innovated and applied to overcome the pollution challenge. This dissertation focuses on utilizing heterogeneous catalysis to eliminate carbon monoxide (CO), hydrocarbons (CH$_x$) and nitric oxides (NO$_x$) emissions produced from fossil fuel combustion.

The first type of catalyst is Pd supported on Mn-Ce solid solution. It achieves 100% CO conversion at room temperature. The high activity is attributed to superior lattice oxygen transfer interaction between Pd and support, which is discovered by multiple in situ and ex situ characterizations. When tested under practical simulated diesel exhaust condition, including extra water, CH$_x$ and NO$_x$, the CO light-off temperature increased to 170$^\circ$C due to competitive adsorption of CH$_x$ and NO$_x$. The comparison of structure characterization before and after hydrothermal aging shows that the Pd is attempting to aggregate and solid solution support is tending to segregate. However, such minor change is not significant enough to change catalysts activity. Doping additional Sn into MC support can improve sulfur resistance of catalysts for low temperature CO oxidation.
The second type of catalyst is Pd supported on shape and surface facet controlled Fe and Mn-Fe nanorods. Mn can be successfully doped into Fe nanorod and form solid solution. The Pd/Mn-Fe catalyst shows over 90% CO conversion at 50°C which is much higher than the inactive Pd/Fe catalyst. The Pd structure and reactivity change on doped oxide surface with controlled facet will be elucidated. The goal of this study is to provide new fundamental insight on metal-support interaction and active sites design approach.

The third type is SSZ-13 zeolite based catalyst, which has small pore structure and excellent hydrothermal stability. By ion exchange method, metal cations can be introduced into the zeolite pores and function as active sites. The active sites can be used in the ammonia selective catalytic reduction (NH₃-SCR) of NOₓ, which is a major NOₓ reduction technology in heavy duty trucks and coal power plants. Cu-SSZ-13 zeolite catalysts show the best NO conversion (over 95%) from 150-450°C when compared with Fe and Ce based SSZ-13. Moreover, in the presence of SO₂ and H₂O, which usually can poison SCR catalysts, Cu-SSZ-13 still keeps a relatively high sulfur resistance at temperatures between 250-450°C.
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Chapter 1

Introduction

1.1 Environmental catalysis

Environmental catalysis refers to catalytic technologies for reducing emissions of environmentally unacceptable compounds [1]. It includes a broad range of catalytic technologies. The first typical type of technology is directly converting pollutions to harmless product. This category includes mobile emission control, NO\textsubscript{x} reduction from stationary sources (e.g. power plants), sulfur compounds and VOC (volatile organic compound) conversion, conversion of ozone, formaldehyde and other organic indoor pollutants, photocatalytic antibacterial air purification, liquid and solid waste treatment (polymers and other solid waste), and greenhouse gas abatement or conversion. The second type of environmental catalysis is improving chemical reaction process and reduces the production of pollution from the process. This category contains the application of catalysis for eco-compatible refinery, chemical catalytic processes, and new catalytic routes to valuable products without forming undesirable pollutants. Energy-efficient catalytic technologies are the third type. It includes catalytic combustion, catalysis in fuel cells, catalytic devices for using renewable energy sources like solar energy or biomass. Finally, the reduction of the environmental impact in the use or disposal of catalysts should also be cited as part of the objectives of environmental catalysis.
Among various environmental catalysis applications, this dissertation focuses on researching two specific directions for air pollution control. The investigation of new catalysts for low temperature diesel engine exhaust control was first explored. Next screening for sulfur resistant catalysts for NOx reduction in coal power plants was investigated.

1.2 Diesel engine exhaust emission control

The emissions from a diesel engine are composed of solids, liquids and gases. The combined solids and liquids are called total particulate matter (PM) and are composed of soot, sulfates and soluble organic fractions (SOFs). Gaseous hydrocarbons (HC), carbon monoxide, nitrogen oxides, and sulfur dioxide make up the gas phase emissions. Several strategies have been developed in order to reduce the quantity of pollutants emitted to the atmosphere. The diesel oxidation catalysts (DOC) are used to oxidize CO and HC to CO$_2$ and water before release to the atmosphere. Another potential role of the DOC is to oxidize NO to NO$_2$ for the passive regeneration of the diesel particulate filter (DPF). This is located downstream of the DOC in the engine exhaust. DOC can also be used to enhance NO$_x$ reduction in the selective catalytic reduction (SCR) process. The limiting factor for the DOC efficiency is its light off temperature (the temperature below which oxidation is kinetically limited), which can reduce its efficiency, especially during urban operating conditions [2]. Up to 80% of CO and hydrocarbon emission can emit during the automobile cold start phase [3-5].

Many categories of catalysts were developed for low temperature oxidation of CO. Cobalt oxide (Co$_3$O$_4$) shows very high CO oxidation activity at and below ambient temperatures [6]. Different CO oxidation light-off temperatures ($T_{50}$) for Co$_3$O$_4$ have
been reported. Cunningham et al. [7] found a $T_{50}$ of $-54^{\circ}C$ for pure Co$_3$O$_4$ and Thormahlen et al. [8] reported a $T_{50}$ of $-63^{\circ}C$ for Co$_3$O$_4$ supported on Al$_2$O$_3$. It was only the pre-oxidized cobalt oxide catalyst that showed activity at these low temperatures. Upon adding Pt or Pd to a Co$_3$O$_4$/Al$_2$O$_3$ catalyst, Meng et al. [9] found that the temperature required for full conversion in CO oxidation could be decreased by -213$^{\circ}C$.

However, in the complex diesel exhaust gas conditions, the low-temperature activity of Co$_3$O$_4$ is inhibited by the presence of water [7, 10], hydrocarbons, and NO [10]. Moreover, even without these inhibitors, a slow decrease in activity was observed during steady-state CO oxidation at low temperature due to accumulation of carbonates on the catalyst surface [7]. Like Co$_3$O$_4$ catalysts, the discovery of gold catalyst for low temperature CO oxidation [11] made by Haruta and colleagues motivated a considerable amount of research on the activity of gold-based catalysts. Gold catalysts supported on transition metal oxides exhibited high CO oxidation activities at very low temperatures below the freezing point (0$^{\circ}$ C) when the gold particles are smaller than about 10 nm [12, 13]. Specifically, small gold particles (2-4 nm in diameter) have an activity at 273 K that is more than 2 orders of magnitude larger than larger gold particles (20-40 nm in diameter) regardless of the support being reducible or irreducible oxide [14]. Even though gold catalysts preform good CO oxidation activity at low temperature its applications are limited. This is due to catalyst deactivation and low stability under reaction conditions which is caused by accumulation of carbonates on the surface and the agglomeration of Au particles [15,16].

In practical automobile CO and hydrocarbon oxidation, the current DOC typically consists of platinum group metals (PGMs) (Pt, Pd, Rh) as an active phase that are placed
on high surface area supports and oxygen storage materials [17-19]. Among them, Pd catalysts drew much attention due to the low cost, fast light-off performance, high oxidation capability, and sintering resistance compared to Pt and Rh catalysts [20-24]. Despite the high performance of Pd catalysts, Pd has poor CO oxidation activity at low exhaust temperatures and deactivates by the presence of sulfur compounds in the exhaust gas [25-26]. For instance, Pd based DOCs can emit up to 80% of CO at temperatures below 200°C during the cold-start stage of a vehicle [20,27-28]. For diesel and efficient lean-burn internal combustion engines, the average exhaust temperature is low, which ultimately affects the CO oxidation performance of the catalyst [17, 29-30]. The low CO oxidation activity of DOCs at low exhaust temperatures is typically explained with the blocking of active sites by HCs [30-31]. Thus, novel catalysts that can maintain a high oxidation performance at low exhaust temperatures while resisting inhibition by HCs are desired.

CeO$_2$ is a widely used component in DOCs due to the Ce$^{3+}$/Ce$^{4+}$ redox cycle. CeO$_2$ can store and release oxygen, depending on the exhaust gas composition. This ability is known as oxygen storage capacity (OSC), and improves oxidation of CO and HCs during lean and rich cycles [32]. Ceria promoted Pd catalysts exhibit high catalytic activity for CO oxidation at low-temperatures (100°C-200°C) due to the OSC and strong-metal support interaction (SMSI) [33-35]. In addition, CeO$_2$ promotes noble metal dispersion [36] and increases the activity for water-gas shift and steam reforming reactions [37-38]. Despite the high performance of CeO$_2$, it has low thermal stability and tends to deactivate at temperatures above 800°C [39]. The incorporation of a secondary metal into the ceria lattice can improve the OSC and prevent its sintering [39-41].
The development of automobile catalysts meanwhile facilitates the fundamental reaction mechanism study. For CO oxidation, the most cited mechanism over metal or supported metal are the Eley-Rideal (E-R), Langmuir-Hinshelwood (L-H), and Mars-van Krevelen (MvK) mechanisms. The E-R mechanism is based on two reaction steps in which one reactant (e.g. O$_2$) is first adsorbed to the surface and the second reactant directly reacts with it in the gas phase without an adsorption step. For example, Manuel et al. proposed an E-R reaction mechanism in which CO(g) would react on a Rh$^{x+}$ site surrounded by two O vacancies partially filled with oxygen species[42]. On the other hand, the L-H mechanism includes the adsorption of both CO and O$_2$ on the catalyst surface. For example, it is widely accepted that the reaction of CO oxidation over unsupported Pt proceeds according to an L-H mechanism, in which the determining steps occur in the adsorbed phase. CO is not dissociated whereas O$_2$ is generally dissociated above 170 K[42]. The adsorbed CO then reacts with O to produce CO$_2$. Such mechanism is also suitable to be employed in alumina- or silica-supported catalysts, which are considered as inert supports. It is important to note that in L-H mechanism, CO with -1 kinetic order has a strong inhibiting effect on metal sites, whereas the reaction is first order with respect to oxygen on all the studied metals[42].

In MvK mechanism, CO reacts with lattice oxygen directly at the surface of metal oxide catalysts leaving an oxygen vacancy. The vacancy then can be replenished by gas phase oxygen or by mobile bulk oxygen. For instance, ceria allows the metals to work in transient conditions when the oxygen pressure in gas phase decreases much below the stoichiometry[ 43, 44]. Yu Yao investigated the impact of ceria on the kinetics of CO oxidation reaction [45]. Contrary to alumina-supported catalysts, the kinetic order with
respect to oxygen decreases and is close to zero when ceria is added to the support. Still more remarkable, the kinetic orders with respect to CO become positive, whereas they were negative over metal/Al₂O₃ catalysts. This finding was interpreted as the result of a cooperative effect between metals and ceria (dual-site mechanism). Carbon monoxide would be adsorbed on metal sites whereas oxygen could be adsorbed and activated on ceria sites in close vicinity of metal particles. The kinetic orders with respect to CO and O₂ are both between 0 and 1.

1.3 NOₓ emission control from stationary source

The major source of nitric oxides (NOₓ) emission is combustion of fuels in engines and power plants. NOₓ emission and SOₓ emissions are components of acid rain. Furthermore, NOₓ and hydrocarbons can react in atmosphere and form photochemical ozone (smog). NOₓ is formed in the combustion process by combination of the N₂ and O₂ in the air.

NH₃-SCR reaction is a widely used technology for the reduction of NOₓ emissions in stationary sources (e.g. gas-, oil-, and coal-power plants) and mobile sources (e.g., diesel engines). It was discovered that NH₃ can react selectively with NOₓ, producing N₂ and H₂O. When sulfur is present in the flue gas, the oxidation from SO₂ to SO₃ results in formation of H₂SO₄ on reaction with H₂O, which can cause corrosion of equipment. The reaction of NH₃ and SO₃ results in formation of (NH₄)₂SO₃ and NH₄HSO₄, which can deposits on SCR catalysts and cause the deactivation of catalysts.

Nowadays, the commercial catalysts used for SCR units in industry are mainly TiO₂-supported V₂O₅, promoted with WO₃, with operation temperature window at 350–450°C [46-51]. This type of catalyst has also been used for HD diesel vehicles in Europe.
as well. However, with higher reaction temperature 550°C, the catalyst loses selectivity leading to NH₃ oxidation. In addition, the active anatase structure of TiO₂ with a surface area of 80-120 m²/g irreversibly converts to rutile with a surface area of less than 10 m²/g, which can deactivate the catalyst. Addition of WO₃ and MoO₃ can improve the redox properties and activity. Although vanadium catalysts have been introduced into the market for power plants and diesel vehicles, some problems still need to be solved, such as rapid catalyst activity decrease above 550 °C due to the high activity for oxidation of SO₂ to SO₃, and the toxicity of the vanadium species to the environment [51–53].

Many studies have shown that zeolites are promising catalysts for coal combustion flue gas conditions due to their wide working temperature from 200°C to 600°C[54-60]. Zeolites comprises of tetrahedra units (TO₄) through corner sharing to form a three dimensional microporous framework. Framework TO₄ generally refers to [SiO₄]⁴⁻ and [AlO₄]⁵⁻. Isomorphous substitution of Si⁴⁺ with Al³⁺ renders the zeolite framework negatively charged. This charge is neutralized by exchangeable cations, such as Cu²⁺, Na⁺, and K⁺ located in the channels or cages of the structure. Cations will try to maximize their coordination number through interacting with O ions from the zeolite. The O ions around the tetrahedral Al³⁺ are preferential anchor sites for Cu²⁺ cations due to the electron neutralization [51, 54]. Compare to V-Ti based catalysts, commercially available zeolites can keep good activity at 600°C without oxidizing NH₃ to NOₓ. While in a high water concentration stream from coal power plant or automobile sources, zeolite tend to deactivate by a process called dealumination, where Al³⁺ in the zeolite framework migrates out of the structure. This leads to irreversible change and, in the extreme case, collapse of crystalline structure.
Aqueous ion exchange is the most commonly used method for preparing zeolites with transition metal ions located at exchange sites. For instance, Cu ion-exchanged zeolite contains aqueous Cu in the pores and cavities of the zeolite. Upon high-temperature treatment, water is removed and the Cu cations coordinate to the surface oxygen of the exchange sites. Cu active sites formation depends on the Si to Al ratio and Cu loading in the zeolite framework [51]. For example, in Cu-SSZ-13 with Chabazite structure, isolated Cu$^{2+}$ in coordinated in a 6-member ring is generally considered as active site for selective catalytic reduction of NO by NH$_3$ (NH$_3$-SCR). Complexes of Cu$^{2+}$ can also be ion-exchanged in the cages and channels of zeolites and can also be synthesized in situ by ligand adsorption. The coordination chemistry of Cu$^{2+}$ with extra-framework ligands is different from the coordination chemistry in aqueous solution. This is due to the geometric constraints in the cages. Even if the complex is similar with regard to its ligands, encapsulation in zeolite cages and pores may also impose additional constraints in the complex, inducing significant changes in bond lengths and angles. Such variations could substantially influence their reactivity in activating molecules [54].

Different ion exchanged zeolites were reported to be active for NH$_3$-SCR reaction, such as Fe [54,55], Cu[56,57], Mn [58], and Ce [59,60]. Among such a wide family of catalysts, iron and copper zeolites are particularly active in NH$_3$-SCR and have been extensively studied. Yang et al reported a Fe-ZSM-5 catalysts, with surprisingly high NO conversions in a broad temperature window (375-600 °C) under a high gas hourly space velocity (GHSV) of $4.6 \times 10^5$ l/h. However, at high temperatures, in the presence of water vapor (steam), the catalyst deactivates and exhibits greatly diminished SCR activity. This is due to dealumination of the zeolite framework. At elevated
temperatures, the aluminum in the framework becomes unstable and detaches from the tetrahedral framework positions [61–66]. Previous work from our group indicates that Cu-SSZ-13 zeolite catalyst exhibits higher hydrothermal stability and NOx conversion than other Cu loaded zeolite catalysts, such as ZSM-5, in an ideal flue gas condition (NO, NH3, O2 and N2) [67]. Moreover, Cu-SSZ-13 has found as a NH3-SCR game changing catalyst due to its high catalytic activity, N2 selectivity compared to other ion-exchanged SSZ-13 catalyst [68, 69]. Active sites and reaction mechanisms on Cu-SSZ-13 have been reported in many recent papers [70-73].

Co-cations, i.e. alkali, alkaline-earth elements and rare earth metal, can direct the Cu species and change the location of Cu species, which can further change the Cu site structure and activity. The coordination chemistry of Cu2+ in zeolites is well established [74]. Cu2+ preferentially coordinates in 6 membered rings with 1, 2 or 3 Al tetrahedra. It coordinates preferentially with the oxygen atoms of the Al-tetrahedra, which are more basic than those of the Si-tetrahedra. Some research has been performed with Ni on FAU zeolite, where the Na+ co-cations are competing and hindering the migration of the metal to the 6-MR channels from the super cages during thermal treatment [75]. In Cu-SSZ-13 zeolite, on the other hand, a recent study shows that Na+ cannot change the location of Cu2+ in 6-MR, but only weaken the interaction between Cu and SSZ-13 framework, while other larger alkali metals, such as K+ and Cs+, can limit the number of Cu2+ ions able to reside at such sites [76].
Chapter 2

Experimental and Techniques

2.1 Catalyst preparation

2.1.1 Precipitation

Precipitation method is one of the most widely used catalyst preparation methods in industry. A common procedure for precipitation method is mixing an aqueous metal salt solution with an aqueous alkali or ammonium carbonate. This results in the precipitation of an insoluble metal hydroxide or metal carbonate, which is followed by filtration, washing, drying and calcination. In the calcination step at high temperature, these insoluble sediments can be converted to metal oxides. The metal precursors and precipitant are generally chosen because of their high water solubility and easy removal of unwanted elements at high temperature (e.g. NO$_3^-$, Cl$^-$).

The final particle size and shape of catalysts can be controlled by a variety of factors, such as solution pH, metal precursor/precipitant type, temperature and stirring rate, surfactant e.g. PVP. Some advantages of the precipitation methods make it the most widely and simply used methods. First, it generally provides a relatively uniform particle size and shape distribution. In addition, pore size and distribution of catalysts can be well controlled.
If two or more metal compounds are present, they may precipitate at different rates or in sequence, which will cause final phase separation of the catalysts. However, if two metal or more metal compounds can precipitate simultaneously and could finally form uniform crystal structure, such solid might have special chemical properties in catalytic reactions due to its unique structure and components. The solid is unusually called solid solution. More detailed synthesis steps are explained in the experimental section of chapter 3 and 4.

2.1.2 Wet impregnation method

A carrier or support is contacted with aqueous solution of one or more metal precursors. The water present from solution must be removed from the support through drying in order to release the metal precursor. When most of the moisture is removed by evaporation of liquid water, the result is that a substantial fraction of dissolved precursor is deposited on the surface or/and pores of the support. The mixture is then dried and calcined at high temperature to crystalize or stabilize the catalyst and removal unwanted elements. In this step, the metal precursor decomposed to metal oxide and gas. For example, Pd(NO$_3$)$_2$ precursor can decompose to PdO and NO$_2$ at 550°C.

This method is preferred in preparing supported noble metal catalysts. Because it can spread out the metal in a finely divided a form without washing and filtering compared to precipitation method that may cause the loss of precious metal. The noble metal is unusually used 1wt% or less. This could greatly reduce the consumption of expensive ingredient meanwhile maintain the active components on the surface or in the pores of support. More detailed synthesis steps are explained in the experimental section of chapter 3 and 5.
2.1.3 Zeolite synthesis

A general route for zeolite synthesis is the hydrothermal synthesis method that converts a mixture of silicon and aluminum compounds, alkali metal cation (optional), organic molecules and water through supersaturated solution into a microporous crystalline aluminosilicate. Colloidal silica, waterglass, pyrogenic silica or silicon alkoxides are common sources of silicon. Gibbsite, pseudo-boehmite, aluminate salts, aluminum alkoxides are unusually used as aluminum source. Cationic and neutral organic molecules are added as structure-directing agents or so called templates to construct Si/Al framework.

The presence of OH ions solubilizes the gel and de-polimerizes the precursors into silica and alumina, directing them around the cation of the structure-directing agent (organic template). This step is known as primary nucleation and is driven by micro-processes such as the pH of the solution and macro-processes such as stirring of the gel. After the primary nucleation, the primary structural units form polyhedra and join to form the zeolite crystal, produced mostly by the driving force caused by the stirring of the solution. This process is known as secondary nucleation. Once the polyhedral is formed, it is combined with other polyhedral and multiplied; performing the crystallization process. For this process, higher temperatures are required to promote the formation of larger crystals.

By definition, the primary nucleation is governed by the driving force caused by the super saturation of the solution. In other words, if the solution is too diluted in water, no driving force exists to incorporate atoms into the zeolite framework. The primary nucleation can be both a homogeneous and heterogeneous process. It is a homogeneous
process when the nucleation is driven by the solution components itself (e.g. silicon and aluminum precursors, organic template). On the other hand, it is a heterogeneous process when it is driven by a material that will not become part of the framework. An example for this process is the use of mineralizers such as fluorine sources or the addition of seeds. The crystallization step is carried out in a Teflon-lined autoclave reactor under autogenous pressures and temperatures above 140°C. The antogenous pressure is produced by the vapor generated by the gel inside the Teflon autoclave when it is heated. Various parameters can affect the formation and growth of zeolites, such as molar composition, pH, temperature and time, precursor spicous and templates. More detailed synthesis steps are explained in the experimental section of chapter 6.

2.2 Characterization

2.2.1 X-ray powder diffraction (XRD)

X-ray powder diffraction (XRD) is a quick analytical technique primarily used for phase identification of a crystalline material and can give information on unit cell dimensions. X-ray diffraction is a bulk technique. XRD is based on constructive interference of monochromatic X-rays and a crystalline sample. The X-ray is generated by a cathode ray tube. The interaction of the incident rays with the sample produces constructive interference when conditions fulfill Bragg's Law ($n\lambda=2dsin\theta$). This law connects the wavelength of electromagnetic radiation to the diffraction angle and the lattice spacing in a crystalline sample. Because of the random orientation of the powdered material all possible diffraction directions of the lattice can be obtained. Conversion of the diffraction peaks to d-spacings results in identification of the mineral because each
mineral has a set of unique d-spacings, which can be by compared with standard reference patterns.

The mean crystallite size of a catalyst can be determined from the broadening of a diffraction peak, measured at one-half the height, which is called full half maximum width. The line broadening is inversely proportional to the crystallite size and can be used to provide an approximation of particle size with same crystal structure. The numerical particle size calculation can be calculated by Scherrer Equation:

\[
\tau = \frac{K\lambda}{\beta \cos \theta}
\]

Where \( \tau \) is the mean size of the ordered (crystalline) domains, which may be smaller or equal to the grain size; \( K \) is a dimensionless shape factor, with a typical value of about 0.9, but varies with the actual shape of the crystallite; \( \lambda \) is the X-ray wavelength; \( \beta \) is the line broadening at half the maximum intensity (FWHM); \( \theta \) is the Bragg angle (in degrees). It is important to note that the lattice strain, the instrumental broadening and other factors that can cause peak width change are simplified and neglected. To determine the absolute particle size of a catalyst, electron microscopy imaging should be utilized as compensate technique.

2.2.2 Electron Microscopy

Catalysts morphology, composition, surface structure and particle size are factors that can affect reaction activity. Electron microscopy allows for imaging the surface to a resolution of at least the nanometer scale. Two main electron microscopy techniques were used in this dissertation are scanning electron microscopy (SEM) and scanning transmission electron microscopy (STEM).
SEM is used to obtain image by rastering a beam of high-energy electrons across a sample surface of varying topography. The most commonly used imaging mode employs secondary electrons that are emitted when the sample is excited by the electron beam. These electrons have low energy and ensure that the signal comes from the surface region of the specimen. The number of emitted electrons greatly depends on the angle of the sample surface with respect to the electron beam and the detector, which construct differences in brightness and therefore reveal the sample topography. Another imaging mode is based on backscattered electrons, which has higher energy. This mode is sensitive to the image intensity depends on the composition of sample, which can provide good atomic number contrast. SEM imaging allows for viewing of a large area of sample and it is very useful for identification of particle morphology.

Species identification is accomplished by collecting the characteristic X-rays emitted from the sample, in a technique known as Energy Dispersive X-ray Spectroscopy (EDS). Electron excitation causes ionization within the sample leading to X-Ray emission which can be analyzed by solid state energy dispersive detector. Before imaging, powder catalyst samples were placed on carbon tape adhered on an aluminum stub without conductive coatings. SEM images were obtained using a Zeiss Ultraplus Thermal Field Emission Scanning Electron Microscope.

While SEM provides a topographical image of a sample surface using backscattered and secondary electrons, STEM uses a focused beam of high-energy electrons to form a small spot that is raster-scanned over a thin sample to image the entire depth by detecting scattered or transmitted electrons. One useful imaging mode in STEM is high angle annular dark field. The intensity distribution of electrons scattered at high
angles follows approximately a $Z^{1.85}$ dependence corresponding to the Reutherford scattering cross-section. Due to the incoherent scattering the HAADF-STEM images refers to as Z-contrast images and are very useful to study catalysts containing small metal particles. However, when the Z of the support is higher than metal particle, there is no good contrast and thus cannot distinguish the small particle from support. In this case, spectroscopic imaging utilizing the inelastic scattered electrons for EDS can be exploited to generate elemental maps.

### 2.2.3 X-Ray Photoelectron Spectroscopy (XPS)

X-Ray Photoelectron Spectroscopy (XPS) is a surface sensitive technique to analyze catalysts surface elemental composition and elemental oxidation states. The physical principle is based on the photoelectric effect, which was first discovered by Albert Einstein in 1905. Photons of a specific energy are used to excite the electronic states of atoms below the surface of the sample. Electrons ejected from the surface are energy filtered via a hemispherical analyzer before the intensity for a defined energy is recorded by a detector. Since core level electrons in solid-state atoms are quantized, the resulting energy spectra exhibit resonance peaks characteristic of the electronic structure for atoms at the sample surface. While the X-ray may penetrate deep into the sample, the escape depth of the ejected electrons is limited to less than 10nm for energies around 1400 eV. The photoemission process, obeys the following energy conservation rule:

$$hν = E_b + E_k$$

Where $hν$ is the photon energy, $E_b$ is the electron binding energy, and $E_k$ is the kinetic energy of the photoelectron. Conventional sources typically exploit the Kα radiation emitted by an Mg or Al anode to produce photons at a fixed energy of 1256 and 1486 eV,
respectively. The chemical environment in which the core electron is found prior to the photoemission event (the type of bonding, the oxidation state, the possible presence of adsorbates) results in distinctive BE shift.

2.2.4 X-ray absorption spectroscopy (XAS)

Synchrotron-based x-ray absorption spectroscopy (XAS) has proven to be a versatile structural probe for studying the local environments of atom in catalysts. It is a bulk characterization method and gives averaged results.

When a beam of X-ray photons passes through a material, the incident intensity will be decreased due to the adsorption of the material being irradiated. For a path length dx of the radiation through the material, the decrease dI is given by:

\[ dI = -u(E)I \, dx \]

where the linear absorption coefficient \( u(E) \) is a function of the photon energy. Integral form of the equation is called Lambert's law:

\[ I_t = I_0 e^{-u(E)x} \]

When the energy of the incoming photons is large enough to excite an electron from a deeper core level to a vacant excited state, a sharp rise in the adsorption intensity appears. This sharp rise is denoted as absorption edge.

An X-ray absorption spectrum is typically divided into two energy regions: the X-ray Absorption Near-Edge Structure (XANES) region, which extends from a few eV below an element's absorption edge to about 50 eV above the edge, and the Extended X-ray Absorption Fine Structure or EXAFS region, which extends from about 50 eV to as much as 1000 eV above the edge. The EXAFS region can be used to resolve structural information including the average bond distance between neighbored atoms, coordination
number of a selected atom species, while the XANES region can be used to indicate oxidation states of the selected element.

2.2.5 Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTs)

DRIFTs is a technique for analyzing surface catalytic reaction, adsorbate, adsorption sites and reaction intermediate. It offers the advantages of easy sample preparation. The electromagnetic radiation reflected by roughened surfaces is collected and analyzed in IR region, which is termed as diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS). IR beam incident onto a solid sample surface can have specular reflection, diffuse reflection, and partly penetrates into the sample. The beam penetrated the sample can be absorbed within the particles or be diffracted at grain boundaries, giving rise to diffusely scattered light in all directions. In diffuse reflectance spectroscopy, there is no linear relation between the reflected light intensity (band intensity) and concentration, in contrast to traditional transmission spectroscopy in which the band intensity is directly proportional to concentration.

2.2.6 Temperature programmed reduction (TPR)

TPR is widely used to determine catalysts reducibility, which is greatly correlated with catalysts activity in redox reactions. The basic chemistry is utilizing H₂ to reduce lattice oxygen of catalysts and forming H₂O. The A typical process of TPR is flowing H₂ in an inert gas with fixed flow rate over a catalysts in furnace. Then the catalyst is heated up with a constant temperature ramping rate. The outlet gas passing catalysts is detected by a mass spectrometer, from which we could tell the H₂ consumption peak at certain temperature. A H₂ concentration calibration is employed to quantify the H₂ consumption peak. The higher the H₂ consumed, the richer lattice oxygen can be involved in the redox
reaction. The lower temperature the peak occurs, the more likely the catalysts can work at lower temperature.

2.2.7 Atomic adsorption spectroscopy (AAS)

Atomic absorption spectroscopy (AAS) is used to determine the elemental composition of catalyst samples. Here, AAS is used to quantify the amount of Pd loading present in prepared catalysts. It is known that ground state atoms strongly absorb light at a characteristic wavelength and that the amount of light absorbed at low atomic concentrations is linearly related to the concentration of the element. In AAS, samples are atomized and exposed to the path of a light source emitting at the characteristic wavelength of the material. To calculate the concentration of an unknown sample, the absorbance at the characteristic wavelength is measured and compared with a calibration curve prepared using standards of known concentrations.

For each analysis, the calibration samples were diluted to five different concentrations, which cover the expected concentration of the metal of interest. An example procedure for Pd samples is described as follows. Standard solutions of 0, 1, 2, 4, and 6 ppm Pd were prepared by diluting appropriate fractions of a stock solution of 1 mg/mL Pd in 10% HCl (Acros Organics). In the diluting procedure, 10 vol% HCl and 0.5% LaCl₃ were added to the samples for better sensitivity and accuracy. The Pd-containing samples and the five standard solutions were nebulized into an air/acetylene flame. A Pd hollow cathode lamp (Hamamatsu Photonics K.K.) was used as a light source. An example of AAS calibration curve is shown in figure 2.1, which gives the absorbance as a function of Pd concentration. The calibration curve indicates good agreement with a
linear fit over the 0-6 ppm range. This calibration was applied to the synthesized Pd catalyst samples in order to measure the actual Pd weight loadings on those samples.

![Pd concentration calibration curve measured from AAS.](image)

**Figure 2.1** Pd concentration calibration curve measured from AAS.

### 2.3 Reactor and catalyst evaluation

#### 2.3.1 Reactor design

A schematic diagram of the reactor system is shown in figure 2.2. The design consists of two tube furnaces with temperature controllers, H₂O injection system, carrier gas, mass flow controller. 1/2” stainless steel tube coated with inert silicon coating (Silcoalloy 1000) or 3/8” quartz tube is used to load the powder catalyst sample. Swagelok Teflon front and back ferrules are used to seal the reactor. The maximum temperature limit for these ferrules is ca. 250°C. Since they are more than 3 inches far away from the heating part of the reactor, the real temperature of is much lower than the reactor temperature. After multiple reaction test with temperature range from 500-800°C, the Teflon ferrules will be aged and lose the sealing. Leak check by using leak detector or
soap is necessary for each reaction test. If there is a leak, then the old ferrules should be changed. The reactor operated at near ambient pressure over a temperature range from 25-800°C. Industrial grade flue gases including 1%NH₃/N₂, 1%NO/N₂, 2%SO₂/N₂, O₂, CO, 2%C₃H₆/He and balanced N₂ or Ar that simulate coal and automobile emission conditions are each connected to mass flow controllers (Brooks 5850E). H₂O is combined with the carrier gas feed into a heated evaporator. The product stream was sent directly to a mass spectrometer (MS, Hiden HAL IV RC) for analysis. One reactor is used for catalysts reaction test, while the other is a blank one used for gas concentration calibration during the reaction. The reason for this design is because catalyst in a single reactor can covert reactant during temperature ramp and the MS reading of outlet gas concentration is unknown. In the blank reactor, there is no reaction occur. So the known concentration of a gas passing the blank reactor will not change between inlet and outlet, which is representative for real gas concentration and can be used for calibration.

Flow rate ratio of these two reactors w adjusted by a needle valve before the blank reactor. The flow rate is measured by a Sensidyne 800266-1 Gilibrator. Each flow rate is measured at least 3 times in steady state to make sure the reading is repeatable and accurate. The total flow is maintained at 800 sccm. The amount and volume of both catalysts and quartz wool could change in different tests, so the needle valve needs to be adjusted in each reaction test to achieve the targeted flow rate.
2.3.2 Temperature control

The thermocouple setup is shown in figure 2.3 K-type thermocouple 1 (Omega Engineering, Inc., KMQ316SS-032U-12) was fitted into catalyst bed for reactor temperature monitoring. An additional thermocouple 2 is fitted into furnace for the purpose of interfacing with the temperature proportional integral derivative controller (PID controller, Omega Engineering, Inc., part number CN760000). The thermocouple 1 is placed into the catalyst bed to evaluate the impact of exothermic or endothermic catalytic reactions. The catalysts reaction temperature is reported by using the catalysts bed temperature. Since the furnace is not openable, the catalysts actual location in it is not visible. The length between the catalysts bed and the top of quartz tube is measure before loading the reactor. Then the length of thermocouple is marked as the same length so that it can reach the catalysts bed.
The process of temperature control is based on following steps: read the temperature using a K-type thermocouple (Omega), set the desired temperature, and control via a PID controller using LabView software. The reactor furnace is a high temperature ceramic radiant heater, supplied by Omega Engineering (CRFC-112/120-C-A). These furnaces are insulated with ceramic fiber and can go up to 900°C (requiring a maximum of 5 Amps). A K-type thermocouple transmits signal to the chassis from National Instruments (NI CDAQ-9174), which sends an input signal to the PID controller in the PC. Once the temperature is set in the PC, the PC sends an output-trIGGER signal (ON-OFF command) to the 4-channel relay module (NI-9481), placed in the second slot of the NI chassis. The solid-state relay (Omega Engineering – SSRL240AC25) requires a...
range of 90-280 V for operation and a circuit prior the SSR was added to obtain the needed power and voltage (120 V).

The final section of the temperature control system is the loop that allows the powering of the furnaces. Each furnace requires a 500 W (4.16 Amp, 120 V) for long furnaces. A variac autotransformer allows to step-up or step-down the voltage needed by the furnace. In the case of this temperature control system, the variacs are set at around 50%-70% of 120 V. For cases when the furnace’s loop is overpowered, a 5 Amp fuse would work as a safety device, shutting down the circuit to prevent the breakdown of the furnace or the solid-state relay. During a reaction, the temperatures of blank reactor and the reactor with catalyst are set the same to maintain the similar flow distribution.

2.3.3 Mass spectrometer

A quadruple mass Spectrometry (Hiden Analytical (HAL 201-RC), operated with the MasSoft software) is used to analyze the outlet gas from reactors. The gas molecules entering the ultra-high vacuum(UHV) chamber are ionized via electron ionization to be converted majorly into positive charges. Then, the ionized molecules are accelerated from the ion source through a set of 4 rods with a hyperbolic electric field.

A UHV chamber for the mass spectrometry was built-in-house using vacuum components obtained from Kurt J. Lesker and/or Duniway Company. The chamber includes one 4-way reducing cross (C-0275) with 2 ¾” conflat flanges at two ends of 4 ¼”conflat flanges. At one end, the cross has a 45° elbow (L45-0275) and a 979 Series Pressure Transducer (Kurt J. Lesker) used to monitor the pressure of the chamber. The transducer is capable of obtaining pressure measurements in a wide range of conditions (atm–10⁻¹⁰ torr). The second end of the standard cross has the mass spectrometer from
Hyden Analytical, while the third end has a LVM Series Leak Valve (Kurt J. Lesker), which provides molecular gas flow into the chamber (leak rate: $3.0 \times 10^{-5}$ torr/s). Generally, the achievable leak rate for leak valves are as small as $1 \times 10^{-10}$ torr/s and they are bake-able up to $T = 450^\circ$C. The last end of the 4-way standard cross has a conical reducer nipple (Kurt J. Lesker: CRN600X450) and a turbo molecular pump (TurboVac 151, SN: 20900101555). The turbo molecular pump has a similar appearance to a turbine compressor in jet engines; i.e. it uses rotating blades mounted on a shaft to direct gas molecules into the vacuum chamber in the molecular flow regime.

In order to start the turbo molecular pump, the chamber needs to be at rough vacuum conditions first; therefore, a 2-stage rotary vane mechanical pump (Varian SD-451) was attached to the turbo pump exhaust to initially pull gas from the chamber and achieve the rough vacuum conditions. The pulled gas from the chamber goes into the roughing pump’s low-pressure stage, then to its high-pressure stage, compresses it and then sends it to the exhaust at atmospheric pressure. It should be noted that oil is used in the internals of the roughing pump to lubricate the pump’s mechanical components (e.g. bearings, seals, rotor and vanes). Any failure in the roughing pump’s operation (e.g. not enough oil, oil leaks, power outage etc.) will cause malfunction of the turbo molecular pump and eventually damage it. Also, a valve was added to the mechanical pump (rough pump) to prevent back-diffusion of oil vapors to the vacuum chamber in cases when the turbo is turned off.

In order to achieve UHV conditions it is also necessary to bake-out the chamber. The baking procedure will remove any contaminants in the UHV chamber (e.g. water and minimum traces of hydrocarbons). Typically, the chamber is baked at temperatures
around 110-130°C, while the elbow around the pressure transducer is baked at lower temperatures (ca. 80°C) due to the transducer’s temperature limitations. The ultimate pressure achieved with this turbo pump is $8 \times 10^{-10}$ torr. (The maximum baking temperature during operation at conflat flange of turbo pump is 55°C).

The mass/charge (m/z) ratio of the ions is detected either with the Faraday or SEM detectors in the 100 amu mass range. Maximum operable pressure of the Faraday detector is $1 \times 10^{-4}$ torr. The disadvantage of this detector is the low sensitivity and delay time in the amplification system, which would explain why the signals vs. time appear noisy compared with the signals acquired with SEM detector. On the contrary, maximum operable pressure of the SEM detector is $5 \times 10^{-6}$ torr and can give higher sensitivity than the Faraday. Both of detectors are used in the experiments depending on the concentration range of the gases.

The reference mass to charge ratios that needs to be monitored were obtained from the NIST chemistry web book. The detectors used for each gas component depend on the concentration that needed to be analyzed. For trace level (ppm) concentrations, the SEM was selected due to its higher sensitivity, accuracy and lower noise level. Carrier gases like Ar and N$_2$ were analyzed by Faraday detector. When the MS operation pressure is within $3 \times 10^{-7}$ torr, all gases will be detected by SEM.

The volumetric flow of the gas sample going to MS was reduced from 100 sccm to 20 sccm using a 50 µm orifice provided by Swagelok. Reducing the volumetric flow to 20 sccm allows a steady pressure in the UHV chamber, which is convenient when monitoring gas concentrations in steady conditions. However, the gas volume between
the orifice and leak valve is still very high compared to the volumetric flow that goes into the MS when we open the leak valve. This is the so called “dead volume”, which can cause longer response time in the MS. In order to shorten the response time, a vacuum was created between the orifice and the leak valve using a roughing pump (Varian-SD-40) to improve the flow rate in such “dead volume”, as shown in figure 2.4. With this design, the MS can catch the composition change in seconds and enables characterizations like H₂-TPR and CO-O₂ pulse reaction.

**Figure 2.4** Mass Spectrometer sample line set schematic.

The operation sequence of this vacuum system is critically important. When gas flows are introduced into the system, valve 1 and 2 should be opened first, and then the leak valve can be opened slowly. After the reaction and calibration tests, the leak valve should be closed first, and then valve 1 and 2 can be closed. The reason is that the pressure in the MS is in $10^{-6}$ to $10^{-10}$ torr, which is much lower than the roughing pump ($10^{-1}$ to $10^{-2}$ torr). If valve 2 is closed while valve 1 and the leak valve are open, the pressure difference can easily suck pump oil from the roughing pump to the MS chamber. This can cause contamination, which is a disaster for the high vacuum system and may need months to clean up the chamber.
For a typical reaction test, a MID mode in the MS is used to monitor the pressure change of each gas component as a function of time. The MS is turned on for 30 min, then Ar or N$_2$ inert gas flow is started and the leak valve is opened until the chamber pressure reaches $3 \times 10^{-7}$ torr. Then the other gas flows and the temperature ramp are started. After the temperature and MS signal reach steady state, the reaction data is taken for analysis. Gas concentration calibration is done after each temperature ramp.

In the CO oxidation reaction, the m/z ratio for each gas is selected as follows: CO=28, O$_2$=32, Ar=40, H$_2$O=18, CO$_2$=44. It is important to note that CO$_2$ has ca. 10% fraction of m/z=28, which is overlapped with the m/z of CO. Hence, to calculate the CO conversion, such CO$_2$ contribution is subtracted from the CO signal. In the NH$_3$-SCR reaction, the m/z ratio of each gas is selected as follows: NO=30, NH$_3$=17, H$_2$O=18, O$_2$=32, N$_2$=28, CO$_2$=44, SO$_2$=64. The NO conversion is calculated by the formula: $(\text{NO}_{\text{inlet}}-\text{NO}_{\text{outlet}})/\text{NO}_{\text{inlet}}$, where NO inlet and NO outlet represent the concentration of NO inlet and outlet of the reactor, respectively.

2.3.4 Gas concentration calibration

MS is sensitive to a wide variety of gas concentrations. Prior to the reaction experiments, the mass spectrometer was calibrated at different concentrations to obtain a calibration curve for each respective gas component of interest. The concentration of the gas components were determined by back-calculating the calibration trend-line equation, shown in figure 2.5. The calibration experiments demonstrated a mass spec response time of 10 min every time a different concentration is selected. It would take more than around 20 seconds to receive response from the mass flow controllers because of the length of
the lines. Figure 2.5 shows the raw spectra and the calibration curve of CO in the range of 0% to 10% diluted in Ar. The concentration of CO is linear to the MS signal intensity (CO pressure).

Figure 2.5 CO concentration calibration on the MS.

C₃H₆ has a much lower concentration than CO in diesel oxidation reactions, which is in the ppm level. The C₃H₆ calibration was carried out to make sure it is detectable by the MS, shown in figure 2.6. The calibration curve shows good linear relationship between concentration and the MS intensity. It is important to note that in this
case, the C\textsubscript{3}H\textsubscript{6} pressure is normalized by the Ar pressure, which is the carrier gas. This is because the Ar pressure may fluctuate during the test and can lead to C\textsubscript{3}H\textsubscript{6} pressure or signal fluctuation in the MS. Through normalization, the pressure fluctuation effect can be greatly reduced and the data quality was improved.

**Figure 2.6** C\textsubscript{3}H\textsubscript{6} concentration calibration on the MS.
2.3.5 Benchmark catalyst tests

The commercial 0.5% Pt/Al₂O₃ catalyst (Alfa Aesar) was used as a benchmark sample to validate traction and analysis systems. The catalyst was tested for CO oxidation under 150, 250, 350, and 450°C for one hour at each temperature and the reactivity corresponds to steady state activity. A gas mixture of 2.0% CO (99.999% CO, Airgas), 5% O₂ (99.9999% O₂, Airgas) and balance Ar (99.9999% Ar, Airgas) was fed to the reactor via mass flow controllers. 200 mg of catalyst supported with quartz wool, was placed in the reactor for each run and no pretreatment was performed before the reaction. The corresponding gas hourly space velocity (GHSV) is 40,000 h⁻¹. CO conversion is calculated by the formula: \( \frac{(\text{CO}_{\text{inlet}} - \text{CO}_{\text{outlet}})}{\text{CO}_{\text{inlet}}} \), where CO inlet and CO outlet represent the concentration of CO inlet and outlet of the reactor, respectively. Calibration of the CO concentration was carried out by switching to the blank reactor with known inlet concentrations, which generates 4 calibration curves at each temperature. One of the disadvantages of using mass spectrometry as analytical technique is the occurrence of spectral skewing. By definition, spectral skewing is the term used to describe how the relative intensities of mass spectral peaks vary due to the change in concentration of the analyte in the ion source. In addition, the intensity of signal in the MS can gradually decrease as running time increases. Hence, multiple calibrations could improve the data accuracy. The CO concentration was achieved by using the calibration function and averaged CO pressure during the reaction at each temperature.

In figure 2.7, the benchmark Pt/Al₂O₃ catalyst shows almost 0% CO conversion at 150°C and over 95% conversion from 250°C to 450°C. The ramp up and ramp down curves match each other well, indicating good temperature control quality and
consistency. The conversion curves fit quite well with many reported Pt/Al$_2$O$_3$ catalysts. These tests validate the function and accuracy of the reactor and the MS. Most of the catalytic reaction experiments in this dissertation are based on this reactor system.

Figure 2.7 CO oxidation activity of benchmark 0.5% Pt/Al$_2$O$_3$ catalyst. CO/O$_2$ ratio of 2:5 and GHSV = 40,000 h$^{-1}$
Chapter 3

Superior oxygen transfer ability of Pd/MnO$_x$-CeO$_2$ for enhanced low temperature CO oxidation activity

3.1 Introduction

Carbon monoxide is a toxic pollutant and produced due to the incomplete combustion of carbon-containing fuels [77-78]. The majority of CO emissions come from mobile sources and catalytic oxidation of CO is the most widely used control technology to remediate CO emissions [78]. Even though the current commercialized platinum group metal (PGM) catalysts can reduce most of the CO content at temperatures above 200$^\circ$C, up to 80% of CO is still emitted during the cold-start stage of a vehicle due to the low operating temperature of the catalyst [78-80].

CeO$_2$ is a widely used component in mobile emission control catalysts due to the Ce$^{3+}$/ Ce$^{4+}$ redox cycle [81-93]. CeO$_2$ can utilize lattice oxygen reversibly for CO oxidation depending on the exhaust gas composition, improve the dispersion of noble metals and enhance catalyst stability at high temperatures [81]. All these promoting effects shift the light-off temperature for CO oxidation to lower operating temperatures and provide a stable catalyst structure [82-93]. Addition of a PGM on CeO$_2$ as an active phase can create adsorption sites for CO and promote CO oxidation [88,92]. Among the PGMs, Pd based CeO$_2$ catalysts are shown to have fast light-off performance, high
oxidation capability, and better sintering resistance [93]. Recently, the effect of synthesis methods, incorporation of a different metal oxide into CeO$_2$, and the structural change of pure CeO$_2$ support have all been investigated to promote the low temperature activity (LTA) of the Pd/CeO$_2$-based catalysts for CO oxidation at reaction temperatures below 150°C [94]. Generally, LTA can be determined by $T_{90}$, which denotes the temperature at which 90% CO conversion occurs. For instance, Meng et al. [95] reported a PdO/Ce$_{1-x}$Pd$_x$O$_{2-\delta}$ catalyst prepared by solution-combustion method, which showed a $T_{90}$ of 130°C. This catalyst exhibited a CO oxidation rate 100 times higher than PdO$_x$ (x=1,2) species on pure CeO$_2$ at 130°C and its increased activity was mainly attributed to a synergetic effect between the PdO$_x$ species and the Ce$_{1-x}$Pd$_x$O$_{2-\delta}$ solid solution. In addition, another Ce$_{1-x}$Pd$_x$O$_{2-\delta}$ solid solution catalyst prepared via a plasma-arc method showed a lower $T_{90}$ of 75°C due to its high specific surface area and high defects concentration on the catalyst [96]. On the other hand, highly ordered mesoporous CeO$_2$ supported Pd catalyst showed excellent LTA for CO oxidation. For example, Jin et al. [97] reported that Pd supported on mesoporous CeO$_2$ synthesized by a KIT-6 silica hard template method showed a $T_{90}$ of 90°C. After H$_2$ reduction at 150°C for 1 h, the $T_{90}$ decreased to 50°C. Moreover, Pd supported on mesoporous Co$_3$O$_4$-CeO$_2$ prepared by a surfactant-template method resulted in a $T_{90}$ of 75°C without performing a H$_2$ pretreatment [98]. A $T_{90}$ of room temperature was also reported over Pd/CeO$_2$-TiO$_2$ catalysts, synthesized by sol-gel precipitation and subsequent application of supercritical fluid drying [99]. However, the LTA over Pd/CeO$_2$-TiO$_2$ did not remain stable at room temperature and the CO conversion dropped down to 20% in 2 h.
The low CO oxidation activity of the Pd/CeO₂ catalyst can be attributed to the existence of small PdO nanoparticles and Pd²⁺ ions in the form of a Ce₁₋ₓPdₓO₂₋₅ solid solution. Both of these Pd species can be obtained via conventional synthesis techniques, such as wet impregnation, co-precipitation, and solution combustion [87, 91, 95, 100, 101]. Pd²⁺ ions substituted into the CeO₂ framework by solution combustion show better CO oxidation activity at temperatures below 120°C if compared to the Pt, and Rh metal ions [83]. However, up to 94% of Pd content in the solution combustion synthesis remains in the bulk and may have a little contribution to CO oxidation [91,95]. On the other hand, conventional wet impregnation can concentrate most of the Pd species on the CeO₂ surface, while still maintaining a high CO oxidation activity at low temperatures [94].

In addition to the synthesis methods, the OSC of CeO₂ could be enhanced by substituting Ce⁴⁺ with other cations, such as Y⁴⁺, Zr⁴⁺, La³⁺, Sm³⁺, Sn⁴⁺, and Mn³⁺, while still maintaining its cubic fluorite structure [102-107]. Among these metal oxides MnOₓ has taken particular attention due to the unique catalytic redox performance of CeO₂-MnOₓ and formation of large amounts of surface oxygen species on the Mn doped ceria. [108] For instance, Luo et al synthesized a series of Pd-doped mixed oxides CeO₂-MOₓ (M = Mn, Fe, Co, Ni, Cu) by a surfactant-assisted co-precipitation method followed by a 2-day hydrothermal treatment, in which Pd-MnOₓ-CeO₂ showed the best CO conversion with a T₉₀ of 50°C [108].

In this work, we present Pd supported on ceria based catalysts active for room temperature CO oxidation. Mn ions were incorporated into the CeO₂ support through a simple co-precipitation method. The catalysts were tested from room temperature to
450°C. The low temperature CO oxidation activity of Pd doped MC solid solution catalysts is investigated by means of in-situ X-ray absorption spectroscopy (XAS) and X-ray photoelectron spectroscopy (XPS). Dynamic reduction behavior of Pd$^{2+}$ species in the presence of CO at low temperatures is characterized by in-situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTs). H$_2$ temperature-programmed reduction (TPR) and CO/O$_2$ transient pulse experiments are conducted to evaluate the lattice oxygen reducibility of Pd/CeO$_2$ and Pd/MC.

3.2 Experimental

3.2.1. Catalysts synthesis

The MC supports were prepared by an ultrasonic assisted co-precipitation method, where Mn(NO$_3$)$_2$, and Ce(NO$_3$)$_3$, with a mole ratio of 1:1, were used as the catalyst precursors and (NH$_4$)$_2$CO$_3$ (1 mol L$^{-1}$) as a precipitator. The paste obtained from co-precipitation was treated by ultrasound for 2 h, followed by subsequent filtration. The samples were then washed with deionized water, dried in stagnant air overnight at 105°C, and calcined in stagnant air at 500°C for 6 h. Pd/MC with 1 wt% Pd loading was synthesized by impregnation. The MC support was immersed in aqueous Pd(NO$_3$)$_2$ solution and dried at room temperature while stirring. Then the solid was calcined in stagnant air at 550°C for 3 h. Similarly, Pd/CeO$_2$ was synthesized using the precipitation and impregnation method. The Ce(NO$_3$)$_3$ precursor was only mixed with the (NH$_4$)$_2$CO$_3$ (1 mol L$^{-1}$) precipitator and synthesized following the aforementioned procedure described for Pd/MC. The actual Pd loadings of Pd/MC and Pd/CeO$_2$ were measured by atomic absorption spectroscopy, and found to be 1.1±0.05 wt% and 1.0±0.05 wt %, respectively. Additionally, 5 wt% and 0.5 wt% Pd/CeO$_2$, and 5 wt% Pd/MC samples
were synthesized as a reference sample to compare Pd speciation. The Pd loading on 5 wt% samples were measured to be 5.1±0.05 wt% and 4.4±0.05 wt% on Pd/MC and Pd/CeO₂, respectively. The actual Pd loading on 0.5 wt% Pd/CeO₂ was 0.49±0.05 wt%.

3.2.2. Catalytic testing

CO oxidation experiments were conducted in a plug flow reactor under atmospheric pressure. A gas mixture of 2.0% CO (99.999% CO, Airgas), 5% O₂ (99.9999% O₂, Airgas) and balance Ar (99.9999% Ar, Airgas) was fed to the reactor via mass flow controllers (Brooks 5850E). 200 mg of catalyst supported with quartz wool was placed in the reactor for each run and no pretreatment was performed before the reaction. The catalyst temperature was recorded using a thermocouple placed inside the catalyst bed. The gas hourly space velocity (GHSV) for all experiments was 40,000 h⁻¹. The amount of CO before and after the reaction was measured using a differentially pumped mass spectrometer (MS, Hiden HAL IV RC). CO conversion was reported at steady state at each temperature and calculated by using the following formula: \( \frac{(\text{CO}_{\text{inlet}} - \text{CO}_{\text{outlet}})}{\text{CO}_{\text{inlet}}} \), where \( \text{CO}_{\text{inlet}} \) and \( \text{CO}_{\text{outlet}} \) represent the concentration of CO inlet and outlet of the reactor, respectively. The conversion error is calculated to be less than ±5% after repetitive tests.

The turnover frequency (TOF) of the Pd catalysts was calculated by using the following equation:

\[
\text{TOF} = \frac{F \times X}{n(Pd)}
\]
where F is the flow rate of CO in mol s\(^{-1}\), X is the CO conversion at 50°C, and n(Pd) is the mole of Pd in the catalyst.

### 3.2.3. Catalyst characterization

Powder X-ray diffraction (XRD) data for fresh samples were collected on a RigakuMiniflex II desktop diffractometer using a Cu K\(\alpha\) source with D/teX Ultra 250 silicon strip detector. XPS was carried out on a Kratos AXIS Ultra DLD XPS system equipped with a hemispherical energy analyzer. A monochromatic Al K\(\alpha\) X-ray source (1486.6 eV) was operated at 15 kV and 120 W. All spectra were calibrated to the adventitious carbon at 284.8 eV (C1s). The high-resolution elemental mapping and imaging of particles were collected using a FEI Talos F200X scanning transmission electron microscope (STEM).

XAS was collected at X-ray beamline 4-1 at the Stanford Synchrotron Radiation Lightsource (SSRL), Menlo Park, CA. The storage ring electron energy was 3 GeV with a current of 500 mA. Pd K-edge spectra were collected in the transmission mode with a Si (220) double-crystal monochromator that was detuned by 30% to minimize effects of higher harmonics in the X-ray beam. A Pd foil reference compound was placed between the \(I_1\) and \(I_2\) ion chambers to serve as a continuous energy calibration standard. A reference sample (PdO, 50 mg, Sigma-Aldrich) was mixed with boron nitride (BN, Sigma-Aldrich) (150 mg) to give an appropriate absorbance at the edge energy, whereas other samples (200 mg) were used without mixing with BN. Samples were then hand pressed inside the sample holder and loaded into the reaction cell, which was then evacuated down to \(10^{-5}\) Torr [109]. PdO were cooled down using a liquid N\(_2\) cryostat and
the Pd K-edge XAS of the sample was collected. Both Pd/CeO$_2$ and Pd/MC samples were first exposed to He at room temperature (ca. 25°C) for 1.5 h. Subsequently, 1% CO and 0.7% O$_2$ balanced with He was introduced into the cell. The in-situ reaction was conducted at the reaction cell temperatures of room temperature (RT), 50°C and 100°C. Pd K-edge XAS of the samples was collected at each condition. The X-ray absorption near edge structure (XANES) analysis of the samples was performed using the Athena software [110].

Time resolved DRIFTs experiments were performed on a Bruker Equinox 55 spectrometer equipped with a deuterated triglycine sulfate (DTGS) detector. CO adsorption was performed over the Pd/CeO$_2$ and Pd/MC samples at 50°C and atmospheric pressure. 2% CO balanced with Ar was injected to the reaction cell at a total flow rate of 50 sccm for 10min. The sample spectra were collected during CO adsorption with an accumulation of 32 scans at a resolution of 4 cm$^{-1}$. Background spectra were collected in Ar without the presence of CO.

The reduction properties of the catalysts were characterized through H$_2$-TPR experiments. 200 mg of a catalyst supported with quartz wool was placed in a quartz tube and no additional pretreatment was performed. A reduction gas of 10% H$_2$ balanced with Ar was introduced with a flow rate of 50 ml min$^{-1}$. The sample was heated up to 800°C with a rate of 10°C min$^{-1}$. H$_2$ consumption was monitored by a differentially pumped MS and calculated by integrating the peak area.

CO/O$_2$ transient pulse experiments were conducted in the aforementioned plug flow reactor used for CO oxidation experiments. 200 mg of the 1wt % Pd/CeO$_2$ and Pd/MC catalysts were placed in the reactor and tested under the flow rate of 100 sccm.
Initially, the catalysts were pretreated with 5% O$_2$ for 30 min at 50°C. Subsequently, the catalyst was purged with pure Ar for 30 min. Following the pretreatment, 2% CO balanced with Ar and 5% O$_2$ balanced with Ar were each cycled to the reactor every 10 min. Between each pulse, pure Ar was introduced to purge the residual gas for 10 min. The CO$_2$ (m/e=44), O$_2$ (m/e=32), CO (m/e=28), and Ar (m/e = 40) signals were monitored by the differentially pumped MS.

3.3 Results and discussion

3.3.1. Catalysts structure characterization

XRD was carried out to analyze the crystal structure of the samples. As shown in figure 3.1, the observed diffraction patterns in all samples can be attributed to the (111), (200), (220), (311) and (222) lattice planes of the cubic fluorite structure of CeO$_2$, indicating that Mn and Ce form a solid solution without appreciable phase separation. The change in the lattice parameter of CeO$_2$ after Mn addition and the physical properties (particle size, surface area, pore size) of Pd/CeO$_2$ and Pd/MC have been discussed in detail and published elsewhere [25]. The 1 wt% Pd/CeO$_2$ and Pd/MC catalysts do not show any diffraction peaks corresponding to Pd metal (40.2°) or PdO (34°, 42°) [25,100]. The lack of Pd diffraction peaks can be due to the small amount of Pd loading or formation of highly dispersed small Pd nanoparticles [95,100]. Indeed, increasing Pd loading to 5 wt% on MC leads to the formation of a weak diffraction peak at 42°, corresponding to crystalline PdO [100]. In the case of 5 wt% Pd/CeO$_2$, an even weaker diffraction peak at 42° is observed. The broader full width at half maximum of the PdO peak for the Pd/CeO$_2$ sample indicates that smaller PdO nanoparticles might be forming on Pd/CeO$_2$ in comparison to Pd/MC.
To “find” Pd, several characterization methods were attempted to show Pd size and structure. Pd dispersion of Pd/MC and Pd/\(\text{CeO}_2\) was tested with 150°C and 250°C \(\text{H}_2\) pretreatment. With 150°C, Pd size of Pd/\(\text{CeO}_2\) and Pd/MC are 1.7 and 4.5nm, respectively. With a followed 250°C \(\text{H}_2\) reduction, Pd size of Pd/\(\text{CeO}_2\) and Pd/MC grow to 2.7 and 7.4 nm, respectively. The XRD of reduced Pd catalysts after chemisorption is shown in figure 3.2. And metallic Pd (111) peak shows up. This indicates Pd dispersion can change with \(\text{H}_2\) reduction and such chemisorption method is not accurate to characterize the initial Pd dispersion.

**Figure. 3.1** XRD of the calcined 1 wt% and 5 wt% Pd catalysts.
Figure 3.2 XRD analysis of reduced Pd/CeO$_2$ and Pd/MC

High resolution STEM was also attempted to identify Pd structure, shown in figure 3.3. Since Pd has lower Z number than Ce, some references reported that the darker area of the catalysts in STEM image should be Pd particles [95]. The left image of Pd/CeO$_2$ shows bright and large CeO$_2$ crystal structure. Two interplanar spacings of 0.38 nm and 0.31 nm attribute to the (110) and (111) planes of CeO$_2$, respectively. The right image of Pd/CeO$_2$ shows a darker area at the edge of particle, which has an interplanar spacing of 0.19 nm. PdO (200) was reported to have a lattice spacing of 0.195nm, which is similar to this number. However, CeO$_2$ (220) has a lattice spacing of 0.19nm as well. Hence, it is very hard to confirm that the darker area is PdO particle due to the
overlapped PdO and CeO$_2$ interplanar spacing. The left STEM image of Pd/MC shows crystallite size around 3 nm, which is much smaller than CeO$_2$. Such observation is consistent with crystallite size calculated by XRD patterns of MC and CeO$_2$, which will be explained in Chapter 4. The right image of Pd/MC again shows a small darker particle with an interplanar spacing of 0.31 nm at the edge. This spacing can either attribute to CeO2(111) or PdO(100) plane, which is again hard to make a judgment of Pd structure. Thus, calculation of lattice distance is not a sufficient way to distinguish PdO from CeO$_2$ structure.

Figure 3.3 STEM images of fresh 1wt% Pd/CeO$_2$ and Pd/MC
As introduced in experimental section, the morphology and elemental distribution of Ce, Mn, and Pd in the 1wt% Pd/MC catalyst can be determined by STEM-EDX, as shown in figure 3.4. The freshly calcined sample comprises nanoparticles with spherical or elliptical shapes and sizes in the range of 20 and 40 nm. The high-resolution elemental mapping of the Pd/MC sample is able to distinguish different elements and indicates that all Ce and Mn are uniformly distributed within the sample structure, confirming the formation of a Mn-Ce solid solution. Pd mapping clearly shows that Pd is highly dispersed on the MC support, in consistent with XRD results.

Figure 3.4 STEM images and high-resolution elemental mapping of the calcined 1 wt% Pd/MC. The STEM mapping was conducted by Dr. Michael J. Lance.
XPS was conducted to investigate Pd oxidation state and speciation on the CeO$_2$ and MC supports. As shown in figure 3.5, the 3d$_{5/2}$ peak of the PdO reference sample locates at 336.6±0.2 eV with a full width half maximum (FWHM) of 1.16 eV, which is consistent with the literature [83]. The Pd 3d$_{5/2}$ peak of 1 wt% Pd-CeO$_2$ can be deconvoluted into two peaks at 337.7±0.2 and 336.5±0.2 eV with a FWHM of 1.46 eV and 1.16 eV, respectively. In the case of 1 wt% Pd/MC, only a high binding energy peak is detected at 337.7 eV with a FWHM of 1.46 eV. The lower binding energy peak at 336.5±0.2 eV is similar to the PdO reference sample and can be attributed to the crystalline PdO phase, while the higher binding energy peak might be due to the formation of highly dispersed Pd$^{2+}$ species or Pd$_x$Ce$_{1-x}$O$_2$$_{-\delta}$ interaction phase [86, 87, 111-112]. The crystalline PdO phase observed on 1 wt% Pd/CeO$_2$ accounts for 21% of the total Pd amount. As shown in figure 3.5, increasing Pd loading to 5 wt% on CeO$_2$ and MC does not affect Pd speciation. The 5 wt% Pd samples show similar Pd 3d core level spectra as the 1 wt% Pd samples. With the increased Pd loading, the MC support can still maintain all Pd species at a high Pd 3d$_{5/2}$ binding energy of 337.7±0.2 eV. The 1.1 eV binding energy shift compared to the PdO reference sample could be due to the particle size influence on metal binding energy that arises from final-state screening effects. As the particle size decreases, the d-electrons are more localized and become less effective to screen the hole created by the photoemission. This effect leads to a decrease in relaxation energy of the final state and thereby increases the apparent binding energy [113-115]. As the Pd loading is decreased to 0.5 wt% on CeO$_2$, the Pd 3d binding energy for crystalline PdO phase disappears and only a high binding energy peak at 337.7±0.2 eV, corresponding to highly dispersed PdO nanoparticles, is observed. These results indicate
that highly dispersed PdO nanoparticles form first on the CeO$_2$ surface with the addition of small Pd loadings (0.5 wt%). The crystalline PdO phase forms at Pd loadings in between 0.5 wt% and 1 wt%, and its relative amount remains stable above Pd loadings of 1 wt%.

**Figure 3.5** Pd 3d core-level XPS of the calcined Pd catalyst.

The oxidation state of Pd is further investigated through XAS experiments. Figure 3.6 shows the Pd K-edge XANES spectra of the 1 wt% Pd/CeO$_2$ and Pd/MC samples in the presence of He at room temperature. Both Pd foil and PdO were characterized as a reference sample. As shown in figure 3.6, the absorption edge of the PdO is measured to
be 24353 eV, which is consistent with the value in the literature [79]. In comparison to the XAS of the PdO reference sample, the Pd K-edge of Pd/CeO$_2$ and Pd/MC samples shifts to higher absorption energies by 0.6±0.2eV and 0.9±0.2eV, respectively. Such shifts are likely due to the chemical interaction of Pd$^{2+}$ species with the support [116]. In any case, the absorption energy of the Pd K-edge for both Pd/CeO$_2$ and Pd/MC samples is above that of the Pd foil and shows similar features to the one of PdO. These results indicate that Pd is likely in the form of Pd$^{2+}$ and no metallic palladium (Pd$^0$) exists in the freshly calcined samples. This is also in agreement with the XPS analysis, in which the Pd 3d$_{5/2}$ binding energy at 335.3 eV corresponding to Pd$^0$ is not pronounced on the freshly calcined samples.

**Figure 3.6** Pd K-edge XANES spectra of 1 wt% Pd/CeO$_2$ and 1 wt% Pd/MC recorded in He flow at room temperature. PdO and Pd foil are shown as a reference.
3.3.2. CO oxidation activity

Figure 3.7 shows the catalytic activity of the CeO$_2$, MC, 1wt% Pd/CeO$_2$ and 1 wt% Pd/MC samples for CO oxidation. The CeO$_2$ support has almost no catalytic activity for CO oxidation under 250°C. After incorporation of Mn into the CeO$_2$ lattice, the $T_{90}$ (temperature at which 90% CO conversion occurs) of the MC support decreases from 400°C to 150°C. The promotional effect of Mn addition for CO oxidation is likely due to a redox cycle between Ce$^{3+}$/Ce$^{4+}$ and Mn$^{4+}$/Mn$^{3+}$/Mn$^{2+}$ ions, which increases the lattice oxygen mobility and redox property [117-118]. The improved oxygen mobility and redox property of the MC support could be associated with the decreased formation energy of oxygen vacancies [117]. It is proposed that the incorporation of Mn$^{x+}$ ions into the CeO$_2$ (111) can decrease the single oxygen vacancy formation energy by inducing an unfilled Mn$_{3d}$-O$_{2p}$ gap state between the O $2p$ valance band and the Ce $4f$ conduction band [118].

After impregnation of 1 wt% Pd, the Pd/CeO$_2$ catalyst shows almost 100% CO conversion at 100°C, but decreases to ca. 40% at 50°C. In the case of Pd/MC, almost 100% of the CO is already converted at 50°C and such high conversion is maintained with increasing temperature.

The TOFs of Pd/CeO$_2$ and Pd/MC can be calculated assuming that either all of the Pd content or highly dispersed Pd species are active for CO oxidation [91]. If all the Pd content on the support is active, the TOFs of Pd/CeO$_2$ and Pd/MC are found to be 0.032 s$^{-1}$ and 0.072 s$^{-1}$ at 50°C, respectively. Although the highly dispersed Pd species are considered as an active site, the TOF of Pd/CeO$_2$ slightly increases to 0.04 s$^{-1}$. These results indicate that CO conversion of Pd/CeO$_2$ and Pd/MC is not linearly correlated with the amount of highly dispersed PdO nanoparticles present on the surface, suggesting that
the dispersion of PdO nanoparticles is not the only factor that controls the catalytic activity at low temperatures.

**Figure 3.7** CO oxidation activity of CeO$_2$, MC and 1wt% Pd supported catalysts: CO/O$_2$ ratio of 2:5 and GHSV = 40,000 h$^{-1}$

CO oxidation is generally accepted to follow the Mars-Van Krevelen mechanism on the Pd-Ce based catalysts [119]. Active supports, e.g. CeO$_2$ and MC can participate the reaction by providing reactive lattice oxygen for CO oxidation [83]. Therefore, the high CO oxidation activity observed over Pd/MC could similarly be related with the lower oxygen vacancy formation energy [117-118]. To further understand the high
activity observed over Pd/MC at low temperatures, a series of in-situ and ex-situ characterization experiments were conducted.

3.3.3. In-situ XAS experiments

In-situ XAS experiments were conducted over the 1 wt% Pd/CeO$_2$ and Pd/MC samples to determine the change in Pd oxidation state during CO oxidation. For these experiments, a higher CO/O$_2$ ratio (1:0.7) was employed compared to the reactor tests (figure 3.7). This higher CO/O$_2$ ratio is not expected to impact the CO conversion mechanism in the presence of excess oxygen, as the reaction order is reported to be positive and nearly zero with respect to CO and O$_2$ on Pd/CeO$_2$, respectively [119]. The reactions with CO/O$_2$ ration (1:0.7) were tested and shown in figure 3.8. The CO conversion of Pd/CeO$_2$ and Pd/MC are similar under both high and low CO/O$_2$ ratio reaction conditions. This also suggests that Pd/MC may be able to work in other lean O$_2$ applications.

![Figure 3.8 CO oxidation activities of Pd catalysts under high and low CO/O$_2$ ratio.](image)

Figure 3.8 CO oxidation activities of Pd catalysts under high and low CO/O$_2$ ratio.
A linear combination fitting is employed to the XANES spectra of Pd/CeO$_2$ and Pd/MC via Pd foil and PdO reference samples to determine the change in the Pd oxidation state [120]. As shown in figure 3.9 and table 3.1, upon injection of CO and O$_2$ at RT, a new feature appears at 24390 eV, corresponding to Pd$^0$ in the Pd/CeO$_2$ spectra. The quantification of Pd$^0$ formations on Pd/CeO$_2$ reveals that approximately 30±5% of Pd$^{2+}$ is reduced to Pd$^0$ at 50°C. In comparison, there is only slight change of the XANES spectra of Pd/MC upon CO oxidation and up to 8±5% of Pd$^{2+}$ is reduced to Pd$^0$. This indicates that the MC support can maintain almost all the Pd content in the oxidized state during CO oxidation.

The Pd K-edge EXAFS spectra of Pd/CeO$_2$ and Pd/MnO$_x$-CeO$_2$ samples were analyzed to determine the change in the local Pd structure during CO oxidation. A PdO bulk structure model is used to fit the data, as shown in figure 3.10. Upon CO and O$_2$ injection, the FT of $k^3$-weighted of Pd K-edge EXAFS spectra of Pd/CeO$_2$ shows new features at around 2.5 Å (phase uncorrected). These new features are visible at all temperatures and correspond to metallic Pd$^0$ (Pd-Pd shell) due to the reduction of PdO during CO oxidation, while Pd/MC does not show significant change. This is consistent with XANES results.
Figure 3.9 Pd K-edge XANES spectra of 1 wt% Pd supported catalysts during CO oxidation.
Figure 3.10 The FT of $k^3$-weighted of Pd K-edge EXAFS spectra of Pd/CeO$_2$ (top) and Pd/MC (bottom) during CO oxidation. The EXAFS data is analyzed by Dr. Erdem Sasmaz.
To identify different Pd\(^{2+}\) species formed on the catalyst surface after the in-situ XAS experiments, the catalysts were re-characterized via XPS. As shown in figure 3.11, Pd/MC shows only one single Pd 3d\(_{5/2}\) peak at 337.7 eV with the same FWHM that was observed on the freshly calcined sample, shown in figure 3.5. In agreement with the XANES analysis, the Pd\(^{2+}\) phase is maintained after CO oxidation on the MC support. In the case of Pd/CeO\(_2\), an additional Pd 3d\(_{5/2}\) peak forms at 335.3 eV, corresponding to Pd\(^0\) [90]. Quantification of the Pd 3d peaks of the Pd/CeO\(_2\) spectrum reveals that 22% of the oxidized Pd amount is reduced to Pd\(^0\) after CO oxidation. The amount of both oxidized Pd phases on CeO\(_2\), i.e. highly dispersed PdO nanoparticles and crystalline PdO, decreases to 66% and 12% after CO oxidation, respectively. The amount of Pd\(^0\) calculated by XPS is lower than the one estimated by in-situ XAS. This difference might be because of the re-oxidation of Pd\(^0\) after air exposure or surface sensitivity of XPS [119].

**Table 3.1** In situ XANES analysis of the Pd catalysts during He treatment and CO oxidation\(^a\)

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Pd oxidation state</th>
<th>Percentage of Pd(^{2+}) or Pd(^0) at different conditions (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>He</td>
</tr>
<tr>
<td>Pd/CeO(_2)</td>
<td>Pd(^{2+}) (±5%)</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>Pd(^0) (±5%)</td>
<td>0</td>
</tr>
<tr>
<td>Pd/MC</td>
<td>Pd(^{2+}) (±5%)</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>Pd(^0) (±5%)</td>
<td>0</td>
</tr>
</tbody>
</table>

\(^a\) The XANES spectra were fitted as a linear combination of the Pd foil spectra and the spectra of PdO reference.
Figure 3.11 Pd 3d core-level XPS of 1wt% Pd supported catalysts after in-situ XAS experiment.

3.3.4. In-situ DRIFTs experiments

In-situ DRIFTs experiments were performed at 50°C to evaluate the Pd adsorption sites during CO exposure over Pd/CeO$_2$ and Pd/MC. The IR spectra were collected as a function of time to determine the reducibility of the oxidized Pd sites on the supports. As shown in figure 3.12, Pd/CeO$_2$ shows a band at 2088 cm$^{-1}$ after 30 s of CO exposure, which is assigned to CO adsorbed on an atop site of Pd$^0$ [42]. At the same time, a weak broad band appears between 1980–1800 cm$^{-1}$, corresponding to chemisorbed CO on Pd$^0$ bridge (1980–1860 cm$^{-1}$) and threefold hollow sites (1920–1800 cm$^{-1}$) [42]. CO adsorbed on Pd$^{n+}$ sites in the range of 2150-2100 cm$^{-1}$ is not observed during these experiments, which could be due to the fast reduction of Pd$^{2+}$ at high CO concentrations,
shown in chapter 4. The integrated peak area of the IR bands for atop, bridge-hollow sites as well as gas phase CO$_2$ for both catalysts is plotted as a function of CO exposure time, as shown in figure 3.12c and 3.12d. Unlike Pd/CeO$_2$, Pd/MC shows significant gas phase CO$_2$ band in the first 30 s of CO exposure, meanwhile no bands for CO adsorbed on Pd$^0$ sites could be detected. After 60 s of CO exposure, a band for CO adsorbed on atop Pd$^0$ sites at 2092 cm$^{-1}$ begins to grow on the Pd/MC sample, while a broad band at 1980-1800 cm$^{-1}$, corresponding to bridge and hollow sites appears only after 120 s of CO exposure. As the reaction continues, the intensity of all these sites grows appreciably. In addition to the CO bands, carbonate species form on the surface of both catalysts in the spectra range between 1650 and 1150 cm$^{-1}$ during the first 30 s of CO exposure (see figure 3.13), indicating that surface oxygen species might be responsible for the formation of carbonate species [121].

The DRIFTs experiments reveal that oxidized Pd on CeO$_2$ can be reduced immediately in the first 30 s of CO exposure, forming Pd$^0$ sites. In the case of Pd/MC, Pd$^{2+}$ species do not get reduced during CO adsorption immediately. Since there is no gas phase O$_2$ fed to the DRIFTs cell, Pd$^0$ is likely get re-oxidized by the lattice oxygen from the supports, which is in agreement with the re-oxidation behavior observed on the Pt/CeO$_2$ catalysts [122]. However, this re-oxidation on MC might be fast enough that the CO-Pd$^0$ band could not be detected until the first 60 s of CO exposure, while there is still CO$_2$ production during this time.
Figure 3.12 a,b) Baseline corrected in-situ DRIFT spectra of CO chemisorption over Pd catalysts. c,d) Peak area integral of CO adsorption sites and CO\textsubscript{2}. Gas phase CO band was subtracted from atop Pd\textsuperscript{0}-CO sites.

Appearance of the bands for the adsorbed CO on bridge and hollow sites after 120 s implies that MC can suppress the formation of adjacent metallic Pd-Pd sites. The higher re-oxidation capability of MC again can be attributed to the decreased formation energy of oxygen vacancies [117-118]. In addition, many studies reported that a charge transfer exists between PGM and CeO\textsubscript{2} [123-125], which could be coupled with oxygen transfer for low temperature CO oxidation activity. During the charge transfer, Pd\textsuperscript{0} can transfer
electrons to Ce$^{4+}$, forming oxidized Pd and Ce$^{3+}$ with oxygen vacancy, which can facilitate the release of lattice oxygen [123-125].

![Figure 3.13](image_url) a,b) Baseline corrected in-situ DRIFT spectra of CO chemisorption over Pd catalysts. c) Peak area integral of peaks range from 1800 to 1100 cm$^{-1}$.

**3.3.5. Reducibility of lattice oxygen**

Reducibility of the lattice oxygen is investigated through H$_2$-TPR and CO/O$_2$ transient experiments. As shown in figure 3.14, the CeO$_2$ support exhibits two weak reduction peaks at around 500°C and 800°C, which can be attributed to the reduction of surface and bulk oxygen species, respectively [126]. The reduction profile of MC also shows two reduction peaks at lower temperatures than CeO$_2$. The first reduction peak of
MC at around 250°C corresponds to the reduction of Mn$^{4+}$ to Mn$^{2+}$/Mn$^{3+}$, while the second peak at 370°C can be attributed to the reduction of Mn$^{2+}$/Mn$^{3+}$ to Mn$^{2+}$ and surface oxygen of CeO$_2$ [127]. The downshift in the reduction temperature after Mn doping might be due to the facile redox cycle and enhanced oxygen mobility [127]. It is also possible that dissolution of MnO$_x$-CeO$_2$ solid solution during H$_2$ reduction can affect the TPR profile. At lower reduction temperatures, e.g. 250°C, the reduced Mn$^{3+}$ may not necessarily separate from the CeO$_2$ fluorite structure, as reported after multiple H$_2$-O$_2$ redox cycles [128]. However, it is possible that further reduction of Mn$^{3+}$ to Mn$^{2+}$ at 370°C might lead to a distortion in the fluorite lattice and eventually a phase separation.

With the addition of Pd, 1wt% Pd/CeO$_2$ shows a reduction peak at 140°C, which can be ascribed to the reduction of PdO to Pd$^0$ [100]. The amount of H$_2$ consumed at 140°C is calculated to be 2.1*10$^{-5}$ mol. This value is close to the amount of Pd (1.9*10$^{-5}$ mol), calculated using the actual metal loading reported in section 2.1. The similarities in between the amount of H$_2$ consumed and the Pd content in the CeO$_2$ was also reported in the literature and is consistent with this work [129]. Based on the XPS and XAS results, we can also assume that all the Pd in the sample is oxidized to PdO. In the case of Pd/MC, the reduction peaks of the MC support observed at 250°C and 370°C disappear and a single reduction peak at 140°C with a total H$_2$ consumption of 4.1*10$^{-4}$ mol is observed. This value is approximately 20 times bigger than the actual Pd amount on MC and close to the measured H$_2$ consumption of the MC support (4.3*10$^{-4}$ mol). The similar amounts of H$_2$ consumed over Pd/MC and MC indicate that the bulk lattice oxygen of MC can be extracted and reacted at lower temperatures in the presence of Pd. The disappearance of the high temperature reduction peaks on the Pd/MC sample can be
attributed to lattice oxygen reduction by H₂ spillover or oxygen reverse spillover from the support [79-81, 130], which is also pronounced in the XAS and DRIFTs experiments. As shown in figure 3.11, the lack of CO-Pd⁰ bands during the first 30 s of CO exposure reveals that the Pd²⁺ can be reduced by CO and then re-oxidized by the lattice oxygen from the MC support. Such oxygen reverse spillover contributes to the stabilization of Pd²⁺ during CO oxidation, as shown in figure 3.9.

Figure 3.14 H₂-TPR profiles of the CeO₂, MC, and 1 wt% Pd catalysts.

In addition to the H₂-TPR experiments, CO/O₂ transient pulse experiments were carried out at 50°C to evaluate the oxygen transfer of the Pd deposited CeO₂ and MC supports. As shown in figure 3.15, CO₂ is immediately produced on Pd/CeO₂ and Pd/MC upon exposure to CO only, which is consistent with the DRIFTs experiments. The initial CO pulse produces 1.5*10⁻⁴ mol of CO₂ on Pd/MC, which is much higher than the amount of Pd²⁺ (ca. 2.0*10⁻⁵ mol) on the catalyst, indicating that the lattice oxygen from.
Figure 3.15 CO/O₂ transient reaction profile of 1 wt % Pd/CeO₂ and Pd/MC. Evolution of CO₂, O₂, CO signals were monitored as a function of time.
the support must be involved in the reduction. On the other hand, a much smaller amount of CO\(_2\) (8.1*10\(^{-6}\) mol) is produced over Pd/CeO\(_2\), suggesting that the lattice oxygen is less likely to react with CO at low temperatures. Upon exposure to O\(_2\), CO\(_2\) is produced more due to the decomposition of carbonate species on the support and reaction of chemisorbed CO on Pd [131-132]. After four pulse cycles of CO and O\(_2\) injection, CO\(_2\) production stabilizes at around 2.0*10\(^{-5}\) mol and 7.4*10\(^{-6}\) mol for Pd/MC and Pd/CeO\(_2\), respectively. The ratio of the steady state CO\(_2\) production (2.7) of Pd/MC and Pd/CeO\(_2\) at 50°C in the CO/O\(_2\) transient pulse experiments is consistent with one (2.5) in the CO oxidation experiments. This suggests that CO adsorption is not the rate limiting step for CO oxidation. The low CO\(_2\) production on Pd/CeO\(_2\) implies that Pd/MC can release lattice oxygen easier than Pd/CeO\(_2\). The decrease in steady state CO\(_2\) production of Pd/CeO\(_2\) and Pd/MC might be due to the limited oxygen transfer rate or accumulation of different carbonate species on the surface that partially block adsorption of O\(_2\) [133].

Ce\(^{3+}\)/Ce\(_{\text{total}}\) ratio sometimes are used to reflect catalysts redox property. Higher Ce\(^{3+}\) amount may lead to higher oxygen storage and release capacity [81-93]. Here Ce 3d XPS spectra of Pd/CeO\(_2\) and Pd/MC are fitted to calculate Ce\(^{3+}\) amount in the catalyst surface regime, shown in figure 3.16. The Ce\(^{3+}\)/Ce\(_{\text{total}}\) ratio of Pd/CeO\(_2\) is 20.4%, while for Pd/MC, the number is only 7%. The Ce\(^{3+}\) amount and actual redox capacity looks contradictory to the trend. Recent study shows that directly compare Ce\(^{3+}\) amount of fresh sample is not accurate to relate with OSC of Ce sample. Researchers demonstrated that active Ce\(^{3+}\) species in a ceria-supported platinum catalyst during CO oxidation are short-lived and therefore cannot be observed under steady-state conditions[134]. Using time-resolved resonant X-ray emission spectroscopy, they could quantitatively correlate the
The initial rate of Ce$^{3+}$ formation under transient conditions to the overall rate of CO oxidation under steady-state conditions and showed that ceria reduction is a kinetically relevant step in CO oxidation, whereas a fraction of Ce$^{3+}$ was present as spectators. In addition, introducing Mn into CeO$_2$ lattice probably improve the redox activity of surface Ce species and lead to higher reaction rate. Hence, it is not necessary to compare Ce$^{3+}$ amount to determine catalysts redox activity and OSC. More reasonable way is to determine the redox rate during reaction.

### 3.3.6 Effect of reaction time and Pd loading on CO conversion

Figure 3.17 illustrates the CO conversion as function of time at room temperature over the Pd/MC catalyst. In this experiment, the furnace was kept off and the initial catalyst bed temperature is room temperature (ca. 25°C). Once introduced CO, the catalyst bed temperature increased to ca. 50°C due to exothermal reaction. Clearly, the CO conversion (ca. 95%) over the Pd/MC catalyst remained unchanged even after 8 h time-on-stream. In addition, the catalyst bed temperature maintains the same at 50°C as well. That is, CO in feed gas was completely oxidized into CO$_2$ over the Pd/MC catalyst. From the previous in-situ XANES, XPS after XAS experiments and CO/O$_2$ pulse results, it is known that the activity comes from the excellent oxygen transfer interaction between Pd and the MC support, meanwhile without Pd oxidation state change. This long time experiment further suggests that such interaction is sustainable. The redox features of the Pd/MC catalysts are quite stable under the CO oxidation atmosphere at low temperature.
Figure 3.16  Ce 3d core-level XPS of the calcined Pd catalysts
Figure 3.17 Effect of reaction time on CO conversion of Pd/MC without heating by furnace.

From the economical point of view, if catalyst can maintain the same activity with the less Pd loading, it will have much lower price since Pd is an expensive material. To evaluate the Pd loading effect, 0.2 wt% and 0.5 wt% Pd/MC sample were prepared using the same method as 1 wt% sample. The effect of Pd loading on activity of 0.2%, 0.5% and 1% Pd/MC catalysts was investigated at a temperature range of 50–450°C (figure 3.18). Decreasing the Pd loading to 0.5% shows similar activity as the 1% sample. Only a slight decrease at 50°C is observed. However, further reducing the Pd loading to 0.2 % can cause significant activity drop from 95% to 70%. The TOF at 50°C of the 0.2% sample is 0.252 s⁻¹, which is 3.5 times higher than the 1% Pd/MC sample. Since not all CO fully
converted to CO$_2$, this TOF can reflect the maximum activity of each Pd site at certain temperature. TOF of 0.2% Pd/MC is ca.8 times higher than the TOF of 1% Pd/CeO$_2$. This comparison is more accurate to reflect the activity of Pd site because both catalysts show less than 100% CO conversion and each Pd site is fully used. Such results further indicate that Pd on MC is much more active than the Pd on CeO$_2$. Comparing with the Pd-Ce catalysts reported in other references, the 0.2% Pd loading on MC still shows higher TOF and CO conversion to those catalysts have even higher Pd loading[94-99]. This indicates that Pd/MC has good potential to lower the cost of CO oxidation catalyst, meanwhile keeps the high activity.

\[\text{Figure 3.18} \quad \text{Pd loading effect on CO conversion. CO/O}_2\text{ ratio of 2:5 and GHSV = 40,000 h}^{-1}.\]
3.4 Conclusion

In this work, the high activity of Pd/MC for low temperature CO oxidation is investigated through a series of characterization experiments. Our results indicate that highly dispersed PdO species can form on freshly calcined CeO$_2$ and MC supports. In-situ XAS experiments reveal that Pd$^{2+}$ species are reduced to Pd$^0$ on CeO$_2$ during CO oxidation, while Pd maintains its initial oxidation state on MC. The presence of stable Pd$^{2+}$ species on MC shows that Pd is re-oxidized by the lattice oxygen of MC.

Participation of lattice oxygen in the low temperature CO oxidation is also supported by the H$_2$-TPR and CO/O$_2$ transient pulse experiments. Despite the similar H$_2$ reduction temperatures observed for both Pd/CeO$_2$ and Pd/MC, the higher amount of H$_2$ consumed on Pd/MC indicates that more lattice oxygen of MC can be extracted at lower temperatures. Similarly, CO/O$_2$ transient pulse experiments imply that Pd/MC shows higher reducibility at 50°C in the presence of CO compared to one for Pd/CeO$_2$. Smaller amount of CO$_2$ produced on Pd/CeO$_2$ suggests that the lattice oxygen in the CeO$_2$ support is less likely to react with CO at 50°C. In the case of Pd/MC, a higher amount of oxygen is replenished and transferred from the gas phase O$_2$, leading to high CO oxidation activity at low temperatures.

Pd/MC redox ability is stable under long time reaction and shows high activity. Lowering the Pd loading to 0.5wt% does not affect activity, but further deceasing the loading to 0.2wt% reduce the CO conversion to 70% at 50°C.
Chapter 4

Evaluation of Mn and Sn modified Pd-Ce based catalysts for low-temperature diesel exhaust oxidation

4.1 Introduction

Diesel oxidation catalysts (DOCs) have been widely applied for the remediation of toxic pollutants, i.e., CO, hydrocarbons (HCs) SO₂, and NOx, from diesel-powered vehicles [135-136]. In previous chapter, the incorporation of Mn into the CeO₂ lattice improves the OSC and lattice oxygen reducibility of CeO₂, in which Pd/MnOₓ-CeOₓ (Pd/MC) catalyst showed high activity for CO oxidation at ambient temperature. It was reported that doping MC solid solution with low amount of Sn (<0.05% atomic) enhanced reducibility of the catalyst and prevented the growth of doped-ceria crystal grains leading to a better OSC and CO oxidation activity in comparison to pure ceria [137]. Another reference suggests that the SnO₂-MnOₓ-CeOₓ (SMC) catalyst indicated a better SO₂ tolerance in the NH₃-SCR, and while still maintaining high NO conversion at low temperature [137].

For practical implementation of a cold start automobile exhaust catalyst, the catalyst preferably maintain its initial activity against severe operating conditions such as changing exhaust temperature, steam, high and low space velocities, and traces of SO₂ [138-140]. However, the effects of these conditions are rarely reported over the Pd/CeO₂
based catalysts that often synthesized via aforementioned complex procedures [94-99,108]. Hence, catalysts having excellent LTA for CO oxidation at room temperature and stability under severe conditions need to be developed using simpler, scalable and more economical synthesis techniques considering the ultimate practical application.

In this work, a new Pd/SnO$_2$-MnO$_x$-CeO$_x$ (Pd/SMC) was synthesized. Then the activity of Pd/CeO$_2$, Pd/MC and Pd/SMC catalysts were evaluated for CO and hydrocarbon oxidation under simulated diesel exhaust gas conditions. Catalyst performance tests were conducted following the low temperature diesel combustion (LTC-D) protocol [141]. The interaction of CO and C$_3$H$_6$ with the surface active sites was investigated using in-situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTs). The evaluation and characterization results were combined to explain HC deactivation over Pd/Ce based catalysts. At last the CO oxidation activity of Pd/SMC and Pd/MC are compared under SO$_2$ poisoning condition.

4.2 Experimental

4.2.1 Catalysts preparation

The SMC supports were prepared by an ultrasonic assisted co-precipitation method, where SnCl$_2$, Mn(NO$_3$)$_2$, and Ce(NO$_3$)$_3$, with a mole ratio of 1:4:5, were used as the catalyst precursors and (NH$_4$)$_2$CO$_3$ (1 mol L$^{-1}$) as a precipitator. The paste obtained from co-precipitation was treated by ultrasound for 2 h, followed by subsequent filtration, washing with deionized water, drying in air overnight at 105°C, and calcination in air at 500°C for 6 h. The Pd/SMC with 1 wt% Pd loading was synthesized by impregnation. The SMC support was immersed into the aqueous Pd(NO$_3$)$_2$ solution and dried at room temperature while stirring. Subsequently, the solid was calcined at 550°C for 3 h in air.
Similarly, Pd/CeO$_2$ and Pd/MC (Mn:Ce ratio = 1:1) were synthesized by the same co-precipitation and Pd impregnation methods. The actual Pd loading over the Pd/SMC, Pd/MC, and Pd/CeO$_2$ catalysts were measured using atomic absorption spectroscopy and were found to be 1.0±0.05 wt%, 1.1±0.05 wt% and 1.0 ± 0.05 wt %, respectively.

4.2.2 Activity tests under simulated diesel exhaust

The low temperature diesel combustion (LTC-D) evaluation protocol was used as specified in the “After treatment Protocols for Catalyst Characterization and Performance Evaluation: Low-Temperature Oxidation Catalyst Test Protocol” published by the Advanced Combustion and Emission Control (ACEC) Technical Team: Low-Temperature After treatment Group. Unless otherwise specified, catalyst amounts and gas flow rates were normalized to give a space velocity of 200 L g$^{-1}$ hr$^{-1}$. Typically, this amounted to 100 mg of sample and a flow rate of ~333 sccm. Before activity was measured, catalysts were degreened once at 700°C for 4 h and then pretreated before each evaluation at 600°C for 20 min in [H$_2$O] = 6%, [CO$_2$] = 6%, and [O$_2$] = 12% balanced with Ar. Activity was then measured as a function of temperature at a rate of 2 °C/min to a maximum temperature of 500°C. This consisted of a mixture of [O$_2$] = 12%, [H$_2$O] = 6%, [CO$_2$] = 6%, [H$_2$] = 400 ppm, [NO] = 100 ppm, [CO] = 2000 ppm, [C$_2$H$_4$] = 833.5 ppm, [C$_3$H$_6$] = 333.3 ppm, [C$_3$H$_8$] = 111 ppm, and balanced with Ar. Water was introduced into the system by bubbling Ar gas through water heated at 50°C and delivered via heated gas lines maintained at 150°C. Oxidation activities were measured using a gas chromatography (Agilent 490 Micro GC). The conversion is calculated using the following expression: (X/C$_{\text{max}}$)*100 where X is the ppm obtained from GC.
integration of the given reactant peak and Cmax is the calibration ppm obtained from the GC during bypass measurement.

In addition to the LTC-D evaluation, CO and C₃H₆ oxidation were conducted in a plug flow reactor under atmospheric pressure and CO conversion was measured by a differentially pumped mass spectrometer (MS, Hiden HAL IV RC). A gas mixture of 2.0% CO (99.999% CO, Airgas), 1000 ppm C₃H₆ (1% C₃H₆ in He, Praxair), 5% O₂ (99.9999% O₂, Airgas) and balance Ar (99.9999% Ar, Airgas) was fed to the reactor via mass flow controllers (Brooks 5850E). 200 mg of catalyst supported with quartz wool was placed in the reactor for each run and no pretreatment was performed before the reaction. The gas hourly space velocity (GHSV) for all experiments was 40,000 h⁻¹. Less than ±5% conversion error is calculated by reparative tests.

The SO₂ poisoning experiments are conducted with a gas mixture of 2.0% CO, 5% O₂ 200 ppm SO₂ (2% SO₂ in N₂) and balance Ar. 500 mg of catalyst supported with quartz wool was placed in the reactor for each run and no pretreatment was performed before the reaction. The gas hourly space velocity (GHSV) for all experiments was 40,000 h⁻¹.

4.2.3 Catalyst characterization

Powder X-ray diffraction (XRD) data for fresh samples were collected on a RigakuMiniflex II desktop diffractometer using a Cu Kα source with D/teX Ultra 250 silicon strip detector. XRD for degreening comparisons were taken on a Panalytical Empyrean XRD operated at 40kV and 40mA using a Cu Kα source. X-ray photoelectron spectroscopy (XPS) experiments were carried out on a Kratos AxidUltra DLD XPS
system equipped with a hemispherical energy analyzer. A monochromatic Al Kα X-ray source (1486.6 eV) was operated at 15 kV and 120 W. Adventitious carbon at 284.8 eV (C1s) was used as a reference of binding energy. The high-resolution elemental mapping and imaging of particles were collected using a FEI Talos F200X scanning transmission electron microscope (STEM). The surface area of samples were measured on a Micromeritics ASAP 2020 instrument by the N₂ adsorption at 77 K and calculated by the Brunauer–Emmett–Teller (BET) method. The surface area for CeO₂, MC, SMC are 60, 62 and 82 m²/g, respectively.

DRIFTs experiments were performed using a Bruker Equinox 55 spectrometer equipped with a deuterated triglycine sulfate (DTGS) detector. Oxidation reactions at 100°C over these catalysts were studied with an accumulation of 64 scans at a resolution of 2 cm⁻¹. The catalysts were pretreated at 400°C in the DRIFTS cell for 30 min in 10% O₂/Ar. Subsequently, the system was cooled down to 100°C and a background was recorded. CO and C₃H₆ oxidation studies over the catalysts were carried out in the following sequence: 1) CO+O₂ for 30 min, 2) C₃H₆+CO+O₂ for at least 10 min, 3) CO+O₂ for 10 min. Inlet gas concentrations are 0.6% CO, 10% O₂, 0.1% C₃H₆ (when used) with Ar balance.

4.3 Results and discussion

4.3.1 Catalyst structure

The XRD profiles of the Pd impregnated ceria based catalysts are shown in figure 4.1. The diffraction peaks observed over Pd/CeO₂ and Pd/MC can be attributed to the (111), (200), (220) and (311) lattice planes of the cubic fluorite structure of CeO₂,
indicating that Mn and Ce formed a solid solution without appreciable phase separation [11]. The diffraction peaks corresponding to Pd metal (40.2°) or PdO (34°, 42°) are not observed in any catalysts, which can be attributed to the small Pd loading or formation of highly dispersed Pd species [25,100-101]. In the case of Pd/SMC, two additional diffraction peaks at 38° and 52° can be assigned to SnO₂ [142], indicating that SnO₂ segregates from the SMC solid solution. Based on (111) diffraction peak, crystallite size of CeO₂, MC, SMC support are 9.6nm, 3.17nm and 3.29nm, respectively.

Figure 4.1 Wide-angle XRD profiles of the fresh supported Pd catalysts and degreened Pd/CeO₂ (D-Pd/CeO₂) and Pd/MC (D-Pd/MC).

During the LTC-D evaluation protocol, the catalysts were degreened at 700°C for 4 h, which is higher than the calcination temperature (550°C) of the solid solution
catalysts. Possible phase separation of the degreened Pd/CeO$_2$ and Pd/MC samples was investigated via XRD. As shown in figure 4.1, the diffraction profiles of the fresh and degreened samples are similar to each other and no additional diffraction peaks for Pd, PdO and MnO$_x$ were observed after degreening.

The morphology and elemental distribution of Ce, Mn, and Pd for the 1wt% Pd/MC catalyst before and after degreening are shown in figure 4.2. The fresh sample comprises nanoparticles with spherical or elliptical shapes and sizes in the range of 20 and 40 nm. The EDX analysis of the fresh Pd/MC sample indicates that both Mn and Ce are uniformly distributed within the sample structure, confirming the formation of a Mn-Ce solid solution. Pd mapping clearly shows that the majority of the Pd is highly dispersed on the MC support. One small area of aggregated Pd can be seen at the center of the mapping. After degreening at 700°C, the sample shows a similar morphology of nanoparticles as the fresh sample. However, Mn and Ce are not uniformly distributed and some areas of Mn separate from the surrounding Ce. Additionally, Pd is not dispersed as well as in the fresh sample and more areas of Pd aggregates can be observed. The STEM-EDX analysis confirms that both Mn segregation from the Mn-Ce solid solution and Pd aggregation occur after degreening. The lack of MnO$_x$ and PdO diffraction peaks for the degreened sample in the XRD might be due the low concentration of Pd and low concentration of separated MnO$_x$ crystals. Higher magnification of fresh Pd/MC STEM-mapping is shown in chapter 3.
Figure 4.2 STEM images and EDX maps of 1 wt% Pd/MC before (a) and after (b) degreening. The STEM mapping was conducted by Dr. Michael J. Lance.

In the case of Pd/SMC, XPS was conducted to characterize the oxidation state of surface Pd species. As shown in figure 4.3, only one peak at 337.7 eV with a FWHM of 1.46 eV is present, while the lower binding energy peak at 336.5 eV, corresponding to the crystalline PdO phase, is not observed. The formation of high binding energy peak of Pd$^{2+}$ might be due to the SMSI and can be attributed to the formation of small PdO
clusters or palladium ceria interaction phase, Ce$_{1-x}$Pd$_x$O$_{2-\delta}$ [86,87, 111-112], which is similar to the Pd/MC sample.

![Figure 4.3 Pd 3d core-level XPS spectra of fresh Pd/SMC catalyst.](image)

4.3.2 Activity of Pd catalysts under diesel exhausts condition

The performance of the Pd supported catalysts was evaluated under the LTC-D protocol and conversions for CO and HCs are shown as a function of temperature in figure 4.4. For comparison, the light-off temperatures for CO and HCs at 50% conversion (T$_{50}$) and 90% conversion (T$_{90}$) are depicted in figure 4.5. Among the Pd supported catalysts, Pd/MC shows the lowest T$_{50}$ of 173±4°C for CO oxidation. Both Pd/CeO$_2$ and Pd/SMC indicate a similar T$_{50}$ for CO oxidation at 187±4°C and 191±4°C, respectively. The CO light-off curves for Pd/MC and Pd/SMC show a sigmoid shape with higher conversions than Pd/CeO$_2$ at temperatures below T$_{50}$, and spread over a wider
temperature range to reach T₉₀. The total hydrocarbon (THC) conversion includes the conversion of the sum of C₂H₄, C₃H₆ and C₃H₈ on a C₁ basis. Unlike the T₅₀ of CO, Pd/CeO₂ has the lowest T₅₀ (267±7°C) for THC, which is 20°C and 70°C lower than T₅₀ of Pd/MC and Pd/SMC, respectively. The shape of the light-off curves for all three hydrocarbons over Pd/MC and Pd/SMC look similar to that of CO. Oxidation of C₂H₄ and C₃H₈ starts at lower temperatures over Pd/MC and Pd/SMC than Pd/CeO₂, yet increases slower with increasing temperature, leading to a higher T₅₀ and T₉₀. For C₃H₆ oxidation, the conversion starts at similar temperatures for all three Pd catalysts, and both Pd/MC and Pd/CeO₂ demonstrate a T₅₀ of 214°C, which is lower than that of Pd/SMC of 246°C. However, the slope of the C₃H₆ light-off curve for Pd/CeO₂ above T₅₀ is higher than the other two catalysts leading to the lowest T₉₀ of 236°C.
Figure 4.4 Catalytic performance of the degreened Pd/CeO$_2$, Pd/MC, and Pd/SMC catalysts under simulated diesel exhaust oxidation. The tests were conducted by Dr. Andrew Binder and Dr. Todd Toops.
Figure 4.5 $T_{50}$ and $T_{90}$ of Pd catalysts for CO and HC conversion. * represents the maximum conversion if it is under 90%.

The presence of CO, NO, and HCs can inhibit their oxidation at low temperatures [2, 143]. Initially, CO can strongly adsorb onto active sites at low temperatures in the presence of NO and HCs, covering the majority of the catalyst surface. In this case, oxygen access to the catalytic sites is limited, resulting in a low CO oxidation rate [2]. Generally, the presence of HCs can limit CO oxidation, as both CO and HCs compete for the same Pd active sites. Light alkenes (i.e., $C_2H_4$, $C_3H_6$) can strongly adsorb onto active Pd sites, due to their double bonds [144]. When the temperature allows CO oxidation to start, $CO_2$ forms and desorbs from the surface, opening up active sites for CO and alkenes to competitively adsorb [2]. This competition limits CO access to the active sites and thus its subsequent oxidation. At certain temperatures, alkenes also start to react with oxygen
and their oxidation products desorb from the active sites [2,143]. In addition to the alkenes, NO can dissociatively adsorb on the active sites, competing with the adsorption of CO and HCs and inhibiting their oxidation [143, 145].

It was reported recently that crystalline PdO phase has higher activity in hydrocarbon oxidation than highly dispersed Pd\(^{2+}\) due to easier decomposition of intermediate, but highly dispersed Pd\(^{2+}\) and lattice oxygen mobility of support are important for CO oxidation[146]. Both MC and SMC supports demonstrate higher activity at under 170\(^{\circ}\)C. This is because Pd/MC has more highly dispersed Pd\(^{2+}\) and better lattice oxygen reducibility. It is likely that at higher temperatures, competitive adsorption of CO and HCs becomes the limiting factor for CO conversion [42]. At higher temperature above 170\(^{\circ}\)C, which reaches onset of C\(_3\)H\(_6\) oxidation temperature, since Pd/MC has less crystalline PdO phase, C\(_3\)H\(_6\) oxidation activity is lower than Pd/CeO\(_2\) and the slope of light-off curve increases slower. The C\(_3\)H\(_6\) inhibition is more severe on Pd/MC and cannot immediately free many sites for CO oxidation, so that at higher temperature the CO conversion increases slower than Pd/CeO\(_2\).

4.3.3. Effect of C\(_3\)H\(_6\) to CO oxidation

In order to get further insight into the hydrocarbon inhibition, propylene was chosen as a probe molecule to evaluate the change in the light-off curve of CO and surface active sites. CO oxidation was carried out over Pd/CeO\(_2\) and Pd/MC with and without the presence of C\(_3\)H\(_6\) and the light-off curves are shown in figure 4.6. Pd/CeO\(_2\) shows almost 100% CO conversion at 100\(^{\circ}\)C under CO+O\(_2\), but drops below 40% CO conversion at 50\(^{\circ}\)C, while Pd/MC still achieves almost 100% CO conversion at 50\(^{\circ}\)C [25]. Upon introduction of 1000 ppm C\(_3\)H\(_6\), the CO oxidation activity for both catalysts
drops significantly and both Pd/CeO₂ and Pd/MC show CO conversions below 10% at 50°C. As the catalyst temperature increases to 150°C, both catalysts can achieve over 95% conversion for CO and C₃H₆. The oxidation of C₃H₆ and CO show similar light-off curves, indicating that both molecules are attracted by the same active sites. The similar activity profiles observed over Pd/CeO₂ and Pd/MC indicate that modification of OSC of supports has little effect on CO oxidation in the presence of C₃H₆ [17,146]. In comparison to the light-off curves shown in figure 4.4, both CO and C₃H₆ oxidize at lower temperatures suggesting that competitive adsorption of C₂H₄ and NO has an influence on the oxidation profiles [143]. In addition, segregation of Mn-Ce solid solution or sintering of Pd can also contribute to the low activity at low temperature after degreening [35, 38-40].

To have a straightforward view of C₃H₆ inhibition effect, MS signals of CO, C₃H₆, O₂ and CO₂ are shown in figure 4.7 during temperature ramp from 100°C to 150°C for the Pd/MC sample. This temperature ramp process depicts the transient reaction state of the CO and C₃H₆ oxidation. Conversion for both CO and C₃H₆ is less than 10% at 100°C but over 95% at 150°C. In the MS, both CO and C₃H₆ show high signal intensity at 100°C. Once the temperature ramps up, both signal start to drop down until they reach to near 0 intensity. On the other hand, O₂ and CO₂ signal show a very significant peak during the ramp. This indicates there is extra carbon source that has been accumulated on the catalyst surface at 100°C. Based on previous discussion, this peak can be attributed to oxidation of adsorbed C₃H₆ that accumulated on the active site. There might be has some adsorbed CO exist on the catalyst as well at 100°C, which is shown from later DRIFTs results in figure 4.10.
Figure 4.6 CO and C₃H₆ oxidation activity of 1wt% Pd/CeO₂ and Pd/MC catalysts. 2% CO, 1000ppm C₃H₆ (when used), 5% O₂ and GHSV = 40,000 h⁻¹.
Figure 4.7 Oxidation of accumulated C$_3$H$_6$ on Pd/MC surface during temperature ramp from 100°C to 150°C. 2% CO, 1000ppm C$_3$H$_6$, 5% O$_2$ and GHSV = 40,000 h$^{-1}$.

It was widely reported that the pretreatment has a significant effect on Pd-based oxidation catalyst performance. In order to determine the degree effect on catalyst activity, Pd/MC was treated under the same LTC-D degreen condition. The XPS of degreened Pd/MC also show the same spectra as fresh sample, shown in figure 4.8.

The catalytic activity of degreened sample was tested in the plug flow reactor again, shown in supporting information figure 4.9. Similar conversion is observed as the fresh Pd/MC under CO oxidation and CO+C$_3$H$_6$ oxidation. This suggests that the level of Mn separation and Pd sintering is not severe enough to deactivate the catalyst.
**Figure 4.8** Pd 3d core-level XPS spectra of fresh and degreened Pd/MC catalysts.

**Figure 4.9** CO and C₃H₆ oxidation activity of degreened Pd/MC catalysts. 2% CO, 1000ppm C₃H₆ (when used), 5% O₂ and GHSV = 40,000 h⁻¹.
To determine the adsorption sites of CO and their evaluation in the presence of C$_3$H$_6$, in-situ DRIFTs was conducted over the Pd/CeO$_2$, Pd/MC, and Pd/SMC samples, shown in figure 4.10. The vibrational bands located in the range of 2110–1800 cm$^{-1}$ can be attributed to the adsorbed CO on metallic palladium (Pd$^0$), while the vibrational bands located at a higher wavenumbers around 2150-2130 cm$^{-1}$ correspond to CO adsorbed on ionic Pd$^{n+}$. The vibrational bands at 2390-2290 cm$^{-1}$ and 2220-2060 cm$^{-1}$ are characteristic for gaseous CO$_2$ and CO, respectively [42]. The bands at 2943 and 2860 cm$^{-1}$ can be assigned to the adsorption of bidentate formate species on Ce ions [39]. During CO oxidation, all three Pd catalysts show CO vibrational bands for CO-Pd$^{n+}$ sites. Despite the overlap with the gaseous CO band, the vibrational bands for the adsorbed CO adsorbed on atop sites of Pd$^0$ at 2100-2090 cm$^{-1}$ can be detected on Pd/CeO$_2$ and Pd/SMC. No obvious vibrational bands for the atop CO-Pd$^0$ sites can be identified on Pd/MC. Chemisorbed CO on the bridge (1980–1860 cm$^{-1}$) and threefold hollow (1920–1800 cm$^{-1}$) sites of the Pd$^0$ are observed over Pd/CeO$_2$ [25,42]. However, no vibrational bands for bridge or hollow sites are detected on Pd/MC and Pd/SMC.

XPS analysis of the fresh samples indicates that Pd is fully oxidized on the surface with an oxidation state of 2+. During CO oxidation, some of the oxidized Pd species are reduced and Pd exists in a mixture of Pd$^{n+}$/Pd$^0$ on Pd/CeO$_2$ and Pd/SMC. For Pd/CeO$_2$, the appearance of CO adsorbed on Pd bridge sites might be due to the formation of larger metallic Pd particles with bridge sites or the lower re-oxidation ability of the CeO$_2$ support [26]. The lack of any adsorbed CO on Pd$^0$ sites over Pd/MC during CO oxidation can be attributed to superior oxygen storage and mobility of the MC support.
Upon introduction of C$_3$H$_6$, the Pd$^{n+}$–CO band disappears due to the competitive adsorption of C$_3$H$_6$ or reduction of Pd$^{n+}$ to Pd$^0$ by C$_3$H$_6$ and its subsequent adsorption [30, 148]. Meanwhile, the gaseous CO$_2$ band intensity decreases and the C-H band in between 3000 and 2800 cm$^{-1}$ grows. CO oxidation is inhibited by C$_3$H$_6$, caused by the competitive adsorption and blocking of the precious metal (Pd, Pt, etc.) active sites by C$_3$H$_6$ [143]. Because the oxidation of hydrocarbons occurs at higher temperatures than CO, the sites with adsorbed C$_3$H$_6$ block CO adsorption and oxidation until the C$_3$H$_6$ is itself oxidized [16].

Upon removal of C$_3$H$_6$ from the gas-phase, the Pd$^{n+}$-CO band recovers on Pd/CeO$_2$ and Pd/SMC, albeit to a lower intensity, implying that CO coverage decreases. The band also shifts from its initial position of 2143 cm$^{-1}$ to 2136 cm$^{-1}$, which could indicate less weakly adsorbed CO. Meanwhile, the gaseous CO$_2$ band returns, also with a lower intensity compared to the spectra taken at initial CO+O$_2$. These results indicate that the activity for CO oxidation is not fully recovered over Pd/CeO$_2$ and Pd/SMC upon C$_3$H$_6$ removal, which is probably due to residual hydrocarbon species adsorbed on Pd$^{n+}$ sites. In the case of Pd/MC, the Pd$^{n+}$-CO band does not reappear after C$_3$H$_6$ removal. The differences observed in recovery of Pd actives sites on MC at 100$^\circ$C might be attributed to the different Pd formations and their interaction with the support.
Figure 4.10 Baseline corrected in-situ DRIFT spectra of oxidation reactions over Pd catalysts.
4.3.4 Effect of SO$_2$ poisoning, steam and GHSV

Figure 4.11 shows the conversion of CO oxidation over the Pd/SMC. Similar to Pd/MC, addition of Mn and Sn to Pd/CeO$_2$ can improve the activity, and the CO conversion reached to more than 90% from room temperature to 450°C, which is above some recently reported supported Pd catalysts [94-107]. For example, Pd/MnO$_x$-CeO$_2$ prepared by a surfactant-assisted co-precipitation followed by a hydrothermal method showed a $T_{90}$ of 60°C [108]. Ramping up and down tests shows overlapped CO conversion curves, indicating the activity is consistent and repetitive.

![Graph showing CO oxidation activity of Pd/SMC. CO/O$_2$ ratio of 2:5 and GHSV = 40,000 h$^{-1}$.](image)

**Figure 4.11** CO oxidation activity of Pd/SMC. CO/O$_2$ ratio of 2:5 and GHSV = 40,000 h$^{-1}$. 

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To be a potential catalyst for low temperature automobile emission control application, not only the catalyst requires high activity, but also its stability under severe exhaust condition is necessary to be evaluated. For instance, SO$_2$ present in an automobile exhaust gas could deactivate the catalyst by forming sulfate species that can block the active sites of the catalyst [149]. Furthermore, H$_2$O present in the range of 5 to 10 vol% in the automobile exhaust gas [150,151]has been reported to deactivate and increase the CO oxidation light-off temperature of Pd/Al$_2$O$_3$ catalysts by the growth of Pd particle[152].

Here, the catalytic activity of the best performed catalysts, i.e. Pd/MC and Pd/SMC, was evaluated as a function of time under 200 ppm SO$_2$ at room temperature. As shown in figure 4.12, both catalysts kept more than 90% CO conversion in the first ca.40min. However, after 40 min, the CO conversion over Pd/MC started to decrease and finally reached to 0% CO conversion at ca.90 min. On the other hand, the Pd/SMC showed better SO$_2$ poisoning resistance with a slower deactivation rate than Pd/MC. Even though the CO conversion over Pd/SMC started to decrease at the same time with Pd/MC, the total deactivation occurred at ca.130 min over Pd/SMC rather than 90 min over Pd/MC. This could be explained with the preferential formation of sulfate species on Mn rather than Ce over the MC catalyst. Once the Mn sites are occupied, sulfate species might form on the Ce sites. However, with the addition of Sn, sulfate species formed preferentially on Ce rather than Mn [137]. Such selective formation of sulfate species could affect the oxygen release and storage ability of the ceria based catalysts at low temperatures. Further tests revealed that SO$_2$ poisoning was reversible over the Pd/MC and Pd/SMC catalysts. As shown in figure 4.13, the catalyst temperature was ramped up
from room temperature to 450°C in the presence of SO₂. Oxidation of CO was completely recovered over both catalysts at temperatures above 250°C. This is attributed to the decrease of the poisoning effect of sulfation at temperatures higher than 200°C [153].

**Figure 4.12** CO oxidation activity of Pd-MC and Pd-SMC catalysts at room temperature with additional 200 ppm SO₂.

**Figure 4.13** CO conversion in the presence of 200 ppm SO₂ with temperature ramp from room temperature to 450°C. CO:O₂=2:5, GHSV=40,000h⁻¹
Due to the better SO₂ tolerance of Pd/SMC at room temperature, the catalyst has further been exposed to 8% H₂O during CO oxidation. Figure 4.14 shows the CO conversion of Pd/SMC in a temperature range of 150°C-450°C. The activity of Pd/SMC did not change compared to the results tested in dry condition indicating that H₂O does not have any effect to CO oxidation over Pd/SMC. Moreover, hydrothermal treatments (5% O₂, 8% H₂O, Ar balance, 12 hours) at 500°C and 750°C for the Pd/SMC catalyst were conducted to test the stability of Pd/SMC. It also shows that the Pd/SMC after steam aging for 12 hours at 500°C keeps the same activity as the fresh catalyst. Even if the aging temperature increases to 750°C, the Pd/SMC still keeps a good CO conversion with only slight deactivation under 150°C.

![Figure 4.14 Effect of H₂O and hydrothermal aging on Pd/SMC for CO conversion. CO: O2=2:5, 8% H₂O (when used), Ar balance.](image-url)

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In addition to the hydrothermal aging, the Pd/SMC catalyst was exposed to higher GHSV=120,000 h\(^{-1}\) and its CO oxidation activity was evaluated as a function of temperature, as shown in figure 4.15. Increasing space velocity did not change the performance of the catalyst from room temperature to 450°C. The Pd/SMC catalyst appears promising for low temperature CO oxidation in the presence of SO\(_2\) and H\(_2\)O.

**Figure 4.15** Effect of GHSV on Pd/SMC for CO conversion. CO: O\(_2\)=2:5, Ar balance.

### 4.4 Conclusion

Here, we evaluated the performance of the Pd impregnated Ce based catalysts for CO and HC oxidation under the LTC-D protocol. Both Pd/MC and Pd/SMC showed excellent CO oxidation activity at ambient temperature. Upon introduction of C\(_3\)H\(_6\), the
CO light-off curve shifts to higher temperatures, indicating a competitive adsorption between CO and C\textsubscript{3}H\textsubscript{6}. Simultaneous oxidation of CO and C\textsubscript{3}H\textsubscript{6} shows a similar light-off profile on both Pd/CeO\textsubscript{2} and Pd/MC, indicating that the OSC and lattice oxygen reducibility do not affect CO conversion in the presence of C\textsubscript{3}H\textsubscript{6}.

In the case of the simulated diesel exhaust gas, all catalysts show a CO oxidation T\textsubscript{50} below 200\textdegree C. Pd/MC achieves the lowest T\textsubscript{50} for CO at 173\textdegree C, whereas Pd/CeO\textsubscript{2} shows the lowest T\textsubscript{50} for THC at 267\textdegree C. The competitive adsorption of CO, NO and alkenes affects the light off curves of CO at both low and high temperatures. Degreening samples at 700\textdegree C can cause segregation of Mn from the solid solution and sintering of Pd nanoparticles. In-situ DRIFTs studies reveal that C\textsubscript{3}H\textsubscript{6} could immediately inhibit CO adsorption, and thereby its oxidation at 100\textdegree C. Upon introduction of C\textsubscript{3}H\textsubscript{6}, CO adsorbed on Pd\textsuperscript{n+} sites disappears over all catalysts and can be partially recovered over Pd/CeO\textsubscript{2} and Pd/SMC after C\textsubscript{3}H\textsubscript{6} is removed from the gas phase. However, Pd\textsuperscript{n+} sites over Pd/MC are completely blocked by C\textsubscript{3}H\textsubscript{6} and are not recovered for CO oxidation.

Pd/SMC showed better SO\textsubscript{2} resistance at room temperature than Pd/MC. Further experiments revealed that SO\textsubscript{2} poisoning was reversible at reaction temperatures above 200\textdegree C. The catalytic activity of the Pd/SMC did not change after hydrothermal aging indicating that Pd/SMC could be a promising catalyst for low temperature CO oxidation.
Chapter 5

Investigation of the Pd structure and reactivity on Mn doped α-Fe$_2$O$_3$ nanorod with controlled facet

5.1 Introduction

One of the classic strong metal–support interactions (SMSI) is the alteration of the charge state of the metal by electron transfer from or to a support which leads to an improvement of reactants activation and thus promotes the catalytic properties [154]. Recently, it was elucidated that d-band electronic perturbation of late-transition-metal catalysts that is induced by a subtle change in the structure of the support has a strong influence on the intrinsic reactivity [155-156]. Iron oxide supported Pd catalysts have been studied as model systems for the effect of SMSI in CO oxidation [157]. Electron transfer from Pd to FeO$_x$ coupled with oxygen transfer from FeO$_x$ to Pd during reaction is the current mechanistic understanding for the Pd-Fe system. However, the effect of d-band electronic perturbation has not yet been studied to get a complete understanding on further promoting the reactivity of Pd-Fe system.

Doping a secondary metal into a metal oxide support can change the support electronic structure; meanwhile maintaining the original crystal structure [158]. One the other hand, different exposed facets in the same metal oxide support can change the electronic structure of surface and greatly influence the Pd structure and reactivity as
well[146]. A feasible way to investigate the unsolved question above is to homogeneously dope a secondary metal into iron oxide support with structurally fixed and spatially uniform surface, to rule out the facets effect.

Herein, we designed Pd supported on α-Fe$_2$O$_3$ and Mn doped α-Fe$_{2-x}$Mn$_x$O$_3$ nanorods with the same hematite structure and exposed facets to study in more detail how SMSI depends on the electronic structure change of support. CO oxidation was used as a probe reaction to evaluate structure-activity relationships.

5.2 Experimental

Preparation of the Mn-doped α-FeOOH nanorods: All of the chemical reagents used here were of analytical grade without further purification. In a typical procedure, 0.256 g polyvinyl pyrrolidone (PVP: MWz 58,000) was dissolved into 20 mL of deionized water, while 1.8 g NaOH was dissolved in 10 mL of deionized water. Then FeCl$_3$ (7×10$^{-3}$ M) and MnCl$_2$·4H$_2$O (3.5×10$^{-3}$ M) were dissolved in deionized water (50 mL) and stirred to form a homogenous solution. The transparent solution of PVP and NaOH were slowly dropped into the above solution in turn. The whole mixture was stirred for another 20 min to obtain a homogeneous solution and then transferred into a 100 mL Teflon-lined stainless-steel autoclave. The autoclave was put into an oven at 120 °C for 12 h. After the autoclave was cooled to room temperature naturally, the resulting product was first washed with 15 wt% HCl solution twice (2 hours each time) and then rinsed with deionized water and absolute ethanol several times. The obtained sample was dried at 60 °C in vacuum for 12 h. In a contrast experiment, α-FeOOH nanorods were prepared through the same procedure but in the absence of MnCl$_2$·4H$_2$O.
Preparation of the Mn-doped $\alpha$-Fe$_2$O$_3$ nanorods: The Mn-doped $\alpha$-FeOOH nanorods were annealed in air at 300 °C for 4 h with a slow ramp rate of 1 °C min$^{-1}$. 1wt% Pd was loaded onto the iron-oxide based supports via an impregnation method and calcined at 300°C to produce Pd/$\alpha$-Fe$_2$O$_3$ and Pd/$\alpha$-Fe$_{2-x}$Mn$_x$O$_3$.

Similar to Pd-Ce based catalysts tests; CO oxidation was conducted in a plug flow reactor, where CO conversion was measured by a mass spectrometer. 200 mg of catalyst was placed in the reactor for each run. The gas mixture of 2.0% CO, 5% O$_2$ and balanced Ar was fed to the reactor at a GHSV of 40,000 h$^{-1}$.

Scanning electron microscopy (SEM) images and EDX of the ZSM-5 catalysts were obtained using a Zeiss Ultraplus Thermal Field Emission Scanning Electron Microscope with an acceleration voltage of 15 kV. STEM were conducted by a JEOL 2100F 200 kV FEG–STEM. XRD, XPS, and TPR characterization were used the same instrument and methods as previous described.

5.3 Results and discussion

The XRD patterns of the as-obtained Mn-doped $\alpha$-FeOOH and $\alpha$-FeOOH are displayed in figure 5.1. The diffraction peaks of the two kinds of products are in agreement with orthogonal $\alpha$-FeOOH (JCPDF Card No. 29-0713, space group Pbnm), and no impurities were found in these XRD patterns. Crystallographic structure of $\alpha$-FeOOH shows the Fe octahedron is linked with other four Fe octahedral through edge sharing and four others are linked through double corner sharing. It appears that the 1D structure of Mn-doped $\alpha$-FeOOH might be reinforced by chemical linkages to maintain the stability of the structure. [159] Comparing the patterns of Mn-doped $\alpha$-FeOOH with
that of pure $\alpha$-FeOOH, no crystalline manganese or manganese oxides were observed in the Mn-doped $\alpha$-FeOOH XRD pattern.

After calcination, $\alpha$-Fe$_2$O$_3$ nanorods with and without Mn doping were obtained. Their patterns can be indexed to pure $\alpha$-Fe$_2$O$_3$ phase (JCPDS No. 33-0664). While an additional peak at 22° shows up in the Mn doped sample, which is corresponding to formation of impure MnFe$_2$O$_4$ particle [159]. Since the peak intensity is very low, the amount of impurity is very small compare to the $\alpha$-Fe$_2$O$_3$ phase. With similar $\alpha$-Fe$_2$O$_3$ phase peaks, the Mn-doped $\alpha$-FeOOH precursor is almost completely transformed into Mn-doped $\alpha$-Fe$_2$O$_3$. The XRD pattern of Pd catalysts shows the hematite Fe$_2$O$_3$ structure is still the dominant structure. For Mn doped sample, a small amount of impure phase still exists. No PdO diffraction peak at 42° appears in both Pd catalysts. The lack of Pd peak could be attributed to the high dispersion or small amount of Pd loading.

SEM images justify the nanorod morphology of Fe, Fe-Mn supports and Pd loaded catalysts, shown in figure 5.2. More detailed Pd structure and surface structure identification is characterized by STEM. Figure 5.3 shows the Pd/Fe$_2$O$_3$ structure STEM image with different resolution. The nanorod support with rectangular shape and 40nm width can be clearly distinguished. The bright spots on the nanorods are Pd particles that exhibit good Z contrast with the Fe. The majority of Pd particle sizes are in the range of 2-5nm. Several bigger aggregated Pd also appears. The Fe$_2$O$_3$ exposed (104) lattice plane with 0.27 nm distance[160]. The Pd particle lattice plane is 0.22 nm, which is corresponding to PdO (110) plane[161].
Figure 5.1 XRD of XRD patterns of \( \alpha \)-FeOOH, Mn-doped \( \alpha \)-FeOOH, \( \alpha \)-Fe\(_2\)O\(_3\), Mn doped \( \alpha \)-Fe\(_2\)O\(_3\), and 1 wt\% Pd catalysts.

![XRD patterns](image)

Figure 5.2 SEM image of Fe based nanorod supports and Pd loaded nanorods after calcination.

![SEM images](image)
Figure 5.3 STEM image of Pd/Fe$_2$O$_3$ catalyst.

In figure 5.4, Pd/α-Fe$_2$O$_3$ nanorod shows almost 100% CO conversion at 150°C, but zero conversion at 75°C. With Mn doping into α-Fe$_2$O$_3$, Pd/α-Fe$_{2-x}$Mn$_x$O$_3$ nanorod shows much higher activity at lower temperature and achieves almost 100% CO conversion at 75°C. Electronic structure and oxidation state of Pd are characterized by X-ray photoelectron spectroscopy (XPS), shown in figure 5.5. The 3d$_{5/2}$ peak of the PdO reference sample locates at 336.6±0.2 eV. The Pd 3d$_{5/2}$ peak of 1 wt% Pd/α-Fe$_2$O$_3$ can be deconvoluted into two peaks at 337.7±0.2 and 336.5±0.2 eV. The lower binding energy peak at 336.5±0.2 eV is similar to the PdO reference sample and can be attributed to the
crystalline PdO phase, while the higher binding energy peak is due to the formation of highly dispersed Pd$^{2+}$, possibly forming single atom sites [158]. In the case of 1 wt% Pd/α-Fe$_{2-x}$Mn$_x$O$_3$, only a high binding energy peak is detected at 337.3 eV, which is different from both peaks of Pd/α-Fe$_2$O$_3$. This suggests different Pd species can form on pure and doped iron oxide surfaces and the support electronic structure change do affect the Pd d-band electronic structure.

Figure 5.4 CO oxidation activity of Pd catalysts. CO/O$_2$ ratio of 2:5 and GHSV = 40,000 h$^{-1}$. 
Reducibility of the lattice oxygen is investigated through H\textsubscript{2}-TPR. As shown in figure 5.6, the Fe\textsubscript{2}O\textsubscript{3} support presents a broad reduction peak above 400\degree C. With Mn doping, additional reduction peaks shows up from 230\degree C to 450\degree C, which is corresponding to Mn reduction steps. The details have been explained in the Pd/MC case. The Pd/\alpha-Fe\textsubscript{2}O\textsubscript{3} catalyst exhibits two reduction regions at around 230\degree C and 400-800\degree C, which can be attributed to the reduction of PdO and Fe\textsubscript{2}O\textsubscript{3} support, respectively [162]. The reduction profile of Pd/\alpha-Fe\textsubscript{2-x}Mn\textsubscript{x}O\textsubscript{3} also shows similar reduction at 210\degree and 400-800\degree C. Interestingly, there is an additional peak at 75\degree. The two peaks at low temperature may both correspond to the reduction of Pd\textsuperscript{2+} to Pd\textsuperscript{0} due to the similar total peak area of

\textbf{Figure 5.5} Pd 3d core-level XPS of Pd-Fe based catalysts and PdO reference.
the PdO reduction peak of Pd/α-Fe₂O₃ sample. Based on XPS, there should be only one Pd species, but two reduction peaks shows up. This might be because Mn doping changes the surface PdO electronic structure or the chemical interaction with the Mn-Fe support, which lead to the reduction of PdO in two steps.

**Figure 5.6** H₂-TPR profiles of Pd catalysts and supports.

In the future CO-O₂ pulse reaction and in-situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTs) will be carried out to give a more comprehensive understanding on metal-support interaction. Density function theory (DFT) calculation will be employed to study the electronic property of Fe-based support surface and the electronic interaction with Pd.
5.4 Conclusion

Pd supported on Fe₂O₃ and Mn doped α-Fe₂O₃ nanorods were successfully prepared. XRD and SEM images justify the catalysts structure, nanorod morphology and size. STEM images of Pd/Fe₂O₃ further distinguished the PdO particle size and exposed facet of α-Fe₂O₃ and PdO. The Pd/Mn doped α-Fe₂O₃ shows over 90% CO conversion at 50⁰C, at which Pd/α-Fe₂O₃ shows almost no activity. XPS of Pd indicate PdO with different electronic structure form on the Mn doped surface. The H₂-TPR comparison indicates the Mn doping results in the lower temperature shift of PdO reduction peak. This may attribute to enhanced metal-support interaction that creates the unique more reducible PdO structure on the Mn doped Fe₂O₃ surface. To elucidate the Pd structure and reactivity change on doped oxide surface with controlled facet, more investigation techniques will be used to provide new fundamental insight on metal-support interaction and active sites design approach.
Chapter 6

Evaluation of sulfur effect on SSZ-13 zeolite catalysts for NO\textsubscript{x} reduction

6.1 Introduction

In NH\textsubscript{3}-SCR reaction, there has been a great deal of attention paid to copper-exchanged molecular sieve Cu-SSZ3-13 as it showed excellent hydrothermal stability [67]. The reason is that its narrow pore structure makes it difficult for aluminium moieties, which are the products of dealumination, to leave. As the Cu/Al ratio became higher due to the fact that the Cu\textsuperscript{2+} in a SSZ-13 cage might form CuO\textsubscript{x} species, the thermal deactivation of Cu-SSZ-13 became more severe. These CuO\textsubscript{x} species might grow and then destroy the cage and channel of the zeolite.

The commercial SCR catalysts for coal power plants contain V\textsubscript{2}O\textsubscript{5}, which is a toxic metal for the environment and human beings. The more environmentally friendly composition of zeolite with excellent hydrothermal stability and wide operation temperature window may be a good candidate to replace current commercial catalysts in power plants NO\textsubscript{x} control.

While hydrothermal stability has been extensively discussed, the stability towards sulfur is another issue that should also be taken into account. The sulfur content in fuels is legislated to be less than 10 ppm. However, in coal power plants, the SO\textsubscript{2} concentration can be up to 500ppm and causing severe catalysts poisoning and deactivation issues. Such high amount of SO\textsubscript{2} effect on the SSZ-13 catalysts have not yet been considered or
tested in the reaction system. In this work, SSZ-13 catalysts loaded with Cu, Fe, Ce are synthesized and tested under SO2 and H2O feed conditions for NH3-SCR activity comparison.

6.2 Experimental

6.2.1 SSZ-13 zeolite catalysts

SSZ-13 was prepared by the following steps: Tetraethyl orthosilicate (TEOS, sigma 98%), N,N,N-trimethyl-1-adamantanamine hydroxide (TMAdaOH, 25 wt %, Sachem Inc.), and DI water were mixed for 2 h, and then Al(OEt)3 (Strem Chemical, 99%) was added to the solution to obtain a final gel composition of SiO2/H2O/TMAdaOH/Al2O3 of 1:20:0.5:0.14 and stirred for another 12 h. The resulting solution was then transferred into Teflon-lined autoclaves and heated at a temperature of 423 K under static conditions for 6 days. After that, the sample was washed with DI water and dried at 353K overnight. The as-made product was then calcined in air at 823 K for 8 h, heating at a ramping rate of 5 K/ min to prepare the starting form of H-SSZ-13.

After calcination, all zeolite samples were ion-exchanged in a 0.1M solution (2 g of zeolite/L of solution) of NH4NO3 (Fisher Scientific) at 80 ºC for 8 h and dried in air at room temperature. 1 g of NH4-zeolite was then added to the 0.1M CuSO4, 0.1M Fe(NO)3, 0.1 M Ce(NO)3 solution and 0.5M Fe(NO3)3+0.5M Ce(NO3)3, respectively. These solutions were stirred in an oil bath at 80 ºC for 1 h. Solutions were then vacuum filtered with deionized water, and the resulting Cu-SSZ-13, Ce-SSZ-13, Fe-SSZ-13 and Ce/Fe-SSZ-13 were dried at room temperature and calcined at 823K for 3 h.
6.2.2 Reaction test and catalysts characterization

The experiments were run in a fixed bed continuous-flow reactor, where the NO conversion was measured by the quadruple mass spectrometer. All catalytic reactions were performed using a feed stream containing 500ppm NO, 500ppm NH₃, 5% O₂, 5% CO₂, 8% H₂O(when used), 500ppm SO₂(when used), and balance N₂. The gas hourly space velocity was 40,000 h⁻¹. The NH₃-SCR activity of all samples was tested from 150 to 450 °C, with 100 °C increments. XRD, SEM, and XPS characterizations were carried out using similar instruments and methods as described in previous chapters.

6.3 Results and discussion

All XRD patterns in figure 6.1 match the standard SSZ-13 pattern and show that no additional peaks appear after ion-exchange, which suggest there is little aggregated metal particle or metal oxide in the catalysts. The (101) peaks shift to a lower angle when the exchanged ion size becomes bigger (Ce>Fe), which suggests lattice cell shrinkage happens after ion-exchange. The peak shift and d spacing calculation based on (101) peak is shown in table 6.1.

![Figure 6.1 XRD patterns of SSZ-13 based catalysts.](image)
Table 6.1 Peak shift and d spacing calculation of SSZ-13 samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>2-Theta</th>
<th>d</th>
</tr>
</thead>
<tbody>
<tr>
<td>H-SSZ-13</td>
<td>9.585 (0.004)</td>
<td>9.2199 (0.0072)</td>
</tr>
<tr>
<td>Fe-SSZ-13</td>
<td>9.553 (0.004)</td>
<td>9.2503 (0.0084)</td>
</tr>
<tr>
<td>Fe-Ce-SSZ-13</td>
<td>9.529 (0.004)</td>
<td>9.2735 (0.0084)</td>
</tr>
<tr>
<td>Ce-SSZ-13</td>
<td>9.518 (0.003)</td>
<td>9.2849 (0.0066)</td>
</tr>
</tbody>
</table>

In figure 6.2, the particle agglomerates are made up of individual jellybeans and a small amount of cube shaped crystals measuring approximately 1μm in size. EDX results indicate that the Si/Al ratio is around 6-7, shown in figure 6.3. After ion exchange, the SSZ-13 crystals maintain their previous morphology, and ICP analysis reveals a total of 1.8 wt % Cu and 0.53 wt % Fe. Ce related ICP results have not yet been performed.

NH₃-SCR reaction experiments were performed using a feed stream containing 500ppm NO, 500ppm NH₃, 5% O₂, 5% CO₂, 8% H₂O (when used), 500ppm SO₂ (when used), and the balance was N₂. The gas hourly space velocity was 40,000 h⁻¹. The NH₃-SCR activity of all samples was tested from 150 to 450 °C, with 100 °C increments.

Figure 6.4 shows the NO conversion for catalysts under simulated flue gas conditions. Without metal loading, H-SSZ-13 is found to have no catalytic activity. After ion-exchanging with Cu, Fe and Ce, the NO conversion of SSZ-13 catalysts jump to more than 80% in a high temperature window (350-450 °C). Moreover, Cu-SSZ-13 show more
than 80% NO conversion in a low temperature window between 150-250 °C, while the NO conversion on other catalysts gradually drops down to less than 30%. Interestingly, the bi-metal exchanged Ce-Fe-SSZ-13 catalyst shows higher catalytic activity than either single metal catalyst, which is probably due to a synergy effect between Fe and Ce in the NH$_3$-SCR reaction system [54]. The commercial catalyst shows over 90% NO conversion above 300°C, but has almost zero activity at 150°C.

Figure 6.2 SEM images of SSZ-13 before (top) and after (bottom) SCR reaction with SO$_2$ and H$_2$O.
Figure 6.3 Si/Al ratio of SSZ-13 based catalysts.

The NH\textsubscript{3}-SCR reaction results with SO\textsubscript{2} and H\textsubscript{2}O in the feed are shown in Fig. 6b. All catalysts are found to deactivate at low reaction temperatures with the addition of SO\textsubscript{2} and H\textsubscript{2}O vapor. Among them, Cu-SSZ-13 shows the best poisoning resistance and keeps more than 90% NO conversion at high temperatures, which is comparable to commercial catalyst. At low temperatures, catalysts deactivate more than at high temperatures, which might be due to the formation of (NH\textsubscript{4})\textsubscript{2}SO\textsubscript{4} on the catalyst [163-165]. The morphology of SSZ-13 keeps the same as fresh catalyst, shown in figure 6.2, suggesting that the catalysts structure is stable after reaction with SO\textsubscript{2}. In figure 6.5 XPS results support the possible formation of (NH\textsubscript{4})\textsubscript{2}SO\textsubscript{4} indicating that both NH\textsubscript{4}\textsuperscript{+} and SO\textsubscript{4}\textsuperscript{2-} are present on the surface of the catalysts.
Figure 6.4 NH$_3$-SCR activity a) without H$_2$O or SO$_2$, b) with H$_2$O and SO$_2$. NO: 500 ppm, NH$_3$: 500 ppm, O$_2$: 5%, CO$_2$: 5%, SO$_2$ (when used): 500ppm, H$_2$O (when used): 8%, N$_2$ balance, GHSV: 40,000 h$^{-1}$.
Figure 6.5 XPS of a) S 2p on Cu-SSZ-13, b) N 1s on Cu-SSZ-13

6.4 Conclusion

In the ammonia selective catalytic reduction (NH$_3$-SCR) of NO$_x$, Cu-SSZ-13 zeolite catalysts show the best NO conversion (over 95%) from 150–450°C when compared with Fe and Ce based SSZ-13. Moreover, in the presence of SO$_2$ and H$_2$O, Cu-SSZ-13 still keeps a relatively high sulfur resistance at temperatures between 250–450°C.
Chapter 7

Conclusions and future work

7.1 Conclusions

This work developed and studied the Pd based catalysts in a relatively comprehensive way from catalysts design to evaluation, fundamental structure-activity relationship characterization to practical application simulation, scalable/industrial synthesis to facet controlled model catalysts preparation. The goal was to improve the current stage of catalysts activity for air pollution elimination. The fundamentals were also carefully investigated to guide the future novel catalysts design.

Pd supported on MnO$_x$-CeO$_2$ and SnO$_2$-MnO$_x$-CeO$_2$ solid solution show excellent room temperature CO oxidation activity. The additional Sn doping can improve the catalyst SO$_2$ resistance and maintain higher CO conversion compare to Sn free sample in a short period of time. The Pd/MC and Pd/CeO$_2$ catalysts were selected to compare doping effect on the Pd structure change and reactivity. The high activity of Pd/MC is attributed to superior lattice oxygen transfer interaction between Pd and support, founded by multiple in situ and ex situ characterizations. This results shows that not only the spillover effect can happen on metal support interface, but also the lattice oxygen reverse spillover.
The practical application of Pd-Ce based catalysts were tested under simulated diesel exhaust condition. The CO light-off temperature of Pd/MC increased to 170°C due to competitive adsorption of CH\textsubscript{x} and NO\textsubscript{x}, while it is still lower than the commercial DOC catalysts (200°C). The comparison of structure characterizations before and after hydrothermal aging shows that the Pd is attempting to aggregate and solid solution support is tending to segregate. However, such minor change is not significant enough to change catalysts activity. It is predictable that extensively increasing the aging or reaction time may finally cause the total phase separation of MC support and formation of much larger PdO particle, which will deactivate the catalysts. So far, the improvement of catalysts stability is a still a challenging topic in industry. The typical method is incorporating stabilizer into the active phase. In the future, self-healing concept may be employed to the catalysts design, which focuses on the reversible transformation of structure under different reaction conditions.

The results of the Pd/Fe-Mn nanorod project shows similar trend as Pd-Ce project. Solid solution structure greatly improves the low temperature CO oxidation activity. The similar well-controlled facet on both Fe and Mn-Fe nanorods provide a good model platform to study the doping effect, meanwhile ruled out many factors that may contribute to activity. The regular nanorod structure is also easier to be modeled by DFT calculation, which is convenient to incorporate theatrical calculation into experimental data.

The Cu-SSZ-13 zeolite was a game changing catalyst for automobile NO\textsubscript{x} emission control. We were interested in transfer such technology into coal power plant application. The high SO\textsubscript{2} condition reaction tests shows that Cu-SSZ-13 has slightly
better NOx conversion than commercial V-W-Ti catalyst, which is toxic to environment. However, the cost of zeolite catalysts is much higher than the metal oxide catalyst due to the use of expensive organic template in the synthesis process. The development of low cost zeolite preparation method and recipe will facilitate and open more market for zeolite application. More and more researchers are developing novel synthesis pathways without templates.

7.2 Future work

In the Pd/Ce based catalytic system, the Mn-O and Ce-O bond characterization during CO oxidation reaction will be studied by time resolved XAS. This could provide more straightforward evidence for the oxygen transfer interaction with Pd. With high resolution in situ XAS, the transient oxidation state change of Mn and Ce could be characterized in XANES spectra. The EXAFS spectra can be used to analyze Mn-O and Ce-O coordination number and bond distance, which can provide information about oxygen transfer effect on dynamic catalysts structure change.

For more active oxidation catalysts design, two pathways may be used. The first is modifying noble metal structure with affinity for the oxygen that is transferred from the support and lower transfer energy barrier. Particle size, shape, facets or bimetallic alloy can be used as design factors to adjust such property. The second path is looking for new support structure that has higher oxygen storage and release ability than Ce4+/Ce3+ and Mn4+/Mn3+/Mn2+ redox couples in fluorite structure. Such structure development may not limit to solid solution concept, but also new and unique multi-metal oxide structure that is developing rapidly in inorganic chemistry research field.
In the Pd/Fe based catalytic system, in situ DRIFTs, STEM, XAS and DFT calculation will be conducted. The DRIFTs can provide details on surface reaction and the Pd sites structure, which is helpful to understand catalysts activity. STEM for Pd/Fe system is crucial important, because it can provide clear images of Pd size and structure. By analyzing size distribution, we may able to further explain whether the assignment of the high and low binding energy in XPS is attributed to size effect or electronic interaction between Pd and support. The regular nanorod morphology of Fe based supports make it easier to model the catalysts structure by DFT, which is convenient to incorporate theatrical calculation with XAS results. Combining DFT and EXAFS could make the catalyst structure model more valid and realistic, which is able to elucidate the Pd structure and reactivity change on the doped oxide surface with controlled facet, and further understand the SMSI.
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Appendix A – List of publication

Chao Wang, Erdem Sasmaz, Cun Wen, Jochen Lauterbach, “Superior oxygen transfer ability of Pd/MnOₓ-CeO₂ for enhanced low temperature CO oxidation activity”, *Applied Catalysis B: Environmental*, 2017 (206) 1–8


Chao Wang, Erdem Sasmaz, Cun Wen, Jochen Lauterbach, “Pd supported on SnO₂-MnOₓ-CeO₂ catalysts for low temperature CO oxidation”, *Catalysis Today*, 2015 (258) 481–486

Erdem Sasmaz, Chao Wang, Jochen Lauterbach, “In-situ spectroscopic investigation of Pd local structure over Pd/CeO₂ and Pd/MnOₓ-CeO₂ during CO oxidation” *Journal of Materials Chemistry A*, under review, 2017
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