Catalytic and Thermodynamic Studies of Supported Core-Shell Catalysts

Chen Chen
University of Pennsylvania, chenc052@gmail.com

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Catalytic and Thermodynamic Studies of Supported Core-Shell Catalysts

Abstract
Interactions between metal catalysts and oxide supports have been known to be important in modifying the catalyst properties for many years, and catalysts with core-shell nanostructures are promising for optimizing these metal-oxide interactions. In this dissertation, core-shell nanoparticles that consist of a metal core and a metal-oxide shell were synthesized and deposited onto an alumina support. These core-shell catalysts exhibit unique catalytic and thermodynamic properties, and were investigated with different core-shell compositions as part of this thesis.

The first part of this dissertation focuses on a Pd@CeO2/Si-Al2O3 catalyst that has been developed and examined for methane-oxidation previously. To better understand this material, I investigated the catalytic, adsorption, and redox properties as they are related to the methane-steam-reforming. I also looked at the effect of calcination temperature on the catalytic properties since the catalysts were strongly influenced by the calcination temperatures, in a manner that is very different from that observed with conventional Pd/CeO2 catalysts. It was found that calcination to higher temperatures improved the performance of the Pd@CeO2 catalyst by modifying the redox properties of the ceria shell.

In the second part of this dissertation, the synthesis and investigation of core-shell catalysts was extended to other precious-metal cores and metal-oxide shells. To determine the effect of shell material, a Pd@ZrO2/Si-Al2O3 catalyst was investigated. The ZrO2 in contact with Pd was found to be reducible and to enhance the methane-oxidation.

A Au@TiO2/Si-Al2O3 catalyst was also synthesized and examined for CO oxidation. It was found that the strong interaction between Au and TiO2 not only enhanced the oxidation activity of Au but also effectively prevented Au sintering up to 873 K.

Additionally, catalysts with Pd or Pt cores and ZnO shells were prepared. The formation of Pt-Zn alloy was suggested by in-situ TEM and coulometric titration results and by catalytic properties for methanol-steam-reforming.

Finally, metal-oxide interactions were compared for Pd@CeO2 and Pt@CeO2. A very strong interaction between Pd and CeO2 helped to stabilize the core-shell structure at higher calcination temperatures and affected the CO accessibility of the core for catalyst calcined at lower temperatures, but these were not observed with Pt.

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CATALYTIC AND THERMODYNAMIC STUDIES OF SUPPORTED CORE-SHELL CATALYSTS

Chen Chen

A DISSERTATION

in

Chemical and Biomolecular Engineering

Presented to the Faculties of the University of Pennsylvania

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Supervisor of Dissertation

____________________________
Raymond J. Gorte, Professor of Chemical and Biomolecular Engineering

Graduate Group Chairperson

____________________________
Raymond J. Gorte, Professor of Chemical and Biomolecular Engineering

Dissertation Committee

John M. Vohs, Professor of Chemical and Biomolecular Engineering
Talid R. Sinno, Professor of Chemical and Biomolecular Engineering
Russell J. Composto, Professor of Materials Science and Engineering
ACKNOWLEDGMENT

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Finally, I would like to dedicate my dissertation of my family for their unconditional love and support over the years.
ABSTRACT

CATALYTIC AND THERMODYNAMIC STUDIES OF SUPPORTED CORE-SHELL CATALYSTS

Chen Chen
Raymond J. Gorte

Interactions between metal catalysts and oxide supports have been known to be important in modifying the catalyst properties for many years, and catalysts with core-shell nanostructures are promising for optimizing these metal-oxide interactions. In this dissertation, core-shell nanoparticles that consist of a metal core and a metal-oxide shell were synthesized and deposited onto an alumina support. These core-shell catalysts exhibit unique catalytic and thermodynamic properties, and were investigated with different core-shell compositions as part of this thesis.

The first part of this dissertation focuses on a Pd@CeO$_2$/Si-Al$_2$O$_3$ catalyst that has been developed and examined for methane-oxidation previously. To better understand this material, I investigated the catalytic, adsorption, and redox properties as they are related to the methane-steam-reforming. I also looked at the effect of calcination temperature on the catalytic properties since the catalysts were strongly influenced by the calcination temperatures, in a manner that is very different from that observed with conventional Pd/CeO$_2$ catalysts. It was found that calcination to higher temperatures
improved the performance of the Pd@CeO₂ catalyst by modifying the redox properties of the ceria shell.

In the second part of this dissertation, the synthesis and investigation of core-shell catalysts was extended to other precious-metal cores and metal-oxide shells. To determine the effect of shell material, a Pd@ZrO₂/Si-Al₂O₃ catalyst was investigated. The ZrO₂ in contact with Pd was found to be reducible and to enhance the methane-oxidation.

A Au@TiO₂/Si-Al₂O₃ catalyst was also synthesized and examined for CO oxidation. It was found that the strong interaction between Au and TiO₂ not only enhanced the oxidation activity of Au but also effectively prevented Au sintering up to 873 K.

Additionally, catalysts with Pd or Pt cores and ZnO shells were prepared. The formation of Pt-Zn alloy was suggested by in-situ TEM and coulometric titration results and by catalytic properties for methanol-steam-reforming.

Finally, metal-oxide interactions were compared for Pd@CeO₂ and Pt@CeO₂. A very strong interaction between Pd and CeO₂ helped to stabilize the core-shell structure at higher calcination temperatures and affected the CO accessibility of the core for catalyst calcined at lower temperatures, but these were not observed with Pt.
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Chapter 1. Introduction

1.1 Background

Metal catalysts play very important roles in many industries, including petroleum refining, and chemicals production, as well as auto catalyst emissions control and other environmental applications. For many reactions, the catalytic activity and selectivity depend upon metal particle size because this in turn affects the surface area and number of catalytic active sites. To enhance the number of active sites per unit mass, most commercial metal catalysts are dispersed in the pores of high-surface-area metal-oxide supports in the form of nanoparticles. Although the primary function of metal-oxides that are used as supports is to maintain metal dispersion, it has been demonstrated that contact between an oxide support and the active metal can strongly influence the activity and selectivity of the catalysts for some reactions. Therefore, understanding and controlling metal-oxide interactions is crucial for developing optimal precious-metal based catalysts. However, interactions between the metal and its oxide support are generally not well understood and need to be further investigated with novel approaches and techniques.

The goal of my work was to understand and enhance these interactions by maximizing the interfacial contact between the support oxide and the metal. In particular, I prepared catalysts with core-shell structures where the active metal is encapsulated in a layer of porous oxide. In addition to catalytic measurements, I also examined the thermodynamic redox properties of the metal-oxide interfaces in these core-shell catalysts using Coulometric Titration, obtaining important information on the energetics associated
with the metal-metal oxide interface for the first time. A number of important metal-
oxide catalytic systems were examined in this work, including Pd-CeO$_2$, Pd-ZrO$_2$, Pd-
ZnO, Pt-CeO$_2$, Pt-ZnO, and Au-TiO$_2$. In addition to developing a better fundamental
understanding of the nature of metal-metal oxide interfaces, methods were developed for
improving catalyst stability at higher temperatures.

1.2 Evidence for Metal-Oxide Interactions

The metal-oxide interactions are complex functions of structure and composition
and will be different for different catalyst systems. While it is difficult to cover all
different types of interaction, in this section, I will choose several representative
eamples to illustrate typical reactions where chemical and physical interactions between
the metal and the metal-oxide support play critical roles in determining the catalyst
properties.

1.2.1 Bi-Functional Catalysts

In some catalytic processes involving the petroleum and petrochemical industries,
the catalyst is considered to be bi-functional in that both the metal and the metal-oxide
are themselves catalytically active. One of the most important examples of this is
dehydrosomerization of methylcyclopentane over Al$_2$O$_3$-supported Pt in naphtha
refining. Pt is well-known to be an efficient dehydrogenation catalyst while Al$_2$O$_3$ has
acid sites that are active for isomerization of olefins. For catalysts in which Pt and Al$_2$O$_3$
are in close contact, methylcyclopentane is first dehydrogenated on Pt to
methylcyclopentadiene, which then migrates to an active sites on Al$_2$O$_3$ to form
cyclohexadiene. Finally, the cyclohexadiene migrates to Pt and is dehydrogenated to benzene [1].

Although this type of metal-support interaction is certainly important, the function of both components is well understood. Also, the support in this case does not change the properties of the metal or affect reactions that occur on the metal. Indeed, it is known that the metallic Pt and the alumina do not even need to be in direct contact for this reaction to proceed. Therefore, I will not consider these types of metal-metal oxide interactions further.

1.2.2 Strong Metal-Support Interaction (SMSI)

The concept of ‘Strong Metal-Support Interaction’ (SMSI) was first introduced in 1978 to refer to the drastic changes in the adsorption properties of group VIII metals that were observed when deposited on a titanium oxide support after high temperature reduction [2]. One of the characteristic properties of group VIII metals is that their surface atoms can chemisorb H₂ or CO molecules at ambient temperature and this property is commonly used to measure the metal dispersion. However, it was found that titania-supported metals exhibited strongly suppressed adsorption following high-temperature reduction. It was suggested that a strong metal-support interaction between the metal and the reduced titania modified the adsorption properties of the metal. Later, it was confirmed by surface science investigations that reduced titania can migrate onto metal particles and then form an overlayer over the metal surface [3], which blocked adsorption of CO and H₂. Even though this later work indicated that the metal properties
are not changed by the reduced titania, the migration of a reduced oxide onto the metal particles is still referred to as SMSI.

1.2.3 Oxygen Storage Capacitance (OSC)

The simultaneous removal of three primary exhaust pollutants (CO, unburned hydrocarbons and NOx) remains a major challenge in emission control for automobile engines. This is because conversion of CO and HC to CO₂ and H₂O requires oxidizing conditions and conversion of NOx to N₂ requires a reducing condition. This objective can be achieved by using a so-called ‘three-way’ catalyst (TWC) within a ‘close-to-stoichiometric’ air/fuel ratio window. A typical TWC consists of a high surface area support, such as Al₂O₃, catalytically active Group VIII metals that are impregnated into the support, and an oxygen-storage component, CeO₂. The facile reducibility of CeO₂ makes it an efficient oxygen capacitor that is able to store oxygen under oxidizing conditions and release oxygen under reducing conditions. Unlike the situation for bi-functional catalysts, ceria reduction cannot occur in the automotive exhaust environment without contact with the catalytic metal [4, 5].

However, there is still debate about how reduction of the ceria occurs, whether oxygen is transferred from ceria to the metal or the reductant is transferred from the metal to the ceria. There is some indication that oxygen is transferred to the metal in some cases but it is not known if the transfer occurs only at peripheral sites or whether oxygen can be transferred to the bulk of the metal.
1.2.4 Alloy Formation

Another possible metal-support interaction involves the formation of alloys. Some oxides may be reduced to their metallic form and then react with the active metal to form an alloy that has superior catalytic properties compared with the elementary metals. For example, PtZn alloys can be formed from Pt/ZnO catalyst upon reduction. The alloy catalysts have been shown to be more selective for hydrogenation of α, β-unsaturated aldehydes to the corresponding saturated alcohols [6]. In another example, CO\textsubscript{2} selectivity for the methanol-steam-reforming reaction was found to be greatly improved when Pd or Pt is supported on ZnO, Ga\textsubscript{2}O\textsubscript{3} and In\textsubscript{2}O\textsubscript{3} due to the formation of Pd–Zn, Pd–Ga, Pd–In, Pt–Zn, Pt–Ga and Pt–In alloys [7].

1.3 Mechanisms of Metal-Oxide Interactions

As pointed out earlier, the nature of metal-metal oxide interactions are not well understood in many cases. Various mechanisms have been proposed to explain how the oxide affects the metal [8-10]. Here, I will briefly discuss some of the more important cases that have been proposed for understanding support effects. Some of these will be relevant for explaining the work I have carried out in this thesis.

1.3.1 Schwab Effect

One of the first models developed for understanding how support oxides and metals interact was proposed by Schwab and Koller [11]. They suggested that, when a catalytic metal is supported on a semiconducting oxide, electrons could transfer between the metal and oxide, causing large changes in the properties of the metal. This mechanism
was invoked initially when the SMSI phenomenon was first observed with titania-supported catalysts. It was suggested at that time that titania became semiconducting under reducing conditions and that it could then donate electrons to the supported metal. Because electron densities of metals are orders of magnitude larger than electron densities in semiconducting oxides, such long-range electron-transfer mechanisms are difficult to explain. Also, electron-transfer mechanisms would imply that support effects should depend on metal loading, which was not observed with SMSI in titania-supported metals. Therefore, electron-transfer mechanisms have grown out-of-favor as a way for explaining support effects.

1.3.2 Bonding Interactions

The effects observed with titania-supported metals are presently thought to arise from bonding between the metal and reduced titania. The attraction between the metal and reduced titania is analogous to wetting phenomena observed at liquid-solid interfaces and results in migration of reduced titania onto the metal particles \([3, 12]\). When the metal surface is completely covered, adsorption suppression is caused by simple site blocking.

In less extreme cases, bonding interactions between a metal and its oxide support could also induce changes in geometry of the metal particles. For example, it was shown that the sublimation energy of Au on SiO\(_2\) is abnormally low (50 kcal mol\(^{-1}\)) at 0.2 monolayers (mL), but increases rapidly with increasing Au coverage to the bulk value (90 kcal mol\(^{-1}\)) at 5mL. The low value of sublimation energy at low Au coverage is effectively explained by repulsive interactions between the Au and silica. In this case, Au
atoms are not attracted to silica; at the edge of small clusters, the Au atoms are bonded to fewer Au neighbors and hence are weakly held to the surface. By contrast, the sublimation energy remains at 50 kcal mol\(^{-1}\) with increasing Au coverage up to 2mL for the case of Au/TiO\(_2\). This has been attributed to a stronger interaction between Au and TiO\(_2\), which in turn leads to greater wetting of TiO\(_2\) by Au compared with the situation for Au/SiO\(_2\). These bonding interactions result in higher Au dispersions and improved the thermal stabilities of Au with TiO\(_2\).[13].

There is evidence that bonding interactions between an active metal and its oxide support can also modify the thermodynamic redox properties of supported metal particles. In a thermodynamic investigation of supported Co catalysts for Fischer-Tropsch synthesis (FTS) [14], it was found that redox properties of Co that had been deposited onto a ZrO\(_2\) support can be affected significantly by the metal-support interface, while redox properties of Co supported on mesoporous silica were indistinguishable from that found for bulk Co. It was reported that this observation is critical for understanding FTS reaction over supported Co catalyst because metallic Co is the active phase for low-temperature FTS reaction. Although bulk thermodynamic calculations indicate that Co should remain metallic under FTS conditions, redox isotherms obtained by coulometric titration of Co/ZrO\(_2\) catalysts suggested that interactions between Co and ZrO\(_2\) can cause particles to be oxidized under FTS conditions. It was further suggested that this effect is due to bonding between highly dispersed Co and oxygen from the zirconia support [15].

It is important to notice that interfacial effects could be very different with metal nanoparticles compared to what happens in the bulk. The electronic properties of
supported nanoparticles differ from bulk materials and this could change bonding interactions with the oxide support. One case where this appears to occur is the situation when Au is supported on titania. Au/TiO$_2$ catalysts prepared by deposition-precipitation were reported to be capable of catalyzing CO oxidation at temperatures as low as 90 K [16], while neither unsupported Au nor TiO$_2$ alone is active for this reaction. The activity of Au nanoparticles is not dependent simply on Au particle size; the composition of the support is also critically important, with rates for water-gas shift reaction over Au/TiO$_2$ that are 20 times higher than rates over the same Au particles supported on Al$_2$O$_3$ [17].

In the Au and TiO$_2$ example, there is a question whether the bonding interactions are important over the entire interface between the metal and the oxide or just at edge sites where the metal and oxide are both exposed to the gas phase. Although many authors have proposed that only the peripheral sites are affected [18-23], it has also been proposed that the active sites on Au particles are those that are separated from the titania by one monolayer of Au [24]. In this case, the entire surface of a “flat” particle, two monolayers thick, would be active. With either model, the active sites are in the proximity of the TiO$_2$ support and the enhanced catalytic activity has been ascribed to the strong bonding interaction between Au and TiO$_2$ support.

The manner by which titania bonding affects Au is uncertain. One recent study of Au supported on highly reduced TiO$_x$ film has suggested that strong bonding between Au and reduced Ti atoms leads to electron-rich Au and it is this form of Au that exhibits exceptionally high activity for CO oxidation [25]. Theoretical studies also show that reduced Ti defect sites at the interface between Au clusters and TiO$_2$ change the
electronic properties of Au clusters through charge transfer from TiO$_2$ to Au [26, 27], which in turn affects the catalytic properties of Au.

It should be emphasized that, while there are numerous studies reporting evidence for electronic interactions between metal nanoparticles and the oxide support, the situation is complicated by the fact that the properties of metal nanoparticles are already intrinsically different from that of bulk materials. Separating effects of particles size and metal-support interactions is challenging.

1.3.3 Oxygen Transfer

For reducible oxides, such as ceria, the role of the support also includes transferring oxygen to and from the supported metal. The ability of ceria to donate oxygen is crucial for three-way catalysis [28, 29], water-gas shift (WGS) catalysis [30-33], hydrocarbon-reforming catalysis [34], and hydrocarbon oxidation catalysis [35, 36]. For example, reaction rates for the WGS reaction on ceria supported Pd has been shown to be orders of magnitude higher than on non-reducible Al$_2$O$_3$ supported Pd [33].

Oxygen transfer appears to be also important for methane combustion over supported-Pd catalysts [37, 38]. It is widely acknowledged that PdO is more active than Pd for this reaction. However, the PdO phase tends to decompose to metallic Pd at high temperatures (over 1073 K) resulting in decreased activity. The re-oxidation only occurs until the temperature decreases to below 873 K [39]. It has been reported that PdO phase can be stabilized when it is supported on reducible oxides such as TiO$_2$ and CeO$_2$, with a significant increase in the temperature for reformation of the PdO.
The key reason for the special properties of ceria-based catalysts is the facile redox shift between Ce$^{4+}$ and Ce$^{3+}$. Under reducing conditions, oxygen atoms can be removed from ceria and result in a non-stoichiometric composition of partially reduced CeO$_{2-x}$. Each released O atom leaves behind an oxygen vacancy and creates two Ce$^{3+}$ cations by transferring two electrons to two Ce$^{4+}$ cations. Under oxidizing conditions, a reverse process takes place.

It has been found that oxygen from the ceria support can be transferred to active metal and then used to oxidize species that adsorbed on the metal. Reduced ceria can be oxidized by molecular O$_2$ or by O from another reactant such as water. This proposed mechanism has been used successfully to explain the enhanced activity observed with several reactions which can be carried out on these catalysts, including CO oxidation [40], water-gas shift [30], and steam-reforming [34]. Considering WGS reaction over Pd/ceria, the mechanism can be written as follows:

\[
2\text{CeO}_2 + \text{Pd} \rightarrow \text{PdO} + \text{Ce}_2\text{O}_3 \quad (1.1)
\]

\[
\text{CO} + \text{PdO} \rightarrow \text{Pd} + \text{CO}_2 \quad (1.2)
\]

\[
\text{Ce}_2\text{O}_3 + \text{H}_2\text{O} \rightarrow \text{H}_2 + 2\text{CeO}_2 \quad (1.3)
\]

Interestingly, this proposed mechanism appears to contradict the thermodynamic redox properties of ceria. Thermodynamics indicates that CeO$_{1.98}$ is the equilibrium stoichiometry at 873 K and P(O$_2$)$\sim 10^{-26}$ atm [41]. Therefore, ceria should not be able to provide oxygen to the supported metal in most reactions, i.e. the reaction conditions are too oxidizing and reduction of ceria should not occur. The likely explanation for these phenomena is that ‘catalytic’ forms of ceria are more reducible than that of bulk ceria.
Usually, ceria that is used in catalysis is in nanoparticle form [42-45] or is promoted by other materials, such as zirconia [46, 47]. It is possible to rationalize why ‘catalytic’ forms of ceria might be more reducible. With regards to pure ceria, Ce$^{4+}$ is the most stable state in stoichiometric CeO$_2$ because the symmetry of the fluorite crystal places the Ce atoms in such a geometry that bonding with the oxygen matches the direction of the 4f orbitals, which is critical for stabilizing Ce$^{4+}$. When ceria is nanostructured, the crystalline structure becomes highly defective and Ce$^{4+}$ are expected to be destabilized relative to Ce$^{3+}$. The presence of additives (for example, Ti$^{4+}$) can also create distortions in the fluorite structures. In both cases, the perfect fluorite structure of CeO$_2$ can be interrupted, causing a relatively high stability of Ce$^{3+}$ that result in an increased reducibility. In the case of zirconia-doped ceria, it has been suggested that Zr$^{4+}$ can pair with Ce$^{3+}$ to form Zr$_2$Ce$_2$O$_7$ locally within the mixed-oxide structure. Again, formation of such compounds would then stabilize Ce$^{3+}$. Finally, small cerium crystallites are expected to have a high surface energy. If this free energy of the surface is large enough, the reducibility of ceria as a whole will be affected.

It should be noted that some have suggested certain crystal surfaces of ceria are more easily reduced than others. For example, theoretical calculations have argued that the (100) surface is preferentially reduced in ceria relative to the (111) surface [48]. Some support for this idea has come from an experimental study which found that nano-rods synthesized to preferentially expose (111) planes were easier to reduce than normal nanoparticles [49]. However, there are also single crystal studies on CeO$_2$ (100) that indicated
the surface could only be reduced with great difficulty [50] (e.g. by sputtering with Ar\(^+\)). Therefore, crystal surface dependence on reducibility has yet to be proven.

While the reducibility of ceria can promote many reactions, questions have been raised regarding the optimal level of reducibility. For example, a study by Bakhmutsky et al. [51] has shown that making ceria too reducible does not always have a positive effect on catalytic activity. In their work, addition of Pr to ceria in a Pd/ceria catalyst leads to a mixed oxide that can give over-reduction of ceria, which in turn gives a much lower activity for the WGS reaction. In this case, oxygen in the praseodymium-ceria mixed oxide was so weakly bound that oxygen could not be restored by oxidation in steam. Therefore, there appears to be an optimum reducibility for ceria that will lead to the most active catalysts.

Zirconia is another support material that has attracted considerable interest in a variety of catalyst systems. Even though ZrO\(_2\) is normally considered an irreducible oxide, and should therefore not promote reaction in the same way that CeO\(_2\) does, there are some indications that interaction between the active metal and ZrO\(_2\) support can affect the catalytic activity for CO hydrogenation [52], methanol decomposition [53], and methane-steam-reforming [54]. This may be associated with the fact that oxygen mobility of ZrO\(_2\) supports is relatively high at moderate and high temperatures, so that oxygen can be exchanged between the active metal and the support. For example, it has been demonstrated that on a conventional Pd/ZrO\(_2\) catalyst, oxygen from a ZrO\(_2\) support may contribute to methane-oxidation reaction, and the involvement of ZrO\(_2\) increases with increasing reaction temperature [55].
In metal-oxide catalytic systems, interactions between phases are crucial for reactions. Whether the mechanism involves bonding interactions, oxygen transfer, or both simultaneously, there must be direct contact between the metal and the oxide support. Therefore, any potential advantages associated with these interactions require maximizing the interface between the metal and the oxide. Some methods that have been developed to maximize interfacial contact will be discussed in the next section.

1.4 Approaches to Improve Metal-Oxide Interaction

For traditional supported metal catalysts which consist of small metal particles deposited onto high-surface-area oxide support, the metal-oxide interaction can be enhanced by simply increasing the metal dispersion. Significant effort in the field of catalysis has gone into synthesizing particles with sizes down to the nanometer scale in order to enhance the specific surface area, the interaction with the support and, consequently, the catalytic properties. However, such enhancement is limited by the ‘single interfacial perimeter’ that forms between the metal particles and the oxide support.

With the rise of nanotechnology, ‘multiple points of contact’ between the metal and the oxide becomes possible; and this provides three dimensional control of the reaction zone and greatly modifies the properties of the catalysts. For example, Pietron et al. [56] formed isolated Au nanoparticles in Au-TiO$_2$ composite aerogels by adding alkanethiolate-monolayer-protected Au clusters to a titania sol before gelation. In the resulting aerogel nanoarchitecture, each Au particle was in contact with multiple TiO$_2$ nanocrystallites. The composite exhibited high catalytic activity toward CO oxidation
with much larger Au particle sizes. Indeed, the particle size in their study was so large that previous reports would have predicted the Au would be inactive.

The ‘3-D’ design can also be used to address another common problem in catalysis: thermal stability of highly dispersed active metal. Nanoparticles tend to rapidly sinter into larger clusters due to their high surface energy, resulting in a loss of activity. It would be desirable to use new approaches to prevent such sintering by encapsulating the dispersed metal nanoparticles with additional materials. Co-precipitation and microemulsion are two of the most commonly used techniques to make encapsulated nanostructures. In the former method, the preformed metal particles (or their precursors) are precipitated together with the metal oxide precursor. The latter one involves using micro-emulsions as a nano-reactor; metal particles are produced inside micelles, which are in turn coated with the oxide precursor to form the encapsulated metal. However, these methods cannot provide great control over the final structures. Our group used both of these methods to prepare Pd in ceria nanostructures for water-gas shift reaction and found that ceria layers made by co-precipitation method were insufficient to prevent sintering of the metal, while with the microemulsion method, the ceria layer underwent condensation that blocked the active sites of the metal [57].

Novel nanotechnologies have allowed great improvements in the synthesis of catalysts with well-controlled size, shape, and surface properties. The deliberate tailoring of the nanostructure can lead to unique catalytic properties, and provide the level of control that is required to maximize the metal-support interface. The controlled structure also allows the systematic investigation of metal-support interactions. One example is
shown in the work of Yeung et al. [58], who prepared Pt@CeO$_2$ core-shell structures by a modified microemulsion procedure with controllable ceria thickness. The Pt core was shown to interact with CeO$_2$ shell in an optimum geometry to form a unique interface, which exhibited high activity for the water-gas shift reaction, but was completely inactive for the undesirable side reaction, methanation. In another example, Zhang et al. [59] prepared Au nanoparticles supported on TiO$_2$/SiO$_2$ core-shell composites, which were in turn encapsulated in mesoporous silica. The small TiO$_2$ particles anchored on SiO$_2$ beads led to a better dispersion of Au and the encapsulation improved sinter-resistance during calcination at 773 K.

Recently, our group used self-assembly method to achieve even more precise control over core-shell structures, allowing finer tuning of the oxide shell and maximizing the metal–oxide interactions [60-62]. A schematic of the method is shown in Figure 1.1. Pd@CeO$_2$ was prepared by reacting preformed 11-mercaptoundecanoic acid (MUA)-protected Pd nanoparticles with cerium (IV) alkoxide, followed by a controlled hydrolysis in the presence of dodecanoic acid.

**Figure 1.1:** Schematic representation of the procedure to obtain dispersible Pd@CeO$_2$ core-shell nanostructures [60].
After forming the dispersible Pd@CeO₂ nanoparticles in solution, they could be deposited onto Al₂O₃ supports by impregnation. However, Pd@CeO₂ particles prepared in this manner are slightly hydrophobic and tend to present as agglomerates rather than as isolated particles adhering to the hydrophilic Al₂O₃ support. In an alternative method, the dispersed Pd@CeO₂ can be adsorbed onto a silane modified Al₂O₃. In this case, the alumina surface is made hydrophobic by reaction with triethoxy(octyl)silane (TEOOS) (Figure 1.2). After adsorption of the core-shell particles, the solid residue can be recovered, crushed, and calcined.

![Figure 1.2](image-url): Schematic representation of the agglomeration of Pd@CeO₂ structures when using the pristine alumina (A) and their deposition as single units after treatment of the same support with triethoxy(octyl)silane (TEOOS) [63].

In previous work, it was demonstrated that these core-shell catalysts exhibit very exciting properties [63]. First, this material shows outstanding thermal stability, with the Pd cores remaining isolated even after heating the catalyst to 1123 K. More importantly, the methane-oxidation activity for the Pd@CeO₂/Si-Al₂O₃ catalyst was exceptional, exhibiting rates that were at least 50 times higher than that of a normal Pd/CeO₂ catalyst, well beyond what a simple optimization of interfacial site concentrations would provide.
While it has been inferred that this exceptional activity may result from improved metal-oxide interaction between the Pd core and the ceria shell, many questions remain. A further investigation on metal-oxide interaction and a better understanding of the properties of this core-shell material are needed.

1.5 Scope of the Thesis

My thesis work fell into two categories. The first part focuses on Pd@CeO$_2$/Si-Al$_2$O$_3$ catalysts. The goal was to gain a better understanding of the properties of this material that make it such good catalyst. The second category involved extending the synthesis to other metal@oxide systems and into investigations of metal-oxide interactions with different core-shell compositions.

The thesis is divided into 8 chapters. Chapter 2 provides descriptions of the sample preparations, characterization techniques and experimental methods used in this work. In Chapter 3, I describe an investigation of Pd@CeO$_2$/Si-Al$_2$O$_3$ catalysts for the methane-steam-reforming reaction. In this work, I looked at the effect of calcination temperature for this catalyst and this reaction. The oxidation and reduction properties of Pd@CeO$_2$/Si-Al$_2$O$_3$ calcined at different temperatures were explored using pulse measurements and related to the catalytic rates.

Chapter 4 focuses on the interactions between Pd and ZrO$_2$ in Pd@ZrO$_2$/Si-Al$_2$O$_3$ catalysts, and investigates how they relate to the observed high activity this material has for the methane-oxidation reaction. This work provides for the first time a quantitative explanation for support interaction modifying methane-oxidation rates over Pd. In
addition, because steam has been reported to strongly inhibit catalytic reactions and cause severe deactivation over Pd-based catalysts, the stability of Pd@ZrO₂/Si-Al₂O₃ for methane-oxidation in the presence of steam was also investigated.

Chapter 5 reports the synthesis and characterization of Au@TiO₂/Si-Al₂O₃ core-shell catalysts. Two of the major issues with Au-based catalysts are poor thermal stability due to the very low surface energy compared to other transitional-metal based catalysts and a strong particle-size dependence on activity. The interaction between Au and TiO₂ in the core-shell catalysts helped stabilize the materials against sintering, maintaining a high activity.

In Chapter 6, the synthesis and characterization of Pt@ZnO/Si-Al₂O₃ and Pd@ZnO/Si-Al₂O₃ core-shell catalysts are described. In order to investigate whether Pt-Zn alloys can be formed upon mild reduction due to the intimate contact between the core and the shell, in-situ TEM and coulometric titration experiments were conducted. The applications of these catalysts in methanol-steam-reforming reactions were also discussed and compared to that of the conventional supported catalysts.

Chapter 7 compares the catalytic and adsorption properties of Pd@CeO₂/Si-Al₂O₃ with Pt@CeO₂/Si-Al₂O₃ catalysts. The interactions between the ceria shell and the different metal cores were inferred from their thermodynamic isotherms and used to explain different stabilities that were observed on these two catalysts.

Finally in Chapter 8, the results and conclusions of this work are summarized.
Chapter 2. Experimental Techniques

This chapter will describe the methods used to synthesize the catalysts, as well as the experimental principles and applications of the various techniques used to characterize the catalysts.

2.1 Catalyst Synthesis

All catalysts used in this thesis were synthesized in our laboratory. The catalysts can be categorized into two types: core-shell catalysts supported on hydrophobic alumina (referred as metal@oxide/Si-Al₂O₃); and metal-oxide, supported, precious-metal catalysts (referred as metal/oxide). In this section, general synthesis methods will be discussed, while the details of the preparation procedure, such as ingredients and calcination temperatures for particular metal-metal oxide combinations, will be described in corresponding chapters.

2.1.1 Core-Shell Catalysts

The general method for synthesis of the dispersible core-shell nanostructures includes 3 steps [61, 62]: 1) preparation of 11-mercaptoundecanoic acid (MUA) protected metal nanoparticles, 2) the self-assembly of a metal alkoxide on the MUA protected metal particles by reaction of metal alkoxide with the acid functionality of the MUA ligand, and 3) the controlled hydrolysis of the remaining alkoxide functionality in the presence of protective ligands (dodecanoic acid) to obtain metal@oxide nanoparticles that dispersible in tetrahydrofuran (THF).
The metal@oxide nanoparticles, dispersed in THF, were then adsorbed from solution onto an Al$_2$O$_3$ support that had been modified by reaction with Triethoxy Octyl Silane (TEOOS) [63]. This modification of the support is required to make the Al$_2$O$_3$ hydrophobic so that core-shell nanoparticles could adsorb onto the surface as isolated units. The Al$_2$O$_3$ itself was purchased from Alfa Aesar as γ-Al$_2$O$_3$ and then stabilized by calcining to 1173 K for 24 h. After removing the catalysts from solution by centrifugation and drying, the resulting powders were calcined to various temperatures with a heating ramp of 3 K min$^{-1}$.

2.1.2 Supported Catalysts

For comparison purpose, two types of metal/oxide catalysts were prepared in this thesis. Conventional types of supported catalysts were prepared by impregnation of metal-oxide support with aqueous solutions of metal ammonium nitrate precursors. The amount of precursor and support were carefully chosen to obtain the desired weight loadings. The slurry was then dried and calcined in air to decompose the precursors and obtain a catalyst in the oxidized state.

Nanoparticles deposited on metal-oxide support were also prepared from the MUA-protected metal nanoparticles without oxide shells. In this case, oxide supports were first dispersed in THF, and then an appropriate amount of MUA-protected metal nanoparticles, also dispersed in THF, were added to the mixture dropwise. After stirring overnight to allow complete adsorption, the solid residue was recovered by centrifugation, washed with THF, dried and calcined.
2.2 Equilibrium Measurements

2.2.1 Coulometric Titration

The redox properties of the catalysts were measured using coulometric titration, which is an electrochemical technique that provides the equilibrium oxygen stoichiometry of the oxide sample as a function of P(O\textsubscript{2}) that above the sample. For instance, for the Pd-PdO equilibrium:

\[ 2\text{Pd}_{(s)} + \text{O}_{2(g)} \leftrightarrow 2\text{PdO}_{(s)} \]  

(2.1)

The equilibrium constant can be calculated using:

\[ K_{eq} = \frac{a_{\text{PdO}}^2}{a_{\text{Pd}}^2 \times P(O_2)} = (P(O_2))^{1} \]  

(2.2)

where the activity of solids is equal to 1. The differential Gibbs Free Energy of the oxidation reaction can then be calculated using the following equation:

\[ \Delta G = RT \ln(K_{eq}) = -RT \ln[P(O_2)] \]  

(2.3)

It is important to recognize that the experimental P(O\textsubscript{2}) values are so low that they are not actual partial pressures of O\textsubscript{2} over most of the range reported in this thesis, but rather oxygen fugacity established by an equilibrium with another reaction:

\[ 2\text{H}_2 + \text{O}_2 \leftrightarrow 2\text{H}_2\text{O} \]  

(2.4)

If the initial concentrations of H\textsubscript{2} and H\textsubscript{2}O are known, the P(O\textsubscript{2}) can be determined by:
\[
\log[P(O_2)] = -2\log(K_{eq}) + 2\log\left[ \frac{P(H_2O)}{P(H_2)} \right]
\] (2.5)

The coulometric titration setup used in this thesis is shown in Figure 2.1 [64]. The setup consists of a YSZ (yttria-stabilized zirconia) tube with Ag electrodes painted on both inside and outside. Pt wires were attached to the inner and outer electrode using Ag paste. The inner Pt wire was then spot-welded to an Ultra-Torr Swagelok fitting which had been fitted over one of the ends of the YSZ tube.

**Figure 2.1**: Schematic diagram of coulometric titration setup [64].

During measurements, approximately 1g of sample was placed in an alumina crucible that was then inserted into the coulometric titration cell. The entire apparatus was heated to 873 K; and a mixture of 5% O\textsubscript{2}, 11% H\textsubscript{2}O, and 84% Ar was allowed to flow through the YSZ tube at this temperature for 1 h. This pretreatment insured that the...
measurements were started from the oxidized state of the samples. After stopping the flow, the ends of the YSZ tube were sealed using glass stoppers. To perform the actual measurements, oxygen was electrochemically pumped out of the YSZ tube by applying a potential across the electrodes with a Gamry Instruments potentiostat. The amount of oxygen removed was determined by integrating the current as a function of time. After removing the desired amount of oxygen, the system was allowed to come to equilibrium with the electrodes at open-circuit. The criterion that used for establishing equilibrium was that the open-circuit potential across the electrodes changed by less than 3 mV day$^{-1}$, which typically took 4 to 10 days. Finally, the equilibrium P(O$_2$) was calculated from the Nernst equation (equation 2.6) and the open-circuit voltage (OCV).

$$OCV = \frac{RT}{4F} \ln\left(\frac{P(O_2)_{in}}{P(O_2)_{out}}\right)$$  \hspace{1cm} (2.6)

As an additional check that equilibrium was achieved and that there were no system leaks, most isotherms were measured again starting with the reduced sample and pumping oxygen back into the electrochemical cell.

2.2.2 Transient-Pulse Measurement

The oxidation and reduction of some of the samples were also examined by the transient-pulse experiments. By separating interactions between the catalyst and different reactive molecules sequentially, pulse measurements could be used to investigate the redox properties and deactivation mechanisms on the core-shell catalysts. These measurements were performed in a tubular reactor that had an online quadrupole mass
spectrometer to analyze the concentrations of the effluent gases [65, 66]. Computer-controlled solenoid valves allowed step changes in the gas composition. In all measurements, helium was the major component of the gas phase, with a total flow rate of 20 mL min$^{-1}$, while the concentrations of the reactive component (either CO, O$_2$, H$_2$, or H$_2$O) were chosen to be 10% of the total gas stream. Water was introduced to the reactor by saturation of a He carrier gas flowing through deionized water and condensed with an ice-trap before the products were analyzed. 1.0 g of catalyst was used for these experiments. Prior to loading the samples in the reactor, each sample was pressed into thin wafers that were then broken into smaller pieces. Integration of the partial pressures of the reactor effluent as a function of time allows determination of the amounts of oxygen that could be added or removed from the catalyst by the various reactive components at different temperatures. No attempt was made to analyze the shapes of the pulses because coupling between desorption, re-adsorption, reaction, and diffusion does not allow for a unique determination of rate processes in transient experiments of this type [67].

2.3 Other Characterization Techniques

2.3.1 TEM

Transmission Electron Microscopy (TEM) characterization was performed on a Jeol JEM 2100 operating at 200 kV. Samples were prepared either by drop-casting the particles directly from THF solution onto 300 mesh carbon-coated Cu grids (Electron Microscopy Sciences) or by dispersing the powders into isopropanol and then drop-casting of the dispersion onto holey carbon coated 300 mesh Cu grids.
2.3.2 XRD

Powder X-ray Diffraction (XRD) was used to determine the structures and the chemical phase composition of the core-shell catalysts. The XRD patterns were recorded on a Rigaku Smartlab diffractometer equipped with a Cu Kα source (λ=1.5405 Å). The sample powders were finely dispersed in 2-propanol by sonication and then drop-cast onto glass slides. The intensities of the diffracted beam were measured while sampling different diffraction angles. The crystallite particle size (d) could be estimated using the Scherrer equation:

\[ d = \frac{\kappa \lambda}{B(2\theta) \cos \theta} \]  

(2.7)

where \( \kappa \) is a shape factor usually equal to 1, \( \lambda \) is the X-ray wavelength, \( B \) is the peak width at half the maximum intensity, and \( \theta \) is the diffraction angle.

2.3.3 Chemisorption

The apparent metal dispersions were measured using CO chemisorption at room temperature in a home-built adsorption apparatus [68]. Two different protocols, with different reducing temperatures, were used to pretreat the core-shell catalysts. The calcined samples were first placed in the adsorption apparatus, oxidized at 673 K in 200 Torr O\(_2\) for two minutes, evacuated, and then re-oxidized. After repeating the oxidation step three times, the samples were evacuated and then reduced by exposure to 200 Torr H\(_2\) at either 423 K or 673 K for 5 minutes, followed by a second evacuation. The exposure to H\(_2\) was repeated several times until no measurable H\(_2\) consumption was
observed. CO chemisorption was performed at room temperature by adding small pulses of CO to the samples until a pressure rise in the sample cell was detected [69].

2.3.4 FTIR

Fourier Transform Infrared Spectroscopy (FTIR) was used to analyze the adsorption properties on the catalyst surface. The spectra were recorded using Mattson Galaxy 2020 FTIR spectrometer. The spectrometer was equipped with a Spectra-Tech Collector II diffuse-reflectance accessory to allow measurements on powdered samples with control over temperature and atmosphere.

2.3.5 TPO

In order to determine the temperature required for removing the organic protecting agents from core-shell nanoparticles, Temperature Programmed Oxidation (TPO) measurements were performed in the same system used in the transient-pulse measurements on samples dried at 338 K. Experiments were conducted with either 0.1 g or 1.0 g of sample to determine when most of the carbon leave the sample and to look for the possibility of sulfur contamination from the 11-mercaptoundecanoic acid (MUA) ligands used in preparing the metal nanoparticles. The gas-phase composition during TPO was 20% O₂ in He, with a total flow rate of 25 mL min⁻¹; and the heating rate was 3 K min⁻¹.
2.4 Catalytic Studies

2.4.1 Steady-State Rates Measurements

Several reactions were used in this thesis to characterize catalytic properties of the core-shell catalysts with different metal-metal oxide compositions. The steady-state rates were measured using 100 mg of sample in a ¼-in, quartz, flow reactor with an on-line gas chromatograph (SRI8610C) equipped with a Hayesep Q column and a TCD detector. The reactor pressure was always atmospheric. The partial pressure of each reactant was controlled by adjusting the relative flow rate of each component, with a total flow rate of 120 ml min\(^{-1}\), corresponding to Gas Hourly Space Velocity of 72,000 mL g\(^{-1}\) h\(^{-1}\). Detailed reactant gas-phase composition for each reaction was summarized in Table 2.1. For those experiments in which H\(_2\)O was added, H\(_2\)O was introduced by bubbling He through a H\(_2\)O saturator and the content of H\(_2\)O was controlled by the temperature of the saturator. For all measurements where rates are reported, the conversions of reactant were kept well below 15%, so that differential conditions could be assumed.

**Table 2.1**: Reactant gas-phase composition.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Catalyst</th>
<th>Reactant composition (balanced in He)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane oxidation</td>
<td>Pd@CeO(_2), Pd@ZrO(_2)</td>
<td>3.8 torr (0.5%) CH(_4), 38 torr (5%) O(_2)</td>
</tr>
<tr>
<td>Methane steam reforming</td>
<td>Pd@CeO(_2)</td>
<td>35 torr (4.6%) CH(_4), 70 torr (9.2%) H(_2)O</td>
</tr>
<tr>
<td>CO oxidation</td>
<td>Au@TiO(_2)</td>
<td>25 torr (3.3%) CO, 12.5 torr(1.65%) O(_2)</td>
</tr>
<tr>
<td>Water-gas shift</td>
<td>Pd@CeO(_2), Pt@CeO(_2)</td>
<td>25 torr (3.3%) CO, 25 torr(3.3%) H(_2)O</td>
</tr>
<tr>
<td>Methanol steam reforming</td>
<td>Pd@ZnO, Pt@ZnO</td>
<td>45 torr (5.9%) MeOH, 45 torr(5.9%) H(_2)O</td>
</tr>
</tbody>
</table>
2.4.2 Light-Off Measurements

The light-off measurements were performed in the same system used in the transient-pulse measurements using 100 to 400 mg of sample. For CO oxidation reaction, the composition of the reactant mixture was chosen to be 1% CO and 20% O₂ in He and the total flow rate was maintained at 60 ml min⁻¹. For methane oxidation, the composition of the reactant mixture was chosen to be 1% CH₄ and 5% O₂ in He and the total flow rate was maintained at 120 ml min⁻¹. In both cases, the conversions of reactant were measured as the temperature ramping up from room temperature.
Chapter 3. High Temperature Calcination Improves the Catalytic Properties of Alumina-Supported Pd@Ceria Prepared by Self Assembly

3.1 Introduction

High activity and thermal stability are required for catalysts used in high-temperature reactions, such as methane-oxidation. The most active catalysts for methane-oxidation are based on Pd [38, 70], which is susceptible to sintering at high temperatures; but both activity and thermal stability can be improved through the proper choice of oxide support [71-77]. Ceria can affect rates on supported Pd catalysts because its redox properties can provide an additional channel for oxygen on the Pd. Further improvement of these catalysts requires the optimization of the Pd-support interactions and one approach for accomplishing this is through the development of core-shell catalysts in which a porous oxide “shell” surrounds the metal “core”.

Various methods have been reported for preparing catalysts with a core-shell structure [78]; and, not surprisingly, the different preparation methods can result in materials with vastly different structures and catalytic properties. For example, materials having an “egg-yolk” structure, in which the metal core is in a void volume made from a larger oxide shell [79], will have very different properties from materials prepared using microemulsions, in which the metal core will be in physical contact and completely surrounded by an oxide shell that is typically thicker [80]. Additionally, many of the methods for preparing core-shell structures for catalysis have been developed with
supports that do not participate in the catalytic cycle, such as silica or alumina for example [78].

A catalyst based on a new type of core-shell structure that can be made with catalytically active oxides in the shell has recently been prepared by some of us using self-assembly methods [60, 62]. In this case, the core-shell structures are prepared in solution by exploiting favorable interactions between the constituent building blocks (protected palladium nanoparticles and a cerium alkoxide) and are then dispersed in monolayer form onto engineered oxide supports [63]. The alumina-supported, Pd@CeO$_2$ variant exhibited outstanding performance both in terms of activity and stability for methane-oxidation [63]. The core-shell structure of the supported nanoparticles appears to remain intact, even after calcination to temperatures as high as 1123 K, with the ceria (CeO$_2$) shell being porous and formed by small crystallites that allow adsorption of reactants on the Pd core. In catalytic tests, the Pd@ceria/alumina catalyst showed much higher methane-oxidation activities than either conventional Pd/ceria or Pd/ceria/alumina catalysts prepared by impregnation methods having the same Pd loading. Even more intriguing, the core-shell catalyst exhibited no loss in activity following either calcination at 1123 K for 12 h or repeated cycling to 1123 K under reaction conditions.

Literature reports indicate that conventional Pd/ceria catalysts are very active for the water-gas shift (WGS) and methane-steam-reforming (MSR) reactions [32, 34]. It has been argued that the high activities result from oxidation of either CO (WGS) or methane (MSR) on the Pd using lattice oxygen from ceria, with subsequent re-oxidation of the reduced ceria by H$_2$O. Although the close proximity of the Pd and ceria in the Pd@CeO$_2$
core-shell catalysts suggests that these materials might be even better WGS and MSR catalysts, earlier studies of the WGS reaction on catalysts formed by impregnation of Pd@CeO\textsubscript{2} particles onto alumina showed rates that were lower than those of conventional Pd/ceria and were also unstable with time [69]. Because the Pd@CeO\textsubscript{2} catalysts were deactivated by treatment in H\textsubscript{2} and reactivated by treatment in O\textsubscript{2}, it was argued that the ceria in the core-shell catalysts became heavily reduced in the WGS environment and could not be oxidized by H\textsubscript{2}O. A similar argument had been used to explain the low activity of praeoseodymia-supported Pd for WGS, since H\textsubscript{2}O is also not an effective oxidant for Pr\textsubscript{2}O\textsubscript{3} [51].

In the present chapter, I set out to investigate the characteristics of the Pd@ceria/alumina catalysts for MSR and to determine the effect of catalyst calcination temperature on their properties. The results showed that these catalysts are very strongly influenced by the calcination temperature. For catalysts calcined at 773 K, the behavior under MSR was similar to that reported earlier for the WGS reaction on Pd@CeO\textsubscript{2} nanoparticles in that rates decreased rapidly with time, apparently due to deep reduction of the ceria shell. Calcination to higher temperatures improves the performance of the core-shell catalysts, possibly by tailoring the reduction properties of the ceria shell so that it can be oxidized by steam. These observations clearly demonstrate the different behavior of the core-shell systems compared to conventional materials and introduce a new way for tailoring the redox properties and catalytic activity of nanostructured materials.
3.2 Experimental Methods

The Pd@CeO$_2$/Si-Al$_2$O$_3$ catalysts were prepared using methods outlined in detail in other publications [60, 62, 63]. The dispersible Pd@CeO$_2$ nanoparticles were synthesized with a CeO$_2$:Pd weight ratio of 9 and then adsorbed at room temperature from solutions of THF onto functionalized γ-Al$_2$O$_3$ (Puralox TH100/150 obtained from Sasol, calcined at 1173 K for 24 h, 90 m$^2$ g$^{-1}$). The pristine γ-Al$_2$O$_3$ was functionalized by reaction with TEOOS (Triethoxy Octyl Silane) in a toluene solution at 383 K. This process makes the support compatible with the organic solvent used to disperse the core-shell units, allowing a uniform dispersion of the nanoparticles onto the support. As shown previously [63], adsorption of one monolayer of Pd@CeO$_2$ particles onto this support results in a catalyst that is 1-wt% Pd and 9-wt% CeO$_2$. Before use, the powders were heated in flowing air with a ramp rate of 3 K min$^{-1}$ to either 773 K (Pd@CeO$_2$/Si-Al$_2$O$_3$(773)), 1073 K (Pd@CeO$_2$/Si-Al$_2$O$_3$(1073)), or 1123 K (Pd@CeO$_2$/Si-Al$_2$O$_3$(1123)), and then held at the final calcination temperature for 6 h. To achieve reproducible results, the space velocity of the air during calcination was always greater than 1800 h$^{-1}$. Following calcination to 773 K, TEM measurements on identical catalysts showed that the Pd@CeO$_2$ particles were uniform and approximately 6.0 nm in diameter, with Pd cores that were 2.0 nm in diameter.

Conventional catalysts with 1-wt% Pd on either ceria or pristine alumina supports were also prepared for comparison purposes using incipient wetness of (NH$_3$)$_2$Pd(NO$_3$)$_4$ in aqueous solution. For Pd/ceria, the oxide support was obtained by heating Ce(NO$_3$)$_3$•6H$_2$O in air to 873 K, a process that results in an oxide powder with a surface
area similar to $90 \text{ m}^2 \text{ g}^{-1}$ [46]. For the Pd/alumina catalyst, the $\gamma$-$\text{Al}_2\text{O}_3$ support was the same as that used for the core-shell catalysts except that it was not functionalized with TEOOS. After infiltration of the Pd salt, each of the samples was calcined at 773 K for 6 h, again using a heating ramp of 3 K min$^{-1}$.

The MSR and methane-oxidation reactions were studied in a $\frac{1}{4}$-inch, quartz, tubular reactor, using 0.10 g of catalyst. In MSR, water was introduced to the reactor by saturation of a He carrier gas flowing through deionized water. The reactant partial pressures at the inlet were fixed at 35 torr CH$_4$ and 70 torr H$_2$O by adjusting the relative flow rates of each component. For methane-oxidation, the partial pressures of CH$_4$ and O$_2$ were fixed at 3.8 torr (0.5%) and 38 torr (5%), respectively. In determining reaction rates, conversions of CH$_4$ were kept below 10% so that differential conditions could be assumed. For both reactions, rates were measured while maintaining a total flow rate of 120 mL min$^{-1}$; however, identical rates were obtained at lower flow rates, demonstrating that the results shown here were not affected by product inhibition (Figure 3.1-3.2). Because the apparent Pd dispersions varied with pretreatment, the rates in this study were normalized by the catalyst weight and all catalysts used in this study were 1-wt% Pd. Products were analyzed using an on-line gas chromatograph (SRI8610C) equipped with a Hayesep Q column and a TCD detector. Prior to placing the samples into the reactor, each catalyst was pressed into thin wafers and then heated to 693 K in a flowing mixture of 20% O$_2$ and 80% He for 30 min. The rates were taken after one hour of operation.
Figure 3.1: Methane-oxidation rates in 0.5% CH$_4$ and 5% O$_2$ over Pd@CeO$_2$/Si-Al$_2$O$_3$(1073) with total flow rate of 120ml min$^{-1}$ (■), 80ml min$^{-1}$ (○).

Figure 3.2: Rates for MSR reaction over Pd@CeO$_2$/Si-Al$_2$O$_3$(1073) with total flow rate of 120ml min$^{-1}$ (■), 60ml min$^{-1}$ (○). The concentration of CH$_4$ and H$_2$O were held at 35 torr and 70 torr respectively.
The transient-pulse experiments were performed using a system that has been described in other publications [65, 66]. The system consists of a tubular reactor equipped with computer-controlled solenoid valves to allow step changes in the composition of the inlet gases. The reactor effluent could be monitored continuously using an on-line quadrupole mass spectrometer. Helium was always the major component of the gas phase, with a total flow rate of 20 mL min$^{-1}$, while the concentrations of the reactive component (either CO, O$_2$, H$_2$, or H$_2$O) was chosen to be 10% of the total gas stream. 1.0 g of catalyst was used for these experiments. As discussed in previous papers [65, 66], integration of the partial pressures of the reactor effluent as a function of time allows determination of the amounts of oxygen that could be added or removed from the catalyst by the various reactive components at different temperatures.

Temperature Programmed Oxidation (TPO) measurements were performed in the same system used in the transient-pulse measurements on samples dried at 338 K overnight in order to determine the temperature required for removing the organic protecting agents from core-shell nanoparticles. Experiments were conducted with either 0.1 g or 1.0 g of sample to determine when most of the carbon left the sample and to look for the possibility of sulfur contamination from the 11-mercaptopoundecanoic acid (MUA) ligands used in preparing the Pd nanoparticles. Previous work has shown that, if sulfur is present on Pd/ceria catalysts, it is removed as SO$_2$ between 950 K and 1050 K, the same temperature at which Ce(SO$_4$)$_2$ decomposes [81]. The samples that were examined by TPO in this study were not calcined but simply dried at 338 K overnight before placing
them in the reactor. The gas-phase composition during TPO was 20% O$_2$ in He, with a total flow rate of 25 mL min$^{-1}$; and the heating rate was 3 K min$^{-1}$.

To check for the presence of sulfur, X-ray Fluorescence Spectroscopy (XRF) was performed on samples calcined above 773 K. These measurements also failed to detect any S.

The Pd dispersions were measured using CO chemisorption at room temperature on the reduced catalysts. Two different protocols, with different reducing temperatures, were used to pretreat the core-shell catalysts. First, the calcined samples were placed in the adsorption apparatus, oxidized at 673 K in 200 Torr O$_2$ for two minutes, evacuated, and then re-oxidized. After repeating the oxidation step three times, the samples were evacuated and then reduced by exposure to 200 Torr H$_2$ at either 423 or 673 K for 5 minutes, followed by a second evacuation. The exposure to H$_2$ was repeated several times until no measurable H$_2$ consumption was observed. As discussed elsewhere, reduction at 423 K converts PdO to metallic Pd with minimal reduction of the ceria shell, while reduction at 673 K significantly reduces the ceria shell along with the Pd [69].

FTIR spectra were recorded using Mattson Galaxy 2020 FTIR spectrometer. The spectrometer was equipped with a Spectra-Tech Collector II diffuse-reflectance accessory to allow measurements on powdered samples with control over temperature and atmosphere. Infrared spectra were measured on both Pd@CeO$_2$/Si-Al$_2$O$_3$(773) and Pd@CeO$_2$/Si-Al$_2$O$_3$(1073) samples. Prior to exposing the samples to CO, the catalysts were first heated to 673 K in a flowing mixture of 10% O$_2$/90% He, then reduced in
flowing 10% H₂/90% He at either 423 or 673 K. The samples were then flushed with He and cooled to room temperature under He flow before being exposed to a 10% CO/90% He mixture for 5 min. After flushing with He, IR spectra were acquired at room temperature.

Powder X-ray diffraction (XRD) patterns were recorded on a Rigaku Smartlab diffractometer equipped with a Cu Kα source. The powders were finely dispersed in 2-propanol by sonication and then dropcast onto glass slides before analysis.

### 3.3 Results

#### 3.3.1 Materials

The materials obtained immediately following adsorption of the Pd@CeO₂ nanoparticles from solution onto functionalized alumina contain large amounts of organic material, as well as sulfur, because of the various ligands used in assembling the catalyst. To determine the temperatures at which these are removed, TPO measurements were performed, with results obtained using 0.1 g of uncalcined Pd@CeO₂/Si-Al₂O₃ shown in Figure 3.3. The peaks reported in Figure 3.3 correspond to O₂ (m/e = 32), various hydrocarbons (m/e = 43), CO₂ (m/e = 44) and SO₂ (m/e = 64), respectively. Decomposition of the various ligands begins at approximately 450 K, with evolution of CO₂ and hydrocarbons and the concomitant consumption of O₂ occurring in a sharp peak centered at 480 K. All carbonaceous products were removed by 600 K. Based on an estimate of the amount of carbon present in the initial sample and the amount of O₂
consumed in TPO, at least 70% of the ligands leave the sample as organic compounds during calcination, rather than reacting with O_2.

Previous work demonstrated that, if sulfur is present on Pd/ceria catalysts, it is removed during a TPO experiment as SO_2 between 950 and 1050 K, the same temperature at which Ce(SO_4)_2 decomposes [81]. However, no SO_2 was observed leaving the sample in this temperature region, even when 1.0-g samples were used in the TPO measurements. (The m/e = 64 results in Figure 3.3 were obtained with the larger sample to increase the sensitivity of the experiment.) This suggests that the majority of the MUA protecting agent is removed from the sample at relatively low temperatures as organic compounds. Consistent with this observation, XRF experiments failed to identify the presence of S in samples calcined at temperatures above 773 K.

![Figure 3.3](image-url): TPO results for uncalcined samples of Pd@CeO_2/Si-Al_2O_3 in 10% O_2. The data were obtained monitoring O_2 (m/e = 32), various hydrocarbons (m/e = 43), CO_2 (m/e = 44), and SO_2 (m/e = 64). The data for O_2, hydrocarbons, and CO_2 were obtained using 0.1 g of sample, while data for SO_2 were obtained using 1.0 g of catalyst for enhanced sensitivity.
To determine the effect of calcination temperature on crystal structure, XRD measurements were performed on Pd@CeO$_2$/Si-Al$_2$O$_3$(773) and Pd@CeO$_2$/Si-Al$_2$O$_3$(1073), with results shown in Figure 3.4. The diffraction pattern for the γ-Al$_2$O$_3$ sample is shown for comparison. Not surprisingly, features associated with Pd are not observable on samples with only 1-wt% Pd but peaks associated with the CeO$_2$ fluorite structure (near 28 and 57 degrees 2θ) are easily observed by comparison with the pattern for γ-Al$_2$O$_3$. Increasing the calcination temperature caused significant narrowing of the peaks associated with CeO$_2$; however, even after calcination at 1073 K, the peak width at half height for the feature at 28 degrees 2θ was still almost 2°, which would imply a ceria crystallite size on the order of 5 nm. There was also no evidence for reaction between CeO$_2$ and Al$_2$O$_3$.

![Figure 3.4: XRD powder patterns of Al$_2$O$_3$, Pd@CeO$_2$/Si-Al$_2$O$_3$(773), and Pd@CeO$_2$/Si-Al$_2$O$_3$(1073) (Top). Bottom part: reference powder diffraction patterns of bulk Pd and CeO$_2$ phases labeled with Miller indices.](image-url)
3.3.2 Reactor Measurements

Steady-state, methane-oxidation rates were measured under differential conditions on Pd@CeO$_2$/Si-Al$_2$O$_3$(773), Pd@CeO$_2$/Si-Al$_2$O$_3$(1073), and Pd@CeO$_2$/Si-Al$_2$O$_3$(1123) in 0.5% CH$_4$ and 5% O$_2$, conditions similar to those used in the earlier work [63], with results shown in Figure 3.5. The rates per gram catalyst reported here for Pd@CeO$_2$/Si-Al$_2$O$_3$(1123) are very close to those reported in previous work performed on identical samples [63], with the same activation energy of 90 kJ mol$^{-1}$. It is noteworthy that TOF from these catalysts were found to be an order of magnitude higher than of Pd/ceria-based catalysts reported in literature [74] and comparable to those reported for Pd model system [82]. Interestingly, the rates were significantly lower on samples calcined at lower temperatures, with Pd@CeO$_2$/Si-Al$_2$O$_3$(773) exhibiting rates only one third that of Pd@CeO$_2$/Si-Al$_2$O$_3$(1123)). Rates on Pd@CeO$_2$/Si-Al$_2$O$_3$(1073) were intermediate between those of Pd@CeO$_2$/Si-Al$_2$O$_3$(773) and Pd@CeO$_2$/Si-Al$_2$O$_3$(1123). This result was reproduced on multiple batches of catalyst.

![Figure 3.5: Methane-oxidation rates in 0.5% CH$_4$ and 5% O$_2$ for Pd@CeO$_2$/Si-Al$_2$O$_3$(773) ( ■ ), Pd@CeO$_2$/Si-Al$_2$O$_3$(1073) ( ● ), and Pd@CeO$_2$/Si-Al$_2$O$_3$(1123) (▲ ). Data were taken with 3.8 torr CH$_4$ and 38 torr O$_2$.](image-url)
A similar and more pronounced positive effect of calcination temperature was observed for the MSR reaction. As shown in Figure 3.6a), Pd@CeO$_2$/Si-Al$_2$O$_3$(1073) exhibited reasonably stable methane conversions over a period of 10 h, decreasing from approximately 14% to 10%. This is in sharp contrast to what was observed with the Pd@CeO$_2$/Si-Al$_2$O$_3$(773) sample, Figure 3.6b). In this latter case, the MSR conversion dropped dramatically from approximately 6% to near zero after just 1 h. Treatment of the catalyst in O$_2$ at 693 K restored the initial activity, but the conversion again dropped after a short time on stream. Since the amounts of CO and CO$_2$ that could have formed during the period of time the Pd@CeO$_2$/Si-Al$_2$O$_3$(773) catalyst was undergoing deactivation were at least 100 times greater than the amount of oxygen that could be removed from the catalyst, CH$_4$ conversion cannot be due simply to reduction of the catalyst. To distinguish between deactivation due to carbonate formation [83-85] and deactivation due to catalyst reduction, the deactivated sample in Figure 3.6b) was treated in O$_2$ (to remove any carbonates), then reduced in H$_2$, before again measuring the conversion in MSR. Since the conversions after reduction in H$_2$ were low on a sample that could not have had any carbonates, it appears that deactivation is due to reduction of the catalyst.
Figure 3.6a): CH$_4$ conversion as a function of time during the MSR reaction at 693 K over Pd@CeO$_2$/Si-Al$_2$O$_3$(1073). Data were taken with 35 torr CH$_4$ and 70 torr H$_2$O.

Figure 3.6b): CH$_4$ conversion as a function of time during the MSR reaction at 693 K over Pd@CeO$_2$/Si-Al$_2$O$_3$(773). The sample was exposed to oxidizing and reducing treatments as shown. Data were taken with 35 torr CH$_4$ and 70 torr H$_2$O.
Although it was not possible to determine steady-state MSR rates on Pd@CeO$_2$/Si-Al$_2$O$_3$ (773) because of the rapid deactivation, the initial rates on Pd@CeO$_2$/Si-Al$_2$O$_3$ (1073) could be measured and compared to the traditional Pd/CeO$_2$ catalyst. Figure 3.7 indicates that the MSR rates per gram catalyst on these two catalysts, measured under differential conditions, were very similar, both in magnitude and activation energy. (TOF and activation energy of the Pd/CeO$_2$ catalyst shown here were essentially identical to those reported in the literature for catalysts prepared in a similar manner [86].) Furthermore, unlike the case for Pd@CeO$_2$/Si-Al$_2$O$_3$ (773), pretreating Pd@CeO$_2$/Si-Al$_2$O$_3$ (1073) in either H$_2$ or O$_2$ at 693 K had no major effect on the rates.

![Figure 3.7: Rates for the MSR reaction over Pd/CeO$_2$ (■), Pd@CeO$_2$/Si-Al$_2$O$_3$ (1073) after oxidizing in O$_2$ (○), and Pd@CeO$_2$/Si-Al$_2$O$_3$ (1073) after reducing in H$_2$ (Δ). Data were taken with 35 torr CH$_4$ and 70 torr H$_2$O.](image-url)
3.3.3 CO Adsorption

The results in Figure 3.6b) for the MSR reaction over Pd@CeO_2/Si-Al_2O_3(773) are very similar to what was observed in an earlier study of the WGS reaction on catalysts formed from Pd@CeO_2 supported on untreated Al_2O_3 and calcined at 773 K [69]. The earlier study also reported that rates decreased dramatically following reduction of the catalyst in H_2 at 623 K. Furthermore, in that earlier study, adsorption of CO on the Pd cores was completely suppressed after reduction in H_2. It was argued that the reduced ceria crystallites in the shell undergo cell expansion and rearrangement, resulting in reduced shell porosity, thus preventing CO adsorption on Pd.

To gain insights into the effect of calcination and reduction temperatures on the catalysts used in the present study, CO adsorption measurements were performed on the Pd@CeO_2/Si-Al_2O_3(773) and Pd@CeO_2/Si-Al_2O_3(1073) samples after reduction in H_2 at either 423 or 673 K. Table 3.1 provides Pd dispersions determined using volumetric uptakes of CO at room temperature. For reduction at 423 K, both samples showed reasonably good dispersions of 21 and 24%. It is noteworthy that the higher calcination temperature did not significantly decrease the measured dispersion in this case. However, after reduction at 673 K, the CO uptakes on the Pd@CeO_2/Si-Al_2O_3(773) were very low, ~5%, consistent with observations from the previous study. Re-oxidation of Pd@CeO_2/Si-Al_2O_3(773), followed by reduction at 423 K, fully restored the initial CO adsorption capacity of this sample. By contrast, reduction at 673 K had a much smaller effect on the adsorption properties of Pd@CeO_2/Si-Al_2O_3(1073), only decreasing the apparent Pd dispersion from 21 to 18%.
Table 3.1: Pd dispersions, in percent, based on CO uptakes at room temperature for different H₂ reduction temperatures.

<table>
<thead>
<tr>
<th></th>
<th>1&lt;sup&gt;st&lt;/sup&gt; Reduction at 423K</th>
<th>2&lt;sup&gt;nd&lt;/sup&gt; Reduction at 673K</th>
<th>3&lt;sup&gt;rd&lt;/sup&gt; Reduction at 423K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd@CeO₂/Si-Al₂O₃(773)</td>
<td>24</td>
<td>5</td>
<td>22</td>
</tr>
<tr>
<td>Pd@CeO₂/Si-Al₂O₃(1073)</td>
<td>21</td>
<td>18</td>
<td>20</td>
</tr>
</tbody>
</table>

To ensure that the CO adsorption in Table 3.1 was associated with Pd, FTIR measurements were conducted on the Pd@CeO₂/Si-Al₂O₃(773) and Pd@CeO₂/Si-Al₂O₃(1073) samples following reduction at 423 or 673 K, with results shown in Figure 3.8. The spectrum in Figure 3.8a was obtained following room-temperature adsorption of CO on Pd@CeO₂/Si-Al₂O₃(773), after oxidation in 10% O₂/He at 673 K and reduction in 10% H₂/He at 423 K. It is typical of spectra for CO on supported-Pd catalysts. The reasonably sharp peak at 2090 cm⁻¹ is due to CO that is present at “on-top” sites of Pd, while the broad features between 1800 and 2000 cm⁻¹ are typical of “bridge-bonded” CO on Pd. When CO is exposed to this same catalyst after reducing it in 10% H₂ at 673 K, the greatly reduced intensities of the bands in the υ(CO) stretching region of the spectrum in Figure 3.8b) are consistent with suppression of CO adsorption. It is noteworthy that the CO which does adsorb is primarily present at on-top sites and that the bridge-bonded species are almost nonexistent. The υ(CO) vibrational spectrum of Pd@CeO₂/Si-
Al₂O₃(1073), following reduction at 423 K and room-temperature CO adsorption, is shown in Figure 3.8c) and is identical to that obtained on Pd@CeO₂/Si-Al₂O₃(773). Although CO is still able to adsorb on Pd@CeO₂/Si-Al₂O₃(1073) after reduction at 673 K, the spectrum in Figure 3.8d) indicates that adsorption in bridge-bonded sites is again suppressed, so that a larger fraction of the CO is present at on-top sites.

Figure 3.8: Diffuse reflectance FTIR spectra obtained in flowing He after exposure to CO at room temperature for the following samples: a) Pd@CeO₂/Si-Al₂O₃(773) after reduction at 423 K; b) Pd@CeO₂/Si-Al₂O₃(773) after reduction at 673 K; c) Pd@CeO₂/Si-Al₂O₃(1073) after reduction at 423 K; and d) Pd@CeO₂/Si-Al₂O₃(1073) after reduction at 673 K.
3.3.4 Transient-Pulse Studies

To gain insights into the redox properties of the core-shell catalysts and into the reasons behind the changes which occurred with calcination to higher temperatures, we examined selected catalysts using transient-pulse studies. First, we compared the redox properties of Pd@CeO₂/Si-Al₂O₃(773) and Pd@CeO₂/Si-Al₂O₃(1073) with those of the Pd/Al₂O₃ using results from alternating pulses of O₂ and CO, like that reported in Figure 3.9. Figure 3.9 shows the intensities from selected peaks in the mass spectra of the effluent from the reactor during step changes in the inlet composition. These measurements were performed at 673 K using 1.0 g of Pd@CeO₂/Si-Al₂O₃(773). The inlet flow to the reactor was primarily He, at a fixed flow rate of 20 mL min⁻¹, but the gas composition was changed to 10% of either O₂ (m/e=32) or CO (m/e=28) during the step changes in composition. CO₂ (m/e=44) was produced upon exposure to O₂ as a result of cerium carbonate decomposition [65] and upon exposure to CO as a result of PdO and CeO₂ reduction. After the initial pulse of O₂, the sample in Figure 3.9 was exposed to two CO pulses to make sure that complete reduction occurred during the first pulse. As discussed earlier, no attempt was made to extract kinetic information from the pulse data; but the amount of CO₂ formed during the CO and O₂ pulses is easily calculated by integration. In Figure 3.9, the CO₂ formed during the CO pulse corresponded to 250 μmol g⁻¹. An additional 50 μmol g⁻¹ of CO₂ formed during the O₂ pulse due to decomposition of adsorbed cerium carbonates [65], so that the total amount of oxygen that could be transferred in a set of CO-O₂ pulses was 300 μmol g⁻¹. For a catalyst that is 1-wt% Pd, 94 μmol g⁻¹ of oxygen can be attributed to the Pd-PdO transition, while complete reduction of 9-wt% CeO₂ to Ce₂O₃ could account for another 260 μmol g⁻¹.
Figure 3.9: Results from the pulse measurement performed at 673 K on Pd@CeO$_2$/Si-Al$_2$O$_3$(773). The data were obtained monitoring CO$_2$ (m/e = 44), O$_2$ (m/e = 32), and CO (m/e = 28).

Experiments similar to that in Figure 3.9 were conducted as a function of temperature on each of the catalysts and the total amounts of oxygen that could be transferred in a set of CO-O$_2$ pulses were then plotted in Figure 3.10. For Pd/Al$_2$O$_3$, the amount of oxygen that could be transferred in a pulse sequence at temperatures above 650 K was 110 μmol g$^{-1}$, a value that is within experimental error of that expected for
oxidation and reduction of the Pd. More oxygen was exchanged on Pd@CeO$_2$/Si-Al$_2$O$_3$(773) than on Pd@CeO$_2$/Si-Al$_2$O$_3$(1073) but the amounts indicated that significant oxidation and reduction of the Pd cores and the ceria shells occurred in both samples over the entire temperature range that was investigated. As expected, the extent of reduction also increased with increasing reduction temperature. Interestingly, the amount of oxygen transferred on Pd@CeO$_2$/Si-Al$_2$O$_3$(773) at 773 K was $365 \, \text{μmol g}^{-1}$, a number very close to that which would be expected if both Pd and ceria were oxidized and reduced to their theoretical limits.

![Figure 3.10](image_url)

**Figure 3.10:** A plot of the amount of CO$_2$ produced in a set of CO-O$_2$ pulses, measured as a function of temperature, using the Pd/Al$_2$O$_3$(■), Pd@CeO$_2$/Si-Al$_2$O$_3$(773) (○), and Pd@CeO$_2$/Si-Al$_2$O$_3$(1073) (Δ) samples.
The pulse reactor was also used to gain insights into the state of the catalysts under MSR conditions. Figures 3.11a) and 3.11b) show results for Pd@CeO$_2$/Si-Al$_2$O$_3$(773) and Pd@CeO$_2$/Si-Al$_2$O$_3$(1073), exposed to different gases at 673 K, monitoring peaks at m/e =16 (CH$_4$), 28 (CO), 32 (O$_2$), and 44 (CO$_2$). Although data for H$_2$ (m/e =2) and H$_2$O (m/e = 18) would have been desirable, the background signal in the mass spectrometer made it difficult to monitor these peaks. After exposing the catalysts to O$_2$, the catalysts were operated under MSR conditions (35 Torr of CH$_4$ and 70 Torr of H$_2$O, with a total flow rate of 120 mL min$^{-1}$) for 1 h, followed by pulses of CO, two pulses of H$_2$O, another pulse of CO, and finally pulses of O$_2$ and CO. Several important features emerge from the data.

**Figure 3.11a):** A plot of selected peaks from the mass spectra of the effluent from the pulse reactor using Pd@CeO$_2$/Si-Al$_2$O$_3$(773) at 673 K. The peaks that were monitored were CO$_2$ (m/e = 44 and 28), O$_2$ (m/e = 32 and 16), CO (m/e = 28), and CH$_4$ (m/e = 16). The inlet to the reactor is shown at the top.
Figure 3.11b: A plot of selected peaks from the mass spectra of the effluent from the pulse reactor using Pd@CeO$_2$/Si-Al$_2$O$_3$(1073) at 673 K. The peaks that were monitored were CO$_2$ (m/e = 44 and 28), O$_2$ (m/e = 32 and 16), CO (m/e = 28), and CH$_4$ (m/e = 16). The inlet to the reactor is shown at the top.

First, both catalysts exist in a significantly reduced state under MSR reaction conditions, since only about 20 to 30 μmol g$^{-1}$ of CO$_2$ formed on either catalyst during the CO pulse immediately after exposure to MSR conditions. Assuming that the catalysts reach the same oxidation state after the CO pulses in Figure 3.11 as they did in the CO-O$_2$ pulses from Figure 3.10, the average O:Ce ratio during MSR reaction at 673 K must be 1.60 for Pd@CeO$_2$/Si-Al$_2$O$_3$(773) and 1.72 for Pd@CeO$_2$/Si-Al$_2$O$_3$(1073). Since thermodynamic calculations indicate bulk ceria should not be significantly reduced at equilibrium under these MSR conditions [87], the nanocrystals in the ceria shells must be much more easily reduced than bulk ceria.
Second, Pd@CeO$_2$/Si-Al$_2$O$_3$(1073) is easily oxidized by H$_2$O, while Pd@CeO$_2$/Si-Al$_2$O$_3$(773) is not. In the CO pulses following exposure of the samples to H$_2$O, 150 μmol g$^{-1}$ of CO$_2$ were formed on Pd@CeO$_2$/Si-Al$_2$O$_3$(1073) but only 30 μmol g$^{-1}$ of CO$_2$ were formed on Pd@CeO$_2$/Si-Al$_2$O$_3$(773). The fact that there is no CO$_2$ in the subsequent O$_2$ pulse demonstrates that the failure of Pd@CeO$_2$/Si-Al$_2$O$_3$(773) to be oxidized by H$_2$O is not due to formation of carbon-containing deposits during the MSR reaction. This inability of reduced Pd@CeO$_2$/Si-Al$_2$O$_3$(773) to be oxidized by H$_2$O helps explain its low steady-state activity for MSR. Finally, results from the O$_2$ and CO pulses at the end of these experiments show that the redox properties for both catalysts remain unaffected by the exposure to MSR conditions, since both samples could be oxidized by O$_2$ and reduced by CO.

3.4 Discussion

The present study demonstrates that the catalytic properties of catalysts based on Pd@CeO$_2$/Si-Al$_2$O$_3$ depend strongly on calcination temperature. Increasing the calcination temperature from 773 to 1073 K increased the activity of these catalysts for methane-oxidation by more than a factor of two and had a much more dramatic effect on their activity for the MSR reaction. Earlier studies of the WGS reaction using catalysts made from the same Pd@CeO$_2$ core-shell building blocks used here, but calcined to only 773 K, showed very similar characteristics to what we observed with Pd@CeO$_2$/Si-Al$_2$O$_3$(773) for the MSR reaction [69], suggesting that increased calcination temperature would likely have had a large effect on that reaction as well.
Our results rule out the possibility that the positive effect of calcination to higher temperatures is simply to remove impurities introduced from the ligands used in making the Pd@CeO$_2$ particles. First, neither oxidation products nor oxygen consumption were observed above 600 K in the TPO results. Second, there was no spectroscopic evidence for the presence of sulfur, the most likely impurity, in the calcined catalysts. Third, it is difficult to see how the presence of contaminants would cause a catalyst that had been calcined at 773 K to be active for MSR when oxidized and almost completely inactive following reduction. Finally, the loss of CO chemisorption on Pd@CeO$_2$/Si-Al$_2$O$_3$(773) after reduction at higher temperatures is not a result that would be expected from contaminants.

We suggest that increasing the calcination temperature from 773 to 1073 K changed the catalyst properties by affecting the structure of the ceria shell, which in turn affects the reducibility of the ceria and its interactions with the Pd core. The role of ceria in Pd/ceria catalysts is to facilitate oxidation of Pd in both the MSR [34] and methane-oxidation [76] reactions, perhaps by transfer of oxygen from ceria to the Pd [88], so that changes in the redox properties of ceria would be expected to affect catalyst properties for both these reactions. Evidence for changes in the reducibility of the ceria shell upon calcination to higher temperatures comes directly from the pulse experiments which showed that reduced Pd@CeO$_2$/Si-Al$_2$O$_3$(773) could not be re-oxidized by H$_2$O, while reduced Pd@CeO$_2$/Si-Al$_2$O$_3$(1073) could be oxidized by H$_2$O. Based on thermodynamic data for bulk CeO$_2$ [87], ceria should be readily oxidized by H$_2$O at the high H$_2$O:H$_2$ ratios that would occur during exposure to a H$_2$O pulse; however, low-temperature forms
of ceria have been shown to have very different thermodynamic properties from that of bulk CeO$_2$ [89]. Theoretical considerations indicate Ce$^{4+}$ is strongly stabilized by symmetry in the fluorite structure [90], and it has been suggested that defects in low-temperature forms of ceria are responsible for changing its redox properties [91]. Certainly, heating the core-shell catalysts of this study to 1073 K increased the crystallinity of the ceria shell, as shown by the narrowing of the peaks in XRD, and this may be sufficient to allow the shell to be more readily oxidized.

The effect of reduction temperature on the CO adsorption results is also of interest. FTIR and CO chemisorption results both confirm that Pd is accessible to gas-phase reactants in the Pd@CeO$_2$/Si-Al$_2$O$_3$(773) sample if it has been reduced at lower temperatures but largely inaccessible following reduction at higher temperatures. Furthermore, the CO that can adsorb on the sample after high temperature reduction also appears to be restricted to on-top sites, whereas adsorption occurs at both on-top and bridge-bonded sites over the sample reduced at lower temperatures. Both of these observations are consistent with the idea that the ceria shell is highly porous following reduction at lower temperatures but that the pores “close up” after reduction at higher temperatures. A possible mechanism involving the spreading of the ceria shell over the surface of the Pd core has been discussed previously [69]. Although SMSI (Strong Metal Support Interaction) behavior has been reported by others for ceria-supported catalysts [92], past reports of adsorption suppression have always occurred following reduction at temperatures much higher than 673 K with ceria. The fact that this occurs at such low
temperatures in these catalysts is additional strong evidence that they possess a core-shell structure and that the ceria in this shell is easily reduced.

The CO adsorption results on Pd@CeO$_2$/Si-Al$_2$O$_3$(1073) are also interesting. Considering the high temperatures to which this catalyst had been exposed, the measured dispersions of nearly 20% are reasonably good. Although reduction at higher temperatures did decrease the apparent dispersion measured by CO and increase the relative ratio of on-top to bridge-bonded species, the effect was much less significant. The change seems to be due to a decrease in the reducibility of the ceria shell, although we cannot totally rule out that there could be a partial collapse of the core-shell structure.

Obviously, there is much that we still do not understand about these materials. Their high activity for methane-oxidation and excellent thermal stability demonstrates that these materials have great potential but their sensitivity to calcination and reduction temperatures shows that we have much to discover about the nature of their catalytic sites.

### 3.5 Summary

When calcined at 773 K, alumina-supported Pd@CeO$_2$ nanoparticles that have been prepared by self-assembly methods are easily over-reduced, causing suppressed adsorption of CO on the Pd core and decreased activity for reactions carried out under reducing conditions, such as methane-steam-reforming (MSR). Increasing the calcination temperature to 1073 K modifies the reducibility of the ceria shell, allowing for improved activity for methane-oxidation and MSR.
Chapter 4. Methane Oxidation on Pd@ZrO$_2$/Si-Al$_2$O$_3$ is Enhanced by Surface Reduction of ZrO$_2$

4.1 Introduction

The catalytic oxidation of methane has been extensively studied for applications ranging from removal of methane from engine exhausts to catalytic combustion for turbines, and supported PdO has been reported to be one of the best catalysts for this reaction [39, 70, 93-97]. However, major problems remain. First, the activity of conventional supported-Pd catalysts is insufficient at the lower temperatures, typically below 300 °C, required for applications with lean-burn engines [93], especially in the presence of water vapor [37, 98]. Second, metal sintering associated with high reaction temperatures leads to a loss of activity.

Our groups have recently demonstrated that a hierarchically structured catalyst, composed of Pd@CeO$_2$ nanoparticles supported on a functionalized Al$_2$O$_3$, shows great promise in solving some of these problems [63]. The catalysts showed very high activity for CH$_4$ oxidation at temperature below 400 °C and excellent thermal stability. Unfortunately, the Pd@CeO$_2$ catalyst was also very sensitive to the presence of water in the reactant mixture. In addition to the inhibition observed for CH$_4$ oxidation in the presence of water vapor at lower temperatures, suggested as possibly being due to the reversible reaction of PdO to form Pd(OH)$_2$ [99, 100], an additional deactivation of the Pd@CeO$_2$ catalyst was observed when CH$_4$ oxidation was carried out on the catalyst in the presence of water vapor at 600 °C [101]. Under these conditions, the CeO$_2$ shell was
converted to a hydroxide that caused the rates to decrease dramatically by suppressing the
transfer of oxygen from the support to the Pd. Catalyst activity could only be restored by
heating the catalyst above 700 °C to decompose the hydroxide.

Since water affects the performance of Pd@CeO$_2$/Si-Al$_2$O$_3$ catalyst by strong
interaction with reduced ceria, it seemed possible that a core-shell catalyst with a
different oxide shell could better resist water poisoning. An obvious choice for an
alternative oxide shell is ZrO$_2$ because of its good hydrothermal stability [98]. Even
though ZrO$_2$ is normally considered an irreducible oxide, and should therefore not
promote reaction in the same way that CeO$_2$ does, there are some indications that
interaction between Pd and ZrO$_2$ would affect the catalytic activity for CO hydrogenation
[52], methanol decomposition [53], and methane-steam-reforming [54]. Furthermore,
although the reaction order for CH$_4$ oxidation on Pd/ZrO$_2$ has been reported to be -1 in
the H$_2$O partial pressure [102], similar to what is observed on Pd/Al$_2$O$_3$ [98], another
more recent study indicated that Pd/ZrO$_2$ showed superior performance for CH$_4$ oxidation
in the presence of water vapor, even reporting “higher methane conversions in the
presence of water vapor than in its absence” [103].

In this chapter, I first investigated the effect of the shell material on CH$_4$
oxidation. Interestingly, both catalysts exhibit nearly identical properties for CH$_4$
oxidation under dry conditions. Both Pd@ZrO$_2$ and Pd@CeO$_2$ catalysts exhibited higher
rates after calcination to 800 °C compared to materials calcined to only 500 °C.
Equilibrium redox measurements obtained from coulometric titration indicated that the
zirconia at the Pd interface could be reduced and helped stabilize the active PdO phase to
lower $P(O_2)$. Finally, the fact that Pd@ZrO$_2$ catalyst did not undergo deactivation during CH$_4$ oxidation in the presence of water vapor at 600 °C implies that this catalyst should be very interesting for this application.

4.2 Experimental Methods

The synthesis of the Pd@ZrO$_2$/Si-Al$_2$O$_3$ catalyst is described in detail in previous publications [60, 62, 63]. Briefly, Pd@ZrO$_2$ core-shell nanoparticles were obtained by reaction of zirconium butoxide with 11-mercaptooundecanoic acid (MUA) protected Pd nanoparticles (Pd-MUA), followed by hydrolysis of zirconium butoxide to ZrO$_2$ in the presence of protective ligands. The Pd@ZrO$_2$ particles, dispersed in tetrahydrofuran, were then adsorbed from solution onto an Al$_2$O$_3$ support (Si-Al$_2$O$_3$) that had been modified by reaction with Triethoxy Octyl Silane (TEOOS) [63]. This modification of the support was required to make the Al$_2$O$_3$ hydrophobic so that Pd@ZrO$_2$ nanoparticles could adsorb onto the surface as isolated units. The Al$_2$O$_3$ itself was purchased from Alfa Aesar as γ-Al$_2$O$_3$ and then stabilized by calcining to 900 °C for 24 h, after which it had a surface area of 100 m$^2$ g$^{-1}$ as determined by BET isotherms. Catalysts were prepared with ZrO$_2$:Pd weight ratios of either 6, 9, or 12; attempts to produce materials with higher ZrO$_2$:Pd ratios were not successful due to excess ZrO$_2$ that was not associated with Pd. The final catalysts were 1-wt% Pd. After removing the catalysts from solution by centrifugation and drying, the resulting Pd@ZrO$_2$/Si-Al$_2$O$_3$ powders were calcined to either 500 °C or 800 °C for 6 h with a heating ramp of 3 °C min$^{-1}$. Pd@CeO$_2$/Si-Al$_2$O$_3$
catalysts were produced in a similar way, with a CeO$_2$:Pd weight ratio of 9, and were also calcined to either 500 °C or 800 °C for 6 h using the same heating ramp.

Conventional Pd/ZrO$_2$ and Pd/Al$_2$O$_3$ catalysts were prepared by wet impregnation of Pd(NH$_4$)$_4$(NO$_3$)$_2$. The ZrO$_2$ support was obtained by thermal decomposition of ZrO(NO$_3$)$_2$·xH$_2$O at 750 °C. The Al$_2$O$_3$ support used here is the same material used for the supported core-shell catalysts except it was not modified by TEOOS. After impregnation, both catalysts were dried and calcined for 6 h to 500 °C. For comparison purposes, a 1-wt% Pd/Si-Al$_2$O$_3$ catalyst, prepared from the Pd-MUA particles without oxide shells and the TEOOS-functionalized Al$_2$O$_3$, was also synthesized. In this case, Si-Al$_2$O$_3$ powder was first dispersed in THF and then an appropriate amount of Pd-MUA nanoparticles was added to the mixture dropwise. After stirring overnight, the solid residue was recovered by centrifugation, dried and calcined to 800 °C for 6 h.

TEM characterization was performed on a Jeol JEM 2100 operating at 200 kV. Samples were prepared by dispersing the powders into isopropanol and by drop-casting of the dispersion onto holey carbon coated 300 mesh Cu grids. Powder X-ray diffraction (XRD) patterns were recorded on a Rigaku Smartlab diffractometer equipped with a Cu K$_\alpha$ source. The powders were finely dispersed in 2-propanol by sonication and then drop-cast onto glass slides before analysis.

The Pd dispersions were quantified by volumetric CO adsorption measurements at room temperature after the following pretreatments. The calcined samples were placed in the adsorption apparatus, heated in 200 torr of O$_2$ at 400 °C, and then reduced at 150 °C.
in 200 torr of H\textsubscript{2}. Next, the samples were evacuated, cooled to room temperature, and then exposed to CO. O\textsubscript{2} titration measurements were performed in the same apparatus. In this case, the oxidized and reduced samples were heated in vacuum to 500 °C and then exposed to small pulses of O\textsubscript{2} until no additional O\textsubscript{2} was taken up by the sample.

Oxidation-reduction isotherms were measured using Coulometric Titration, as described elsewhere [64]. The sample to be characterized was placed in an alumina crucible that was then inserted into a YSZ (yttria-stabilized zirconia) tube that had Ag electrodes painted on both inside and outside. The sample size was chosen so as to contain ~100 μmol of Pd. The entire apparatus was heated to 600 °C; and a mixture of 5% O\textsubscript{2}, 11% H\textsubscript{2}O, and 84% Ar was allowed to flow through the YSZ tube at this temperature for 1 h. After stopping the flow, the ends of the YSZ tube were sealed. To perform the actual measurements, oxygen was electrochemically pumped out of the YSZ tube by applying a potential across the electrodes with a Gamry Instruments potentiostat. The amount of oxygen removed was determined by integrating the current as a function of time. After removing the desired amount of oxygen, the system was allowed to come to equilibrium with the electrodes at open circuit. The criterion that used for establishing equilibrium was that the open-circuit potential across the electrodes changed by less than 3 mV day\textsuperscript{-1}, which typically took between 4 and 10 days. Finally, the equilibrium P(O\textsubscript{2}) was calculated from the Nernst equation and the open-circuit potential. As an additional check that equilibrium was achieved and that there were no system leaks, most isotherms were measured again starting with the reduced sample and pumping oxygen back into the electrochemical cell.
The transient-pulse and light-off tests were performed in a tubular reactor that had an online quadrupole mass spectrometer to analyze the concentrations of the effluent gases [65, 104]. Prior to loading the samples in the reactor, each was pressed into thin wafers that were then broken into smaller pieces. For transient-pulse measurements, a 1-g sample was held in the quartz tubular reactor at atmospheric pressure. Computer-controlled solenoid valves allowed step changes in the gas composition. In all cases, He was the majority component of the flow, and the concentration of the active component (CO or O2) was maintained at 10%, with a total flow rate of 20 ml min⁻¹. Prior to the actual measurements, the samples were pretreated in O2-He mixtures at 400 °C for 15 min, flushed with He for 10 min, and then reduced in CO-He for 15 min. The amount of CO₂ that formed during CO flow was quantified by integration of partial pressure of CO₂ as a function of time. This O₂-CO sequence was repeated 3 times to ensure the reproducibility of the redox properties of each sample.

The methane-oxidation, light-off tests used 400 mg of sample. The composition of the reactant mixture was chosen to be 1% CH₄ and 5% O₂ in He and the total flow rate was maintained at 120 ml min⁻¹. For those experiments in which H₂O was added, the reactant mixture was bubbled through a H₂O saturator and the content of H₂O was controlled by the temperature of the saturator. Prior to performing a light-off measurement, each sample was exposed to a flowing mixture of 20% O₂ and 80% He for 30 min at 350 °C, then its temperature was ramped at 10 °C min⁻¹ to 800 °C in 1% CH₄, 5% O₂, and 94% He, held at 800 °C for 1 h, and then cooled to room temperature at 10 °C min⁻¹. This last ramping of the sample temperature in the reactant mixture was followed
because steady-state rate measurements showed that this procedure activated and stabilized the catalysts.

Steady-state rates for methane-oxidation were measured using 100 mg of sample in a ¼-in, quartz, flow reactor with an on-line gas chromatograph (SRI8610C) equipped with a Hayesep Q column and a TCD detector. For these measurements, the partial pressures of CH₄ and O₂ were fixed at 3.8 torr (0.5%) and 38 torr (5%) respectively with a total flow rate of 120 ml min⁻¹, corresponding to Gas Hourly Space Velocity of 72,000 mL g⁻¹ h⁻¹. CH₄ conversion was kept below 10% so that differential conditions could be assumed. The catalyst samples were again pressed into thin wafers, cleaned by oxidation at 350 °C in a flowing mixture of 20% O₂ and 80% He for 30 min, and activated by ramping the sample temperature in the reaction atmosphere to 800 °C.

4.3 Results

TEM results for Pd@ZrO₂ catalysts prepared using the methods described here, with a 9:1 weight ratio of ZrO₂ to Pd, have been published previously [62]. Following calcination at 500 °C, uniform core-shell particles are formed, with Pd cores that are approximately 2 nm in diameter and ZrO₂ shells that are approximately 2 nm thick. Figures 4.1A and 4.1B show representative TEM images of the calcined, 1-wt% Pd, Pd@ZrO₂/Si-Al₂O₃ catalyst with this ZrO₂:Pd ratio after calcination at 500 °C. Because of the small Pd particle sizes and the low contrast between Pd and ZrO₂, these two components are not easily distinguishable in the TEM images. However, a few Pd particles were imaged and shown to be surrounded by a thin ZrO₂ layer (~2 nm) in each
case (Figure 4.1A and 4.1B). Even after calcination to 800 °C, a few small particles (2-3 nm), surrounded by a ZrO$_2$ layer, were found in the sample (Figure 4.1C). Due to the small particle size, it is hard to unequivocally attribute the lattice spacing to metallic or oxidized Pd phase. However, lattice profile analysis of individual particles in the samples calcined at 500 °C (Figure 4.1D and 4.1E) support a lattice spacing of ~0.28 nm, in good agreement with the (101) lattice spacing in PdO (0.263 nm). It is likely that the low temperature calcination treatment produces some form of PdO$_x$ that reduces the contrast with the surrounding ZrO$_2$.

**Figure 4.1**: TEM images of Pd@ZrO$_2$/Si-Al$_2$O$_3$ catalysts. Parts A and B correspond to the 500 °C sample, while part C to the 800 °C calcined sample. In parts D and E, a lattice profile analysis of a single particle is presented.
XRD patterns of Pd@ZrO$_2$/Si-Al$_2$O$_3$ catalysts with 1-wt% Pd and varying ZrO$_2$:Pd ratios, calcined to either 500 or 800 °C, are shown in Figure 4.2. The diffraction pattern of tetragonal zirconia phase is also provided for comparison. Not surprisingly, the patterns are dominated by features associated with Al$_2$O$_3$ and peaks associated with Pd are not visible in any of the patterns. More interesting is the fact that the only pattern exhibiting evidence for tetragonal ZrO$_2$, at 30.3 and 50.3 degrees 2θ, is the one with a ZrO$_2$:Pd ratio of 9, calcined at 800 °C, pattern 6). The ZrO$_2$ phase in all of the other samples is either not crystalline or has crystallites too small to be observable by XRD. Even in pattern 6), the ZrO$_2$ crystallite sizes based on the peak width at half maximum, calculated from the Scherrer equation, is only about 4nm. Again, these results are consistent with formation of thin ZrO$_2$ shells in the Pd@ZrO$_2$ structures. At 800 °C and with 9-wt% ZrO$_2$, the shells are sufficiently thick to form crystallites large enough to be observable.
Figure 4.2: Powder XRD patterns of Pd/Si-Al₂O₃(1), and Pd@ZrO₂/Si-Al₂O₃ that calcined at different temperature and with different Pd:ZrO₂ ratio(2-6). 500 °C 1:6 (2), 500 °C 1:9 (3), 500 °C 1:12 (4), 800 °C 1:6 (5), 800 °C 1:9 (6). Reference powder diffraction pattern of tetragonal zirconia is shown at bottom. Al₂O₃ phase was marked by closed squares, ZrO₂ phase was marked with open squares.

The metal dispersions, determined by CO chemisorption, are shown in Table 4.1 for the Pd@ZrO₂/Si-Al₂O₃ catalyst with 1-wt% Pd and 9-wt% ZrO₂, calcined at 500 °C and 800 °C. For the Pd catalyst prepared without a shell, the dispersion after heating to 500 °C in air was 30%. Since 2-nm Pd particles should have a dispersion of ~50%, some sintering must have occurred during calcination. With the core-shell catalyst, the
dispersion after heating to 500 °C in air is lower, ~14%, due to the presence of the shell. The fact that adsorption is still observed implies that the shell must be porous. The CO chemisorption results were essentially unchanged after heating to 800 °C, suggesting that the core-shell helps stabilize the Pd particles, since heating to these high temperatures would normally be expected to cause Pd sintering.

**Table 4.1**: Pd dispersions based on CO uptakes at room temperature.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Dispersion (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1%Pd/Al$_2$O$_3$ 500</td>
<td>30</td>
</tr>
<tr>
<td>1%Pd@ ZrO$_2$/Si-Al$_2$O$_3$ 500</td>
<td>14</td>
</tr>
<tr>
<td>1%Pd@ ZrO$_2$/Si-Al$_2$O$_3$ 800</td>
<td>13</td>
</tr>
</tbody>
</table>

Figure 4.3 shows steady-state rates for CH$_4$ oxidation on selected catalysts as a function of temperature, for 0.5% CH$_4$ and 5% O$_2$, under differential conditions. All of the samples contained 1-wt% Pd and exhibited similar activation energy, ~90 kJ mol$^{-1}$. It is immediately apparent that the core-shell catalysts are significantly more active than the Pd/Al$_2$O$_3$ sample, despite having lower dispersions, implying that the ZrO$_2$ shell is not inert. Indeed, the methane-oxidation rates on the Pd@ZrO$_2$ samples were nearly identical to that observed previously with Pd@CeO$_2$/Si-Al$_2$O$_3$ [104]. Also similar to what is observed on Pd@CeO$_2$/Si-Al$_2$O$_3$ [104], the rates improved when the samples were calcined to 800 °C, rather than 500 °C.
A major issue observed with Pd@CeO₂/Si-Al₂O₃ catalyst is their strong sensitivity to the presence of water vapor in the feed [101]. Not only the rates were found to be much lower in the presence of water vapor, but also that carrying out CH₄ oxidation in the presence of water vapor at 600 °C resulted in a strong deactivation that could only be reversed by heating the sample above 700 °C. Results from previous work indicated that the CeO₂ shell formed a stable hydroxide that was unable to transfer oxygen to the
Pd, causing the Pd to become reduced under reaction conditions. As shown in Figure 4.4, this deactivation process does not occur with the Pd@ZrO\textsubscript{2}/Si-Al\textsubscript{2}O\textsubscript{3} catalyst.

**Figure 4.4**: Effect of high temperature water poisoning over 1-wt\%Pd@9-wt\%ZrO\textsubscript{2}/Si-Al\textsubscript{2}O\textsubscript{3} (A), and 1-wt\%Pd@9-wt\%CeO\textsubscript{2}/Si-Al\textsubscript{2}O\textsubscript{3} (B). Both catalysts were calcined at 800 °C. The aged samples were kept under wet reaction conditions for 4 hours at 600 °C, then cooled to room temperature under He, followed by light-off test. Data were taken with 1% CH\textsubscript{4} and 5% O\textsubscript{2}. The heating and cooling rates are 10 °C min\textsuperscript{-1}.

In Figure 4.4, the CH\textsubscript{4} conversion was measured as a function of temperature in 1% CH\textsubscript{4} and 5% O\textsubscript{2} as the temperature was ramped at 10 °C min\textsuperscript{-1} from 100 °C to 800 °C, then cooled at this same rate back to 100 °C. For the fresh samples calcined at 800 °C, results for Pd@ZrO\textsubscript{2}/Si-Al\textsubscript{2}O\textsubscript{3} and Pd@CeO\textsubscript{2}/Si-Al\textsubscript{2}O\textsubscript{3} are virtually identical. The conversion reached 100% by 400 °C on both catalysts on the upward ramp and showed a
similar, ~50 °C shift to lower temperatures on the downward ramp. Under these conditions, there was also no evidence for a decrease in conversion at higher temperature due to a PdO-Pd transformation, typically observed near 600 °C. However, when the catalysts were aged for 4 h at 600 °C in 1% CH₄, 5% O₂, and 10% H₂O, the results for Pd@ZrO₂/Si-Al₂O₃ and Pd@CeO₂/Si-Al₂O₃ were very different. After this pretreatment, the light-off curve for Pd@CeO₂/Si-Al₂O₃ in a dry reactant stream was shifted by more than 50 °C to higher temperatures on the upward ramp. After heating to 800 °C, the conversions on the downward ramp were the same as with the freshly calcined sample due to decomposition of the hydroxides. With Pd@ZrO₂/Si-Al₂O₃, aging under wet conditions had no effect.

Rates on the Pd@ZrO₂/Si-Al₂O₃ catalyst also seem to be less affected in the presence of water. Figure 4.5 compares light-off curves on the same two catalysts but now with 10% H₂O in the reactant mixture. For both catalysts, there is a shift to higher temperatures when H₂O is present. However, the shift is less with Pd@ZrO₂/Si-Al₂O₃. On the upward ramp, the CH₄ conversion reaches 100% at 500°C on Pd@ZrO₂/Si-Al₂O₃ but this conversion was reached with Pd@CeO₂/Si-Al₂O₃ only after heating to 600 °C.
Figure 4.5: Effect of water on methane light-off curves over 1-wt%Pd@9-wt%ZrO$_2$/Si-Al$_2$O$_3$ (A), and 1-wt%Pd@9-wt%CeO$_2$/Si-Al$_2$O$_3$ (B). Both catalysts were calcined at 800 °C. Data were taken with 1% CH$_4$, 5% O$_2$ and 10% H$_2$O (if present). The heating and cooling rates are 10 °C min$^{-1}$.

While there are differences between the catalysts made with CeO$_2$ and ZrO$_2$ shells, the similarities are perhaps more surprising. CeO$_2$ is well known to promote a wide range of reactions due to its reducibility [91], but ZrO$_2$ is normally considered an irreducible oxide. Because some reports have suggested ZrO$_2$ in contact with metals can be reduced [65, 105-107], we examined the redox properties of our catalysts.
Results from transient-pulse and oxygen-titration studies are shown in Table 4.2 for a series of catalysts with 1-wt% Pd. In the pulse measurements, the samples were exposed to a series of CO and O₂ pulses at 400 °C and the amount of CO₂ formed during the CO pulse was then quantified. If any of the CO₂ that is formed is due to the Bouduard reaction, CO₂ would be formed during the O₂ pulse, which was not observed. For a 1-wt% Pd catalyst, 94 µmol of CO₂/g-catalyst can be formed by reduction of PdO to Pd. For the conventional Pd/ZrO₂ catalyst and for the Pd nanoparticles on the functionalized Si-Al₂O₃, the amount of oxygen that could be removed was within experimental uncertainty of this value. However, for the core-shell catalyst, significantly more oxygen, between 145 and 160 µmol g⁻¹, was removed from the samples than could be explained by reduction of PdO. This was true for samples calcined at both 500 °C and 800 °C. The added amount of oxygen was not dependent on the amount of ZrO₂ in the sample, suggesting that only ZrO₂ that was in contact with the Pd was affected. To confirm these results, O₂ titration measurements were performed in the volumetric apparatus on the Pd/Si-Al₂O₃ and Pd@ZrO₂/Si-Al₂O₃ (calcined at 500 °C, with a ZrO₂:Pd ratio of 6) samples. In addition to using a different apparatus, the O₂ titration measurements used H₂ at 500 °C to reduce the catalysts and measured the amount of O₂ that could be taken up by the reduced samples. The results were in reasonable agreement with the pulse data.
Table 4.2: Results of O\textsubscript{2} titration and pulse study on different Pd based samples that used in this chapter.

<table>
<thead>
<tr>
<th></th>
<th>Sample</th>
<th>Reducibility (μmol O / g\textsubscript{sample})</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO-O\textsubscript{2}-CO pulse study</td>
<td>Pd/Si-Al\textsubscript{2}O\textsubscript{3}</td>
<td>107</td>
</tr>
<tr>
<td></td>
<td>Pd/ZrO\textsubscript{2}</td>
<td>95</td>
</tr>
<tr>
<td></td>
<td>Pd@ ZrO\textsubscript{2}/Si-Al\textsubscript{2}O\textsubscript{3} 1:6 500</td>
<td>160</td>
</tr>
<tr>
<td></td>
<td>Pd@ ZrO\textsubscript{2}/Si-Al\textsubscript{2}O\textsubscript{3} 1:9 500</td>
<td>154</td>
</tr>
<tr>
<td></td>
<td>Pd@ ZrO\textsubscript{2}/Si-Al\textsubscript{2}O\textsubscript{3} 1:12 500</td>
<td>145</td>
</tr>
<tr>
<td></td>
<td>Pd@ ZrO\textsubscript{2}/Si-Al\textsubscript{2}O\textsubscript{3} 1:9 800</td>
<td>145</td>
</tr>
<tr>
<td>O\textsubscript{2} titration</td>
<td>Pd/Si-Al\textsubscript{2}O\textsubscript{3}</td>
<td>87</td>
</tr>
<tr>
<td></td>
<td>Pd@ZrO\textsubscript{2}/Si-Al\textsubscript{2}O\textsubscript{3} 1:6 500</td>
<td>148</td>
</tr>
</tbody>
</table>

To gain additional insight into the redox properties of the core-shell catalysts, coulometric titration experiments were performed. In coulometric titration, a known amount of oxygen is first electrochemically pumped in or out of a sealed vessel containing the sample. After allowing the sample to reach equilibrium, the P(O\textsubscript{2}) is retrieved by measuring the voltage across a YSZ electrolyte [108, 109]. Figure 4.6(A) shows results at 600 °C for Pd/Al\textsubscript{2}O\textsubscript{3} catalysts with 1% and 5% Pd loading. The amount of oxygen removed from the samples, relative to the Pd content, is plotted against the equilibrium P(O\textsubscript{2}). Starting from the oxidized catalyst, the P(O\textsubscript{2}) at which PdO is completely reduced to Pd was found to be ~ 3.5×10\textsuperscript{-3} atm, in reasonable agreement with standard thermochemical data, which indicates the equilibrium P(O\textsubscript{2}) for the PdO-Pd transformation being 2.0×10\textsuperscript{-3} atm [110]. Because no other compounds can influence the
\( P(O_2) \) at this point, removal of even small amounts of oxygen causes the \( P(O_2) \) to decrease to very low levels. It is worth noting that results for 1-wt% and 5-wt% Pd were identical, demonstrating that the Pd loading does not influence the thermodynamics of the PdO-Pd reduction.

The analogous data for a conventional 1-wt% Pd/ZrO\(_2\) catalyst, given in Figure 4.6(B), indicate that much more oxygen can be removed from this sample than it could from the 1-wt% Pd/Al\(_2\)O\(_3\) catalyst and that reduction occurs in two stages. A reduction step with an O/Pd stoichiometry of 1 occurs between \( 10^{-3} \) and \( 10^{-4} \) atm as observed in the case of the Pd/Al\(_2\)O\(_3\) sample, indicating that the support does not influence the thermodynamics of the PdO-Pd reduction. In addition to this first reduction, there is a second process observed at a P(\( O_2 \)) of about \( 10^{-20} \) atm. This second step must be associated with reduction of the support. The isotherms measured in both directions, e.g. starting from an oxidized or a reduced sample, where over imposable demonstrating good reproducibility. In contrast to pulse studies (see above), reduction can be observed in the coulometric titration experiment because of the very reducing conditions that can be achieved with this technique at higher temperature (600 °C compared to 400 °C in the pulse study). It should be noted that, even with these more severe conditions, only a small fraction of the ZrO\(_2\) phase is reduced. Indeed, the extent of reduction is consistent with only the oxide at the Pd-ZrO\(_2\) interface being reduced.
Figure 4.6: Redox isotherms for Pd/Al₂O₃ (A) with 1-wt% Pd (□) and 5-wt% Pd (◆), 1-wt% Pd/ZrO₂ (B), and 1-wt% Pd@9-wt%ZrO₂/Si-Al₂O₃ (C). ◆ symbols were obtained starting from the oxidized state. ◇ symbols were measured while re-oxidizing the sample. All measurements were conducted at 600 °C.
The results for the 1-wt% Pd@ZrO2/Si-Al2O3 catalyst, with a ZrO2:Pd ratio of 9, after calcination to 800 °C, were very different from those of the previous two samples(Figure 4.6(C)). First, the amount of oxygen that could be removed from the sample was greater than that observed in the pulse experiments because of the higher temperatures used in the coulometric titration experiments. The total amount of oxygen removed from this sample in coulometric titration was approximately 2 mol per mole of Pd. (Even so, the average oxygen stoichiometry of the zirconia phase never had a calculated O:Zr ratio less than 1.89.) Also, unlike the isotherms on the conventional catalysts, there is no well-defined step at ~10^{-3} atm corresponding to equilibrium between Pd and PdO. Reduction occurs over a wide range of P(O2) and reduction of both the PdO and the ZrO2 shell appears to occur in single, gradual process. The reversibility of the isotherms demonstrates that these results are not simply due to kinetic effects but to thermodynamic properties of the sample.

An important consideration for interpreting the results from coulometric titration is that the samples are exposed to reducing conditions at 600 °C for long periods of time. Measurement of a complete isotherm like those in Figure 4.6(A-C) typically takes 60 days. For the conventional supported-Pd catalysts, significant sintering of the metal phase occurred during this time. At the end of the experiments, the Pd dispersions for the Pd/Al2O3 and Pd/ZrO2 catalysts were both determined to be below 3%. By comparison, the Pd@ZrO2/Si-Al2O3 was affected to a much lesser extent. Even after this treatment the dispersion was determined to be ~8% by CO chemisorption, suggesting that the Pd had not grown larger than the original 2 nm.
4.4 Discussion

A number of potentially important observations can be drawn from the results of this study. First, Pd@ZrO$_2$, core-shell catalysts are promising materials for CH$_4$ oxidation catalysis. The activity of these materials is comparable to the Pd@CeO$_2$ catalysts, without exhibiting the same deactivation in water vapor that was observed with the CeO$_2$-based catalyst. Second, ZrO$_2$ appears to be reducible, at least when it is in contact with Pd. The extent of ZrO$_2$ reduction is less than that observed with CeO$_2$ and it may be that only the ZrO$_2$ in direct contact with Pd is reduced; however, the fact that ZrO$_2$ may be able to donate oxygen to the metal under reaction conditions may explain why ZrO$_2$ catalyst can be catalytically active. Third, stabilization of PdO phase in the core-shell structure is demonstrated by showing that the equilibrium P(O$_2$) for the Pd-PdO transition is shifted to much lower values compared to those measured on conventional Pd/ZrO$_2$. Fourth, the equilibrium oxidation-reduction properties of the Pd@ZrO$_2$ core-shell catalysts are not a simple sum of those expected for the individual PdO-Pd and ZrO$_2$ phases. These four observations may indeed be related.

It has long been proposed that CeO$_2$-supported catalysts derive some of their attractive properties because of the reducibility of CeO$_2$, with oxygen transfer from CeO$_2$ to the metal playing an important part [111, 112]. Indeed, a very recent study of CO oxidation on CeO$_2$-supported Pt, Pd and Ni catalysts showed a strong correlation between rates and the interfacial contact area between the metal and CeO$_2$ [113]. Maximizing the contact area between the transition metal and CeO$_2$ was a fundamental goal behind preparing Pd@CeO$_2$ core-shell catalysts [63]. Based on the present results with Pd@ZrO$_2$,
it appears that a similar process may be applicable with the ZrO$_2$ analog as well. Transfer of oxygen from ZrO$_2$ to the Pd may occur under reaction conditions.

Contact between the transition metal and ZrO$_2$ in these core-shell materials may also provide opportunities that are not available with CeO$_2$. The Ce(III)-Ce(IV) redox couple is strongly dependent on the local structure and Ce cations can get locked into one oxidation state or the other depending on the local composition and structure. For example, in CeVO$_3$, Ce is locked in the +3 oxidation state; it has been reported that even exposure to oxygen plasmas is not able to oxidize the Ce cations [114]. By contrast, well-crystallized CeO$_2$ is difficult to reduce [89]. The primary reason that ceria-zirconia mixed oxides must be used for oxygen storage in three-way, automotive catalysts is that pure ceria loses its redox properties over time [91]. In the case of Pd@CeO$_2$ catalysts aged in water vapor, it appears that the CeO$_2$ shell converts to the hydroxide, which likely has Ce in its +3 state. The fact that ZrO$_2$ does not form the stable reduced phases under normal conditions may provide an opportunity in that it is unlikely that ZrO$_2$ would be similarly locked in a reduced state.

It is generally accepted that PdO is the active phase for methane-oxidation over Pd-based catalysts. Thermal decomposition of PdO to less active Pd at high temperatures plays an important role in affecting its reactivity. The results of coulometric titration show a significant shift to lower P(O$_2$) for the equilibrium state associated with PdO-Pd transformation, suggesting the metal-oxide interaction between Pd and ZrO$_2$ strongly enhanced PdO stability which in turn improved the catalytic activity.
It is intriguing that the coulometric titration data for the Pd@ZrO\textsubscript{2} catalyst did not exhibit a step at the expected P(O\textsubscript{2}) where PdO and Pd should be in equilibrium and that there was no distinct ranges that could be identified as reduction of Pd or reduction of ZrO\textsubscript{2}. In regards to reduction of PdO, it is possible that surface energies could influence the thermodynamics of the nanoparticles. For example, it has been reported that small supported Co particles can become oxidized under conditions used for the Fischer-Tropsch reaction, even though bulk thermodynamics suggest that metallic Co should be the stable phase [115]. Theoretical considerations have shown that the surface energies of nanoparticle Co are large enough to explain this effect [116]. Although an experimental attempt to verify this effect did not observe changes in the equilibrium P(O\textsubscript{2}) as a function of particle size, shifts to lower values were observed for the equilibrium P(O\textsubscript{2}) for small particles interacting with ZrO\textsubscript{2} [14]. That study suggested that Co-ZrO\textsubscript{2} interactions could be modifying the equilibrium properties. In principle, Pd-ZrO\textsubscript{2} interactions could be causing similar effects. Finally, it is noteworthy that metallic Zr can form very stable alloys with precious metals, referred to as Engel-Brewer intermetallic [117, 118], and this could provide a driving force for reduction of ZrO\textsubscript{2}. Again, some evidence for this has been presented in the literature for Pt [108, 119].

Finally, the fact that the Pd@ZrO\textsubscript{2} catalyst maintained its Pd dispersion to a much greater level after being exposed to reducing conditions at 600 °C for 60 days is a potentially important observation. As reported previously for Pd@CeO\textsubscript{2}, these core-shell catalysts appear to exhibit special stability based on their hierarchical structure. This
property is obviously very important for high-temperature applications, such as methane-oxidation.

There are still many unresolved question about the unique properties of Pd@ZrO$_2$/Si-Al$_2$O$_3$ catalysts that need to be further investigated. However, their high activity for methane-oxidation, good thermal stability, and high resistance toward water poisoning demonstrate the great potential for real catalytic application.

4.5 Summary

In this chapter, I have demonstrated that in the Pd@ZrO$_2$ core-shell catalyst, PdO phase was stabilized through strong interaction between Pd core and ZrO$_2$ shell. The ZrO$_2$ in contact with Pd is reducible and appears to enhance the oxidation activity of the Pd in a manner similar to what is observed with CeO$_2$. However, the ZrO$_2$ shell is distinct from CeO$_2$ in not undergoing deactivation in the presence of steam at high temperatures. Similar to earlier observations with Pd@CeO$_2$, the Pd@ZrO$_2$ catalysts also exhibit good thermal stability against sintering.
Chapter 5. Au@TiO₂ Core-Shell Nanostructures with High Thermal
Stability

5.1 Introduction

When Au is in the form of nanoparticles on certain oxide supports, it can exhibit surprisingly high catalytic activities for CO oxidation [120], propylene epoxidation [121, 122], and water-gas shift [123]. For example, titania-supported Au catalysts prepared by deposition/precipitation were reported to be capable of catalyzing CO oxidation at temperatures as low as 90 K [16]. However, the activities of Au catalysts are not simply dependent on the Au surface area but are strongly dependent on structure [124], with large Au particles exhibiting very low or no activity and specific clusters/structures being responsible for the overall observed catalytic rate [125]. The composition of the support is also critically important; and, although high activities have been reported for Au particles deposited on various oxides [126-128], the best results are usually obtained with titania [129]. Indeed, many authors have reported that a synergetic effect between Au and TiO₂ is responsible for high activity, with the active sites located at the interface between Au and TiO₂ [18-23]. A variation on this model has the active sites being the Au atoms that are separated from the titania by one monolayer of Au [24]. However, with either picture, the Au particle sizes must be very small in order to achieve high activity, with Au particle sizes targeted to be less than 3 nm [24, 130, 131]. Furthermore, the sites must be in the proximity of the reducible oxide support.
Another issue with Au catalysts is that small Au particles tend to sinter easily [131] due to the fact that Au has a very low surface energy compared to other transition-metal catalysts [132]. This problem of poor thermal stability, coupled with the strong particle-size dependence on activity, places severe restrictions on the potential of these materials for commercialization. To circumvent this problem, various approaches have been discussed for the design and synthesis of sinter-resistant materials. The first method of stabilizing metal particles involves modifying the oxide support so as to introduce sites that anchor the Au particles. For example, this has been accomplished on an MgO(001) surface by introducing hydroxyl groups [133]. More commonly, the oxide support is modified by surface substitution of a second oxide (e.g. addition of TiO$_2$ islands to silica [24] or Ti doping of silica [134]), with the Au then stabilized at these sites. A second method involves preparation of structures that isolate the Au particles, preventing them from coming together. One example of this approach is shown in the work of Zhang et al. [59], who prepared Au nanoparticles supported on TiO$_2$/SiO$_2$ core-shell composites, which were in turn encapsulated in mesoporous silica. The small TiO$_2$ particles anchored on SiO$_2$ beads led to a better dispersion of Au and the encapsulation improved sinter-resistance during calcination at 500 °C. In a second example, Ma et al. modified Au/TiO$_2$ catalysts by partially covering the catalyst with an amorphous SiO$_2$ layer deposited via gas-phase Atomic Layer Deposition (ALD) [135]. Although the SiO$_2$ layer stabilized the Au nanoparticles against sintering, it also reduced the activity of the catalyst by blocking the active sites. In a third example, Pietron et al. [56] formed isolated Au nanoparticles in Au-TiO$_2$ composite aerogels by adding alkanethiolate-monolayer-protected Au clusters to
a titania sol before gelation. A fourth approach, proposed by Guttel et al. [136], involves forming egg-yolk, core-shell structures, with Au particles encapsulated in hollow, Ti-doped ZrO$_2$ spheres. This group reported surprisingly high catalytic activities, even though the Au particle size was about 15 nm.

Our groups recently reported a new strategy of making dispersible, metal-core/oxide-shell nanostructures using self-assembly methods [60, 62, 63]. In this chapter, I will show application of the core-shell method to the preparation of Au@TiO$_2$/Si-Al$_2$O$_3$ catalysts. The oxide shell is initiated by reaction of an alkoxide precursor with the carboxyl end group on the thiol ligands bound to the surface of the preformed Au nanoparticles. Core-shell particles are then prepared by controlled hydrolysis in the presence of an organic acid, and these can in turn be adsorbed onto functionalized supports in monolayer form [63].

The resulting materials were found to be very active for oxidation of CO and to exhibit significantly higher thermal stability compared to a more conventional, titania-supported catalyst.

5.2 Experimental Methods

5.2.1 Synthesis of MUA-Au Nanoparticles [137]

0.085 g Et$_3$PAuCl and 0.33 g of 11-Mercaptoundecanoic acid (MUA) were co-dissolved in 10 ml of chloroform, forming a clear, colorless solution that was left stirring in air for 30 minutes. A solution of 0.215 g tert-butylamine-borane complex dissolved in a mixture of 15 ml chloroform and 2.5 ml ethanol was then added in 20 min. The solution
was continuously stirred for 3 h, during which time the color gradually changed from light orange to reddish-purple, finally forming a dark purple precipitate. This precipitate was separated by centrifugation, washed with excess chloroform, and recovered by dissolving in THF.

5.2.2 Preparation of Au@TiO$_2$ Core-Shell Structures

As for Pd@TiO$_2$ particles [62], a THF solution of MUA-Au nanoparticles was added to a THF solution of titanium butoxide (with correct amounts to obtain a final Au/TiO$_2$ weight ratio of 1/9), followed by controlled hydrolysis in the presence of dodecanoic acid. The support for the Au@TiO$_2$ nanoparticles was a functionalized Al$_2$O$_3$ obtained by reaction of pristine γ-Al$_2$O$_3$ (Puralox TH100/150 obtained from Sasol, calcined at 900 °C for 24 h, 90 m$^2$ g$^{-1}$) with triethoxy octyl silane in a toluene solution at 110 °C [63]. The dispersible Au@TiO$_2$ nanoparticles adsorbed onto the functionalized Al$_2$O$_3$ from solution, as evidenced by the solvent turning from dark purple to almost colorless. Then the resulting colored powder was separated from the solution by centrifugation, washed with THF, and dried in an oven overnight. Before use, different portions of the catalyst were calcined at various temperatures (400 °C, 600 °C, or 700 °C) for 4 h using a heating rate of 3 °C min$^{-1}$. The composition of the catalyst was chosen to be 1-wt% Au and 9-wt% TiO$_2$, the rest being Si-Al$_2$O$_3$.

5.2.3 Preparation of Conventional Au/TiO$_2$

A Au(1%)/TiO$_2$ sample was prepared by impregnation of the MUA-Au nanoparticles onto Degussa P25 titania dispersed in THF (20 mL). The resulting powder was again separated by centrifugation, washed with THF, and dried in an oven overnight.
Calcination was performed at various temperatures (400 °C, 600 °C, or 700 °C) for 4 h using a heating rate of 3 °C min\(^{-1}\).

5.2.4 Characterization

TEM characterization was performed on a Jeol JEM 2100 operating at 200 kV. Samples were prepared either by drop-casting the particles directly from THF solution onto 300 mesh carbon-coated Cu grids (Electron Microscopy Sciences), or by dispersing the powders into isopropanol and by drop-casting of the dispersion onto holey carbon coated 300 mesh Cu grids (Electron Microscopy Sciences).

Steady-state rates of CO oxidation reaction were measured in a \(\frac{1}{4}\)-inch, quartz, tubular reactor, using 0.10 g of catalyst. All measurements were conducted at atmospheric pressure, with the partial pressures of CO and O\(_2\) being 25 and 12.5 torr, respectively, and the balance being He. The total flow rate of the gas mixture was maintained at 120 mL min\(^{-1}\). Before testing, each sample was activated by heating to 320 °C at 5 °C min\(^{-1}\) in the reaction mixture before cooling back to the desired reaction temperature. The composition of the reactor effluent was determined using an on-line gas chromatograph equipped with a HayeSep-D column and a thermal conductivity detector. All reported rates were measured with conversions below 15 % in order to ensure differential conditions.

Light-off curves were measured in a similar setup but using an on-line quadrupole mass spectrometer as detector. In this experiment, the concentrations of CO and O\(_2\) were chosen to be 7.6 torr (1%) and 152 torr (20%), the catalyst loading was 0.1 g, and the
total flow rate was maintained at 60 mL min\(^{-1}\). The conversions were then measured from room temperature to 150 °C, while ramping the temperature at 5°C min\(^{-1}\).

**5.3 Results and Discussion**

TEM images of the as-synthesized MUA-Au nanoparticles are shown in Figure 5.1. The low-magnification image in Figure 5.1A) demonstrates the uniformity of the particles, which are also well separated by the thiol ligands. The absolute sizes are more easily seen at the higher magnifications, Figures 5.1B) and 5.1C). These also show that Au particles have an average particle size of 3.1±0.3 nm, with a narrow particle size distribution (σ = 10%). The particles are rich in defects but they show lattice fringes that demonstrate their overall crystalline nature.
Figure 5.1: Representative TEM images of MUA-Au nanoparticles (A, B, C) and histogram of particle size distribution with fit for a Gaussian distribution (D).
Figure 5.2 shows TEM images of the Au@TiO$_2$ particles formed by reaction of MUA-Au with titanium butoxide, followed by hydrolysis of the alkoxide in the presence of dodecanoic acid. The sizes of the Au cores do not appreciably change compared to the initial MUA-Au nanoparticles and the structures are again well separated and dispersed, indicating their excellent colloidal stability. Despite the fact that the titania shells did not show high crystallinity and diffraction contrast, spherical shells of about same size as the Au cores can be observed surrounding the Au particles, with slight contrast on the TEM grid.

**Figure 5.2:** Representative TEM images of as-synthesized Au@TiO$_2$ core-shell structures.
Figures 5.3A-B show the material prepared by deposition of the Au@TiO$_2$ nanoparticles onto the Si-Al$_2$O$_3$ support after calcination to 400 °C to remove all the organic material. Because of the higher electron density of Au, the cores appear as dark spots on the lighter alumina particles. There was no noticeable growth in the diameters of the Au cores, with the Au nanoparticles remaining approximately 3 nm in diameter. The Au particles were surrounded by a thin (~2 nm), amorphous layer of titania (see inset in Figure 5.3B). By contrast, 1-wt% Au/TiO$_2$ samples prepared by depositing MUA-Au onto P25 TiO$_2$, followed by calcination to 400 °C, showed a distribution of Au particles of varying size, between 5 and 15 nm in diameter (Figures 5.3C and D)). Even with this low temperature treatment, the Au particle sizes increased in the Au/TiO$_2$ sample, a clear indication of sintering.
Figure 5.3: Representative TEM images of Au@TiO$_2$/Si-Al$_2$O$_3$ (A, B) and Au/TiO$_2$ P25 (C, D) calcined to 400 °C. Arrows point at Au particles in the two samples.
Steady-state, CO-oxidation rates were measured under differential conditions in 25 torr of CO and 12.5 torr O₂, with results shown in Figure 5.4. Both catalysts were previously calcined in air to 400 °C. Because we observed that rates initially increased with time on stream for both catalysts, each sample was activated by ramping its temperature to 320 °C at 5 °C min⁻¹ in the reaction mixture before cooling back to the desired reaction temperature. The rates on both catalysts exhibited very low temperature dependences, with activation energies of approximately 30 kJ mol⁻¹. Rates on Au@TiO₂/Si-Al₂O₃ were about 8 times higher than those on Au/TiO₂ and therefore comparable to rates obtained on catalysts prepared by deposition/precipitation methods that have previously been reported to be highly active for low-temperature CO oxidation [138, 139]. This result also demonstrates that the TiO₂ shell on Au@TiO₂/Si-Al₂O₃ must be porous in order to allow reactants to access the Au particles. The difference between the two catalysts is primarily explained by the fact that the Au particle sizes are smaller in the core-shell catalyst due to its higher thermal stability.

**Figure 5.4:** CO oxidation rates for Au@TiO₂/Si-Al₂O₃ (■), and Au/TiO₂ (◇). Both samples were calcined at 400 °C. Data were taken with 25 torr CO and 12.5 torr O₂.
As a further indication of the relative stabilities of the Au@TiO$_2$/Si-Al$_2$O$_3$ and Au/TiO$_2$ catalysts, light-off curves were measured on both samples as a function of the calcination temperature. In this case, samples were first calcined in air for 4 h to either 400, 600, or 700 °C. After placing the samples in the reactor, the CO conversions in 7.6 torr CO and 152 torr O$_2$ were measured as a function of temperature, as shown in Figure 5.5. For calcination at 400 °C, both catalysts showed high CO conversions, even at room temperature. The conversion on Au@TiO$_2$/Si-Al$_2$O$_3$ was above 80% but the Au/TiO$_2$ sample was also quite active. When the catalysts were calcined at 600 °C, the light-off conversions for Au@TiO$_2$/Si-Al$_2$O$_3$ showed only a slight decrease while conversion on the Au/TiO$_2$ sample decreased more significantly. Treating the samples at 700 °C caused a more precipitous decline, with the Au/TiO$_2$ catalyst now exhibiting negligible conversions below 70 °C; however, the Au@TiO$_2$/Si-Al$_2$O$_3$ sample remained reasonably active even after this high-temperature treatment.
Figure 5.5: Light-off curves of CO conversion against temperature for Au@TiO$_2$/Si-Al$_2$O$_3$ (A), and Au/TiO$_2$ (B) that calcined at different temperatures. Data were taken with 7.6 torr CO and 152 torr O$_2$. 
TEM images of Au nanoparticle in the Au@TiO$_2$/Si-Al$_2$O$_3$ and Au/TiO$_2$ catalysts after calcination at 600°C for 4 h are shown in Figure 5.6. On the core-shell catalyst, the Au particles remain approximately 3 nm in diameter, Figure 5.6A) and B), while the Au particles on the conventional titania support, Figure 5.6C) and D), have grown dramatically. Typical particle sizes are now above 20 nm. Furthermore, even after treating to this high temperature, the core-shell structure appears to remain intact. The Au particles on the Au@TiO$_2$/Si-Al$_2$O$_3$ sample are always surrounded by TiO$_2$. This indicates that the intimate contact derived from unique core-shell configuration allows the small Au crystallites to remain isolated against sintering.

![Representative TEM images of Au@TiO$_2$/Si-Al$_2$O$_3$ (A, B) and Au/TiO$_2$ P25 (C, D) catalysts calcined to 600 °C. Arrows point at Au particles in the two samples.](image)

**Figure 5.6:** Representative TEM images of Au@TiO$_2$/Si-Al$_2$O$_3$ (A, B) and Au/TiO$_2$ P25 (C, D) catalysts calcined to 600 °C. Arrows point at Au particles in the two samples.
5.4 Summary

In this chapter, I have successfully synthesized Au@TiO$_2$ core-shell nanostructure and deposited them on to modified hydrophobic alumina as single units. This catalyst is not only very active for CO oxidation at low temperatures but also highly stable against sintering. As revealed by TEM images, the Au particles maintained an average size of 3 nm even after calcination up to 600 °C in air. The unique core-shell configuration improved the metal-support interaction, which led to an enhanced resistance of Au particles toward sintering. The excellent thermal stability of Au@TiO$_2$/Si-Al$_2$O$_3$ catalyst made it a potential material for catalyzing other high temperature reactions.
6.1 Introduction

Hydrogen is one promising fuel to replace fossil fuels. The methanol-steam-reforming (MSR) reaction is of interest to produce hydrogen due to high H/C ratio, no C-C bond and can take place at relatively low temperature [140]. In the MSR, to achieve high amounts of H$_2$, the catalysts have to be highly selective to CO$_2$ [141]. Metals of group VIII on different supports have been studied as potential catalysts for MSR [7, 142, 143].

ZnO exhibits interesting properties as a support and as a promoter for Pt and Pd catalysts [7, 141, 144]. The relatively facile reduction of ZnO and subsequent formation of PtZn and PdZn alloys lead to strikingly different catalytic activities compared to the bare metals. For example, PtZn alloys formed from Pt/ZnO catalysts were found to be selective for hydrogenation of $\alpha,\beta$-unsaturated aldehydes to the corresponding saturated alcohols [6]. It has been shown that the addition of Zn to Pt(111) surface changes the reactivity of platinum, the catalysts becoming more selective for deoxygenation of aldehydes and methanol-steam-reforming reaction due the formation of PtZn alloy [145, 146]. Similarly, Zn-promoted, carbon-supported Pt and Pd catalysts are selective for MSR, with CO$_2$ being the primary product, rather than CO [147, 148]. Also, Pd/ZnO has shown high CO$_2$ selectivity in the MSR reaction due to the formation of alloy phase [149].
Other studies demonstrate that the particle size of the PdZn alloy affect the selectivity for the MSR [150-152].

The methods used for the preparation of the catalysts affect their activity and selectivity. The effect of the preparation method in the activity and selectivity of the catalysts towards MSR has been reviewed [141]. Structural and compositional heterogeneity are important considerations for any supported-metal catalyst but they are especially important with alloys. For example, most Pt/ZnO catalysts formed by impregnation of Pt salts onto a ZnO support would have Pt particles with wide size distributions [147]. Pt-Zn alloys form upon reduction, but the Pt:Zn ratio depends on the reduction conditions and the initial Pt particle size. If Zn salts are added to an existing supported-metal catalyst, only a fraction of the Zn will end up interacting with the metal component, and a significant excess of Zn has to be added in order to ensure contact between Zn and Pt components [147]. These issues bring the challenge of finding preparation methods that allow fine tuning of the composition and morphology of the catalysts.

Recent work from our laboratories has provided a method for achieving homogeneous materials with uniform particle sizes and compositions, with good contact between precious metals and oxide phases [63]. The method involves preparing metal nanoparticles with oxide shells in solution, then adsorbing these core-shell particles onto an inert support. Uniform metal particles are produced by reduction of a metal salt in the presence of a bifunctional ligand, 11-mercaptopoundecanoic acid (MUA), in an organic solvent [60, 62]. Uniform oxide
shells are then formed around the metal nanoparticles by reaction of a metal alkoxide with the carboxylic acid end group of the MUA ligand. Following a controlled hydrolysis of the remaining alkoxide groups in the presence of an organic acid, well defined, core-shell particles are produced and remain stable and dispersed in the organic solvent. Finally, the dispersed core-shell structures can be deposited onto engineered oxide supports in monolayer form, and then calcined to remove the remaining ligands. Using these methods, Pd and Pt nanoparticles have been prepared with CeO$_2$, ZrO$_2$, and TiO$_2$ shells [62].

In the present chapter, I will demonstrate that Pt@ZnO and Pd@ZnO core-shell catalysts of uniform size and composition can be prepared by methods similar to those used previously [60]. The core-shell particles can again be adsorbed from solution onto functionalized-alumina supports. In-situ TEM and coulometric titration experiments suggest the formation of alloyed particles of controlled size. The catalytic activity and selectivity of the systems for MSR are also shown to be in agreement with the formation of the alloys. This work provides a general method to prepare alloyed particles of tunable size and composition starting with well-defined core-shell building blocks.
6.2 Experimental Methods
6.2.1 Materials

Potassium tetrachloroplatinate(II) (K$_2$PtCl$_4$, 98%), potassium tetrachloropalladate(II) (K$_2$PdCl$_4$, 98%), diethylzinc (Zn 52.0 wt. %), 11-mercaptoundecanoic acid (MUA, 95%), anhydrous 1-butanol (99.8%), and triethoxy(octyl)silane (TEOOS, ≥ 97.5 %) were purchased from Sigma–Aldrich. Dodecylamine (CH$_3$(CH$_2$)$_{11}$NH$_2$, 98%), lithium triethylborohydride (1.0 M LiBEt$_3$H in THF) and dodecanoic acid (CH$_3$(CH$_2$)$_{10}$COOH, 99%) were purchased from Acros Organics. Anhydrous magnesium sulfate was purchased from Fisher-Scientific. Sodium borohydride (NaBH$_4$, 98%), tetraammineplatinum(II) nitrate (Pt(NH$_3$)$_4$(NO$_3$)$_2$, 99.99%), tetraamminepalladium(II) nitrate solution ((NH$_3$)$_4$Pd(NO$_3$)$_2$, 99.9%), tetraoctylammonium bromide (TOABr, 98%+) and zinc oxide powder (ZnO, 99.9%, 42 m$^2$ g$^{-1}$) were purchased from Alfa Aesar. Al$_2$O$_3$ powder (Puralox TH100/150) was purchased from Sasol and calcined to 1173 K for 24 h prior to use (surface area 90 m$^2$ g$^{-1}$). All of the solvents were HPLC grade from Fisher-Scientific.

6.2.2 Synthesis of the Catalysts

MUA-protected Pt nanoparticles (Pt-MUA in tetrahydrofuran, THF) were prepared following previously reported procedures [62]. Briefly, K$_2$PtCl$_4$ was dissolved in deionized water and transferred to CH$_2$Cl$_2$ using TOABr as phase-transfer agent. The aqueous phase was discarded and the organic phase was dried with anhydrous magnesium sulfate. Dodecylamine was added and the reaction vessel was purged with N$_2$ until after the Pt reduction step. The reducing agent
(LiBEt₃H) was added rapidly, with vigorous stirring, causing the solution to change from orange to black. The solution was then stirred for an additional 5 min. Next, the reaction mixture was washed with water and the solvent removed by evacuation. Ethanol was added to the black solid, which was then centrifuged three times to remove the excess of dodecylamine and TOABr. After dissolving the Pt-dodecylamine nanoparticles in a CH₂Cl₂/THF solution, MUA was added and the solution stirred overnight. After again removing the solvent by evacuation, the solid was washed with CH₂Cl₂ and centrifuged three times to remove excess dodecylamine. Finally, the black solid (Pt-MUA) was redissolved in THF. The Pd-MUA nanoparticles were prepared following previously reported procedures [60].

The synthesis of zinc butoxide (Zn(OBu)₂) was carried out in a nitrogen-filled glove box (<0.1 ppm of water and O₂) following previously reported procedures, with only slight modifications [153]. Diethyl zinc ((C₂H₅)₂Zn, 1 mmol) was added dropwise to anhydrous 1-butanol (C₄H₉OH, 5 mL) with vigorous stirring. (Caution: Flammable gas is generated in this process and the reaction is exothermic.) The zinc butoxide solution produced in this process is stable under air exposure for a limited period of time and was therefore taken out of the glove box and used immediately without further purification. The functionalized, hydrophobic alumina (Si-Al₂O₃) was prepared by allowing pristine Al₂O₃ (10 g) to react with TEOOS (5.8 mL) in toluene (30 mL) [63]. The solution was refluxed for 6 hours, filtered, and washed several times with toluene to remove unreacted TEOOS. The powder was dried in air overnight at 383 K.
Preparation of the catalyst Pt(1-wt%@ZnO(9-wt%/Si-Al_2O_3 was similar to published procedures [60, 62]. An appropriate volume of Pt-MUA solution was added dropwise to an appropriate amount of Zn(OBu)_2 solution under constant stirring to achieve the final desired loadings. Dodecanoic acid (1 mol per Zn), dissolved in THF, was added to the dispersed particles, after which the hydrolysis was carried out by slowly adding a solution containing 0.5 mL H_2O in 10 mL of THF over a period of two hours. Next, the Si-Al_2O_3 was slowly added to the Pt@ZnO solution and the slurry was stirred overnight. During this period, the Pt@ZnO nanostructures were adsorbed onto the Si-Al_2O_3 support, as evidenced by the solution turning from black to translucent white (The translucent white appearance is likely due to a small amount of Al_2O_3 or ZnO remaining suspended in solution.). Next, the solvent was removed by rotary evaporation. Finally, the Pt@ZnO/Si-Al_2O_3 sample was calcined in flowing air at 773 K for 6 h, using a heating ramp of 3 K min^{-1}. The Pd@ZnO/Si-Al_2O_3 sample was prepared following the same procedure described above but using the Pd-MUA solution.

Conventional Pt/ZnO, Pt/Al_2O_3, Pd/ZnO, Pd/Al_2O_3 catalysts with 1-wt% metal were also prepared for comparison purposes by wet impregnation of ZnO or Al_2O_3 with aqueous solutions of Pt(NH_3)_4(NO_3)_2 and (NH_3)_4Pd(NO_3)_2, respectively. The dried powders were calcined in air at 773 K for 6 h using a heating ramp of 3 K min^{-1}. 
6.2.3 Characterization

Transmission Electron Microscopy (TEM) images were obtained using a JEOL 2100 microscope, with an accelerating voltage of 200 kV. CO chemisorption measurements were performed using a home-built adsorption apparatus. To prepare the samples for chemisorption measurements, the calcined sample was first exposed to 200 Torr O\textsubscript{2} at 673 K for 2 min and then evacuated. This pre-treatment was repeated three times. Next, the sample was exposed to 200 Torr of H\textsubscript{2} at either 423 or 673 K for 5 min, followed by evacuation. This reduction step was again repeated three times. CO chemisorption was performed at room temperature by adding small pulses of CO to the sample until a pressure rise in the sample cell was detected.

A detailed description of the coulometric titration apparatus is given elsewhere [64]. Briefly, 1 g of Pt@ZnO/Si-Al\textsubscript{2}O\textsubscript{3} sample that was calcined at 1073 K was put in an aluminium crucible and inserted inside a yttria-stabilized zirconia (YSZ) tube with Ag electrodes that were painted on the inside and outside. After the apparatus was heated to 873 K, a mixture of 5% O\textsubscript{2}, 11% H\textsubscript{2}O and 84% Ar was introduced through the YSZ tube for 1 h, and the two ends of the tube were then sealed. The measurement of the redox isotherms was performed by electrochemically pumping controlled amounts of oxygen into the YSZ tube via the application of a voltage across the electrodes using a potentiostat (Gamry Instruments). The amount of oxygen transferred was quantified by integrating the current, and the system was allowed to reach equilibrium (when open-circuit...
voltage changes are less than 3 mV/day). The equilibrium P(O$_2$) was determined from the open-circuit potential using the Nernst equation. After obtaining the reduction isotherm, oxygen was added in controlled volumes to get the oxidation isotherm to confirm reversibility.

Rates and selectivity for methanol-steam-reforming (MSR) reaction were measured in a ¼ inch, quartz, tubular reactor at atmospheric pressure. 0.10 g of sample were loaded into the reactor and held in place with glass wool. Prior to MSR activity tests, the catalysts were reduced in flowing 5% H$_2$-He mixtures at 523 K for 30 min. After cooling to 453 K in flowing He, methanol/water mixture with partial pressure of 45 torr MeOH and 45 torr H$_2$O were introduced into the reactor with He as a carrier gas. The total volumetric flow rate in the reactor was kept to 110 mL min$^{-1}$. Products were analyzed using an online gas chromatograph (SRI8610C) equipped with a HayeSep Q column and a TCD detector. The catalytic activity and CO$_2$ selectivity were calculated on a carbon basis. The selectivity to CO$_2$ was defined as $S = (\text{moles CO}_2)/(\text{moles CO}_2 + \text{moles CO})$.

6.3 Results and Discussion

The supported Pt@ZnO and Pd@ZnO core-shell nanostructures were prepared in solution by self-assembly methods discussed above. Temperature Programmed Oxidation (TPO) (Figure 6.1) experiments on the uncalcined Pt@ZnO/Si-Al$_2$O$_3$ sample show that the decomposition of the ligands begins at approximately 400 K and that there is a peak in the oxygen consumption centered
at 525 K (Figure 6.1). Slightly higher temperatures (575 K) are required to remove the ligands in Pd@ZnO/Si-Al₂O₃ compared to Pt@ZnO/Si-Al₂O₃. A previous study of Pd@CeO₂/Si-Al₂O₃ shows the O₂-consumption peak at 480 K [104]. The temperature in which the ligands are removed from the samples depends on the metal and the oxide used; but, for all the samples, the ligands were removed by 650 K. For all studies in this paper, the samples were calcined at 773 K to form the core-shell nanostructures.

Figure 6.1: Temperature programmed oxidation (TPO) results for uncalcinated (a) Pt@ZnO/Si-Al₂O₃ and (b) Pd@ZnO/Si-Al₂O₃ samples.

Transmission Electron Microscopy (TEM) investigations were performed to understand nanoparticle morphology and particle size. Figure 6.2 shows representative TEM images of the Pt@ZnO/Si-Al₂O₃ calcined at 773 K in air. The low resolution TEM images (Figure 6.2A-B) show the core-shell particles...
distributed throughout the Si-Al₂O₃ support and the high magnification TEM images (Figure 6.2C-F) show the morphology of the core-shell nanostructures. The images show dark Pt cores surrounded by a crystalline ZnO shell supported onto the alumina grains. The Pt cores are about 2 nm in diameter, the same as the starting Pt-MUA nanoparticles [62], demonstrating that there was no agglomeration of the metal particles after calcination at 773 K. The entire core-shell nanostructures have a diameter of approximately 6 nm, from which a 2 nm-thick ZnO shell is measured. This thickness is similar to what observed in the case of titania, zirconia and ceria [62] and demonstrates the successful implementation of the procedure to the Pt-ZnO combination. The oxide shells in this synthesis procedure are limited to 2 nm by the number of carboxyl end groups present in the MUA ligands surrounding the dispersed metal nanoparticles.
Figure 6.2: Representative low (A, B) and high (C-F) resolution transmission electron microscopy (TEM) images of Pt@ZnO/Si-Al$_2$O$_3$ sample calcined at 773 K in air. Yellow arrows point to core-shell structures where the higher contrast is attributed to Pt cores surrounded by a lighter, ZnO shell.
It was possible to observe the formation of Pt-Zn alloy in the TEM due to the reducing power of the electron beam. Figure 6.3 reports a series of images taken at 20-s intervals where the initial Pt-ZnO core-shell particle dispersed onto the alumina support transforms into a slightly larger Pt-Zn core surrounded by a thinner ZnO shell. During alloy formation, the core Pt particle loses their crystalline morphology (Figure 6.3A) to transform into the disordered alloy (Figure 6.3D). Figure 6.4 shows the representative TEM images for the Pd@ZnO/Si-Al₂O₃ core-shell sample. Despite the lower contrast between Pd and the oxide, the ~2 nm metal cores are discernible also in this case and the metal particles are again surrounded by a ~2 nm oxide shell.

![Figure 6.3: TEM images taken at 20 s interval (from A to D) of two Pt@ZnO core-shell structures (A) that progressively transform into Pt-Zn alloyed particles under the electron beam irradiation. The images were taken at 200 kV.](image-url)
Figure 6.4: Representative TEM image of Pd@ZnO/Si-Al₂O₃ sample calcined at 773 K in air. Yellow arrows point to core-shell structures where the higher contrast is attributed to Pd cores surrounded by a lighter, ZnO shell.

X-ray diffraction (XRD) of the Pt/ZnO sample showed very low intensity and broad peaks near 2θ angles of 39.6° and 46.1° which can be attributed to Pt (111) and Pt (200) family of planes, respectively (Figure 6.5D). In the Pt/ZnO sample, a crystallite size of 45 nm was calculated using the Scherrer equation. Pt-Zn alloy was formed as evidenced by the lattice parameter shift in the Pt/ZnO (0.3942 nm) compared to that of pure platinum (0.3923 nm) [154]. The XRD pattern of the sample Pt@ZnO/Si-Al₂O₃ was dominated by the alumina peaks and only a broad, low intensity peak at ~56° that can be attributed to ZnO was discernible (Figure 6.5E). Similar results were obtained for the Pd and Pd@ZnO/Si-Al₂O₃ catalysts (Figure 6.6). The small crystallite size and the low loadings effectively prevent observation of the PtZn and PdZn XRD peaks.
Figure 6.5: X-ray diffraction (XRD) patterns of (A) Si-Al$_2$O$_3$, (B) Pt/Al$_2$O$_3$, (C) ZnO, (D) Pt/ZnO, and (E) Pt@ZnO/Si-Al$_2$O$_3$. Inset in (D) show magnification of the platinum (111) region.

Figure 6.6: X-ray diffraction (XRD) patterns of (A) Si-Al$_2$O$_3$, (B) Pd/Al$_2$O$_3$, (C) ZnO, (D) Pd/ZnO, and (E) Pd@ZnO/Si-Al$_2$O$_3$ calcined at 773 K.
CO chemisorption results are reported in Table 6.1. In contrast to what is observed for the Pt/Al₂O₃ sample, which shows appreciable CO uptakes, both Pt/ZnO and Pt@ZnO/Si-Al₂O₃ samples show very low CO uptakes corresponding to Pt dispersion values well below 5%. For conventional catalysts, this would imply particle sizes of the order of 10 nm. This result is clearly in contrast with TEM investigations (Figure 6.2), which showed the presence of small (2 nm), well dispersed Pt particles in the core-shell catalyst. The low adsorption uptake is likely due to formation of the Pt-Zn alloy, which has much reduced adsorption compared to the pure Pt particles present in the Pt/Al₂O₃ system. It is noteworthy that a reduction at higher temperatures decreases the CO uptake to almost zero for the ZnO-containing samples. The low CO chemisorption uptake for the core-shell sample can also be partially explained by the ZnO shell coating part of the Pt surface and this has as observed for other core-shell systems [62]. For Pd@ZnO/Si-Al₂O₃, reduction at 673 K slightly increases the dispersion. Oxidizing the samples restores the initial chemisorption values, providing evidence that alloy formation is primarily responsible for the reduced adsorption capacity.
### Table 6.1: Metal apparent dispersions (%) based on CO uptake at room temperature for the calcined samples after different pre-treatment conditions.

<table>
<thead>
<tr>
<th>Sample</th>
<th>1\textsuperscript{st} Reduction at 423 K</th>
<th>2\textsuperscript{nd} Reduction at 673 K</th>
<th>3\textsuperscript{rd} Reduction at 423 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt@ZnO/Si-Al\textsubscript{2}O\textsubscript{3}</td>
<td>4</td>
<td>0</td>
<td>2</td>
</tr>
<tr>
<td>Pt/Al\textsubscript{2}O\textsubscript{3}</td>
<td>34</td>
<td>41</td>
<td>32</td>
</tr>
<tr>
<td>Pt/ZnO</td>
<td>3</td>
<td>0</td>
<td>2</td>
</tr>
<tr>
<td>Pd@ZnO/Si-Al\textsubscript{2}O\textsubscript{3}</td>
<td>3</td>
<td>4</td>
<td>2</td>
</tr>
<tr>
<td>Pd/ZnO</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Pd/Al\textsubscript{2}O\textsubscript{3}</td>
<td>22</td>
<td>18</td>
<td>19</td>
</tr>
</tbody>
</table>

Coulometric titration experiments were also performed on the supported Pt@ZnO core-shell catalyst. Coulometric titration is an equilibrium, electrochemical technique for measuring oxidation state as a function of P(O\textsubscript{2}). Figure 6.7 shows the redox isotherm for the Pt@ZnO/Si-Al\textsubscript{2}O\textsubscript{3} sample at 873 K. Only a single reduction step was observed in the P(O\textsubscript{2}) range of $10^{-15} - 10^{-20}$ atm, which is close to the calculated P(O\textsubscript{2}) for ZnO-Zn equilibrium, $2.3 \times 10^{-16}$ atm. The amount of oxygen that could be removed from the sample is about 50 µmol g\textsuperscript{-1}, corresponding to an O/Pt ratio of 1, further indicating the formation of a PtZn alloy. Interestingly, most of the ZnO in the core-shell catalyst is not being reduced in this experiment, possibly because of interactions with the alumina support. The results also imply that PtZn alloy formation does not significantly affect the Zn-ZnO equilibrium. Temperature programed reduction (TPR) profile for the Pt@ZnO/Si-Al\textsubscript{2}O\textsubscript{3} show the first peak corresponding to the reduction of ZnO in contact with
Pt. The TPR results shows also about 55 μmol g$^{-1}$ of oxygen removed from the sample. This result strongly related with the coulometric titration results of the formation of the PtZn alloy.

**Figure 6.7:** Redox isotherms for Pt@ZnO/Si-Al$_2$O$_3$ at 873 K. Closed symbols were obtained starting from the oxidized state. Open symbols were measured while re-oxidizing the sample.

The core-shell structures were tested as catalysts for methanol-steam-reforming (CH$_3$OH + H$_2$O → CO$_2$ + 3H$_2$), with light-off curves for Pt@ZnO/Si-Al$_2$O$_3$ and conventional Pt/Al$_2$O$_3$ and Pt/ZnO catalysts shown in Figure 6.8A. Before the reaction, each of the materials was exposed to flowing H$_2$ at 523 K for 30 min. Reaction occurred at lower temperatures on Pt/Al$_2$O$_3$, with nearly complete conversion of the CH$_3$OH by 550 K. The reaction started at higher temperatures on Pt@ZnO/Si-Al$_2$O$_3$ and Pt/ZnO, with complete conversion requiring 600 K. However, the selectivities to CO$_2$ with Pt@ZnO/Si-Al$_2$O$_3$ and
Pt/ZnO were much higher than that with Pt/Al₂O₃, as shown in Figure 6.8B. At 573 K (Table 6.2), the selectivity to CO₂ was 66% on Pt/ZnO, 76% on Pt@ZnO/Si-Al₂O₃ and less than 10% on Pt/Al₂O₃. The formation of alloy phases increases the CO₂ selectivity compared to metallic phase.

**Figure 6.8:** (A) Methanol steam reforming (MSR) catalytic activity and (B) CO₂ selectivity over the Pt@ZnO/Si-Al₂O₃ core-shell (triangle symbol), and conventional Pt/Al₂O₃ (circle symbol) and Pt/ZnO (diamond symbol) calcined at 773 K. The catalysts were pretreated in a reducing (5% H₂/He) atmosphere at 523 K for 30 minutes. All catalysts were with 1 wt% of Pt.
Similar trends were observed with the Pd-based catalysts. For a given temperature, the conversions were highest with Pd/Al₂O₃, as shown in Figure 6.9A. However, as shown in Figure 6.9B, the selectivities for CO₂ were much higher on the Pd/ZnO and Pd@ZnO/Si-Al₂O₃ catalysts. The conventional Pd/ZnO exhibited somewhat higher selectivities than did the Pd@ZnO core-shell catalyst, possibly due to particle size effects. Conant et al. observed that smaller crystallites of Pd-Zn alloys were less selective than larger particles [152]. However, in all cases, the Pd-Zn alloy catalysts were more selective for CO₂ than their pure Pd analogues. This agrees with previous observations that the selectivity of ZnO-supported catalysts in MSR depends on the reduction temperature [149, 155-157].

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Conversion (%)</th>
<th>CO₂ selectivity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt@ZnO/Si-Al₂O₃</td>
<td>92</td>
<td>76</td>
</tr>
<tr>
<td>Pt/Al₂O₃</td>
<td>99</td>
<td>10</td>
</tr>
<tr>
<td>Pt/ZnO</td>
<td>92</td>
<td>66</td>
</tr>
<tr>
<td>Pd@ZnO/Si-Al₂O₃</td>
<td>95</td>
<td>34</td>
</tr>
<tr>
<td>Pd/ZnO</td>
<td>93</td>
<td>65</td>
</tr>
<tr>
<td>Pd/Al₂O₃</td>
<td>99</td>
<td>1</td>
</tr>
</tbody>
</table>
Figure 6.9: (A) Methanol-steam-reforming (MSR) catalytic activity and (B) CO$_2$ selectivity over the Pd@ZnO/Si-Al$_2$O$_3$ core-shell (triangle symbol), and conventional Pd/Al$_2$O$_3$ (circle symbol) and Pd/ZnO (diamond symbol) calcined at 773 K. The catalysts were pretreated in a reducing (5% H$_2$/He) atmosphere at 523 K for 30 minutes. All catalysts were with 1 wt% of Pd.

What we have demonstrated in this chapter is that the procedures developed in previous work for making hierarchical core-shell catalysts can be extended to include ZnO shells. An advantage of these materials is that the core-shell particles are highly uniform, both in their metal diameters and shell thicknesses. These core-shell particles can also be attached to any functionalized surface [158]. Therefore,
the self-assembly method can be useful for the synthesis of heterogeneous catalysis with highly tailored and tunable properties.

6.4 Summary

In this chapter, I successfully demonstrated the preparation of Pt@ZnO and Pd@ZnO core-shell nanostructures, well dispersed on a functionalized-alumina support. TEM images proved the formation of Pt@ZnO and Pd@ZnO core-shell nanostructures of 6 nm in diameter composed of a metal core of ~2 nm surrounded by an homogeneous ZnO shell of ~2 nm. The low metal dispersion of the core-shell nanostructures might be attributed to the formation of Pt-Zn alloy. Coulometric titration experiments and methanol-steam-reforming (MSR) reaction strongly suggest that the metal core-oxide shell structures can form alloys upon mild reduction. The MSR results show that Pt/Al₂O₃ and Pd/Al₂O₃ catalysts have catalytic activity with poor CO₂ selectivity, while the alloy catalysts (Pt@ZnO/Si-Al₂O₃ and Pd@ZnO/Si-Al₂O₃) have higher CO₂ selectivity. These finding presents a controlled way of preparing alloys for heterogeneous catalysis.
Chapter 7. A Comparison of Hierarchical Pt@CeO$_2$/Si-Al$_2$O$_3$ and Pd@CeO$_2$/Si-Al$_2$O$_3$

7.1 Introduction

Ceria-supported transition metals often show significantly enhanced catalytic properties, usually because of the reducibility of ceria [89, 159-161]. Because metal-ceria contact is important for promoting catalytic performance, there has been considerable effort at maximizing the interactions between transition metals and ceria [162, 163]. For example, a series of recent papers examined the synthesis of hierarchically structured nanoparticles having a Pd, Pt, or Au core surrounded by a thin oxide shell and showed that these materials can have unique catalytic properties [60, 62, 63, 69, 104, 164-166]. Pd@CeO$_2$ catalysts prepared by these methods showed excellent thermal stability for methane-oxidation upon heating to temperatures as high as 1123 K [104]. However, these same Pd@CeO$_2$ catalysts exhibited very low rates Water-Gas Shift (WGS) [62, 69] and methane-steam-reforming (MSR) [104] when they were calcined to only 773 K and reduced at 673 K. The Pd@CeO$_2$ catalysts calcined at 773 K and reduced at 673 K also exhibited low CO adsorption uptakes, which was interpreted as being due to encapsulation of the Pd by reduced ceria [104]. All of these results suggest that there is a very strong interaction between Pd and CeO$_2$ in the core-shell particles that can stabilize the structure to high calcination temperatures and cause the reduced ceria shell to encapsulate the Pd particles when the CeO$_2$ is reduced.
However, there are differences in how the various transition metals interact with ceria. For example, with ceria-supported Pd, it has been reported that contact with CeO₂ shifts the re-oxidation temperature of Pd, stabilizing the PdO [167]; but, with Pt, it is likely the reduced form of the metal that is in contact with CeO₂ [168]. These differences could potentially have important consequences for the stability of core-shell structures and the activity of the catalysts.

In this chapter, I set out to determine whether similar strong interactions would occur for Pt and CeO₂ in Pt@CeO₂ catalysts prepared by the same methods. I will show that the interactions between the Pt and CeO₂ appear to be much weaker, to the extent that the CeO₂ shell does not suppress adsorption of CO for catalyst calcined at lower temperatures nor stabilize Pt sintering for higher calcination temperatures.

7.2 Experimental Methods

7.2.1 Synthesis of the Catalysts

Synthesis of the Pt(1-wt%)@CeO₂(9-wt%)/Si-Al₂O₃ and Pd(1-wt%)@CeO₂(9-wt%)/Si-Al₂O₃ catalysts followed previously published procedures [60, 62]. The support (Si-Al₂O₃) was made hydrophobic by reacting a commercially available Al₂O₃ (Sasol) with triethoxy(octyl)silane (TEOOS) [63]. To prepare the dispersed core-shell particles, Pt or Pd nanoparticles, dispersed in THF using 11-mercaptoundecanoic acid ligands, were added dropwise to a solution of cerium(IV) tetrakis(decyloxide) under constant stirring. After adding dodecanoic acid (1 mol per Ce) dissolved in THF to disperse the particles, controlled amounts of water were added to hydrolyze the remaining alkoxide
groups. Next, the Si-Al$_2$O$_3$ was slowly added to the Pt@CeO$_2$ or Pd@CeO$_2$ solutions in an amount sufficient to give a final composition of 1-wt% metal and 9-wt% CeO$_2$. After stirring the slurry overnight, the solvent was removed by rotary evaporation. The dried powders were calcined in air at 773 K or 1073 K for 6 h using a heating ramp of 3 K min$^{-1}$.

Conventional Pt/Al$_2$O$_3$, Pt/CeO$_2$, Pd/Al$_2$O$_3$ and Pd/CeO$_2$ catalysts with 1-wt% metal were also prepared for comparison purposes by impregnation of Al$_2$O$_3$ or CeO$_2$ with aqueous solutions of Pt(NH$_3$)$_4$(NO$_3$)$_2$ or (NH$_3$)$_4$Pd(NO$_3$)$_2$. Prior to being used, the Al$_2$O$_3$ was calcined to 1173 K for 24 h. The ceria support was prepared by thermal decomposition of Ce(NO$_3$)$_3$·H$_2$O at 973 K for 6 h with a heating ramp of 3 K min$^{-1}$. The dried powders were calcined in air at 773 K for 6 h using a heating ramp of 3 K min$^{-1}$. The Al$_2$O$_3$, Si-Al$_2$O$_3$ and CeO$_2$ supports had BET surface areas of 100, 90 and 35 m$^2$ g$^{-1}$, respectively.

### 7.2.2 Characterization

Transmission Electron Microscopy (TEM) images were obtained using a JEOL 2100 microscope, with an accelerating voltage of 200 kV. CO chemisorption measurements were performed using a home-built adsorption apparatus and procedures that have been described in detail elsewhere [68]. To prepare a sample for chemisorption, the calcined sample was exposed to 200 Torr O$_2$ at 673 K for 2 min and then evacuated. Next, the sample was reduced by exposure to 200 Torr of H$_2$ at either 423 K or 673 K for 5 min, followed by evacuation. Each pretreatment was repeated three times. CO adsorption uptakes were then determined at room temperature by adding small pulses of
CO to the sample until a pressure rise was detected. In this pretreatment procedure, the reduction step is critical in order to avoid the reaction of CO and subsequent adsorption of CO$_2$ onto the reduced ceria [68].

Coulometric titration is an equilibrium, electrochemical technique for measuring oxidation state as a function of P(O$_2$) and a more detailed description of the apparatus is given elsewhere [64]. Briefly, 1 g of the calcined sample was placed in an alumina crucible and inserted inside a yttria-stabilized zirconia (YSZ) tube with Ag electrodes painted on the inside and outside. After heating the sample overnight to 873 K in flowing air with a temperature ramp of 1 K min$^{-1}$, a mixture of 5% O$_2$, 11% H$_2$O and 84% Ar was allowed to flow through the YSZ tube, over the sample, for 1 h, after which the tube was sealed at both ends using cajon fittings. Controlled amounts of oxygen were then added or removed from inside the tube by applying current across the electrodes using a Gamry Instruments potentiostat. The quantities of oxygen that were transferred were quantified by integrating the current. The P(O$_2$) at 873 K were determined from the open-circuit potential across the electrodes, using the Nernst Equation, after the system came to equilibrium. The ability of coulometric titration to accurately quantify both the amount of oxygen that can be removed from the catalyst and the equilibrium conditions at which this reduction occurs has been verified in previous studies with known samples [108, 109, 166].

The water-gas shift (WGS) reaction was studied in a ¼-inch, quartz, tubular reactor using 0.10 g of catalyst. The samples were first oxidized in flowing 20% O$_2$-He mixtures at 573 K for 30 min. For rate measurements, the reactant partial pressures were
fixed at 25 torr CO and 25 torr H\textsubscript{2}O and the conversions were kept below 10% to maintain differential conditions. For measuring catalyst stability in the WGS environment, the conversion was measured while holding the catalyst temperature at 623 K in a total flow rate of 120 mL min\textsuperscript{-1}. Products were analyzed using an online gas chromatograph (SRI8610C) equipped with a HayeSep Q column and a TCD detector.

7.3 Results and Discussion
7.3.1 Catalyst Characterization

In previous work on Pd@CeO\textsubscript{2}/Si-Al\textsubscript{2}O\textsubscript{3} catalysts, TEM results showed that, after calcination at 773 K, the Pd particles were uniformly 2 nm in diameter and surrounded by ceria nanocrystals to form particles that were 6 nm in diameter. This structure was largely maintained even after calcination to temperatures as high as 1123 K. The results for Pt@CeO\textsubscript{2}/Si-Al\textsubscript{2}O\textsubscript{3} were quite different, as shown in Figure 7.1. Following calcination of the sample to 773 K, the TEM images of the Pt@CeO\textsubscript{2}/Si-Al\textsubscript{2}O\textsubscript{3} in Figure 7.1A show Pt cores that are again approximately 2 nm in diameter, very close to the starting Pt-MUA nanoparticles [62]. It is not possible to tell if there is a ceria shell surrounding the Pt particles. However, after calcination to 1073 K, TEM images of the Pt@CeO\textsubscript{2}/Si-Al\textsubscript{2}O\textsubscript{3} exhibit a number of very large particles, some approaching 40 nm, demonstrating that significant sintering occurred (Figure 7.1B).
Figure 7.1: Representative transmission electron microscopy (TEM) images of Pt@CeO$_2$/Si-Al$_2$O$_3$ samples calcined at (A) 773 K and (B) 1073 K in air. Arrows indicate Pt particles.

The CO chemisorption data in Table 7.1 support the above conclusions. For reference, conventional 1-wt% Pt/Al$_2$O$_3$ and Pt/CeO$_2$ catalysts had dispersions of 41 and 43% after calcination to 773 K and reduction at 673 K. Following calcination at 773 K, the Pt@CeO$_2$/Si-Al$_2$O$_3$ samples had a Pt dispersion between 19 and 21%, essentially independent of the reduction temperature. This is in sharp contrast to what we observed with Pd@CeO$_2$/Si-Al$_2$O$_3$, for which the apparent dispersion depended on the reduction temperature [104], decreasing from 24% after reduction at 423 K to 5% after reduction at 673 K. (Note: This loss in dispersion is reversed by mild oxidation, followed by reduction at 423 K.) With Pd@CeO$_2$/Si-Al$_2$O$_3$, it was previously argued that reduction of the ceria nanocrystals that make up the shell caused the oxide to “close up” around the metal particles and block adsorption. The difference between Pd@CeO$_2$/Si-Al$_2$O$_3$ and
Pt@CeO$_2$/Si-Al$_2$O$_3$ is consistent with stronger attractive interactions between the Pd and CeO$_2$ stabilizing the core-shell structure.

Table 7.1: Pt and Pd dispersions (%) measured by CO adsorption uptakes at room temperature for samples after various pre-treatment conditions.

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Reduction at 423 K</th>
<th>Particle size (nm)</th>
<th>Reduction at 673 K</th>
<th>Particle size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt/Al$_2$O$_3$ – 773 K</td>
<td>34</td>
<td>3</td>
<td>41</td>
<td>3</td>
</tr>
<tr>
<td>Pt/CeO$_2$ – 773 K</td>
<td>36</td>
<td>3</td>
<td>43</td>
<td>3</td>
</tr>
<tr>
<td>Pt@CeO$_2$/Si-Al$_2$O$_3$ – 773 K</td>
<td>21</td>
<td>5</td>
<td>19</td>
<td>6</td>
</tr>
<tr>
<td>Pt@CeO$_2$/Si-Al$_2$O$_3$ – 1073 K</td>
<td>2</td>
<td>54</td>
<td>6</td>
<td>18</td>
</tr>
<tr>
<td>Pd@CeO$_2$/Si-Al$_2$O$_3$ – 773 K</td>
<td>24</td>
<td>5</td>
<td>5</td>
<td>22</td>
</tr>
<tr>
<td>Pd@CeO$_2$/Si-Al$_2$O$_3$ – 1073 K</td>
<td>21</td>
<td>5</td>
<td>18</td>
<td>6</td>
</tr>
</tbody>
</table>

As measured by CO adsorption, heating of Pt@CeO$_2$/Si-Al$_2$O$_3$ to 1073 K caused the Pt dispersion to fall to 6 %, in agreement with the large growth in metal particle size found by TEM. It is noteworthy that the high-temperature treatment had very little effect on the dispersion of Pd@CeO$_2$/Si-Al$_2$O$_3$ [104]. This is again consistent with the core-shell structure stabilizing the Pd particle size but not the Pt particle size.

7.3.2 WGS activity

The Pt@CeO$_2$/Si-Al$_2$O$_3$ catalyst was tested for the WGS reaction (Figure 7.2) and compared to the analogous Pd system (Figure 7.3). As reported in many previous investigations, WGS rates on Pt/CeO$_2$ are significantly higher than those observed over Pt/Al$_2$O$_3$ [64, 169, 170]. WGS rates over the Pt@CeO$_2$/Si-Al$_2$O$_3$ calcined at 773 K were nearly identical to those measured on Pt/CeO$_2$, implying that Pt and CeO$_2$ phases must still be in contact with each other on the hierarchical catalyst, even with the relatively low
CeO₂ loading of 9-wt%. When the Pt@CeO₂/Si-Al₂O₃ catalyst was calcined to 1073 K, the rates were much lower, in agreement with the loss in metal dispersion and the likely separation of Pt and CeO₂ phases.

**Figure 7.2:** Differential reaction rates for the water gas shift (WGS) reaction over (a) Pt/Al₂O₃-773K, (b) Pt/CeO₂-773K, (c) Pt@CeO₂/Si-Al₂O₃-773K and (d) Pt@CeO₂/Si-Al₂O₃-1073K. The samples were pretreated by oxidation in 20% O₂-He mixture at 573 K for 30 min prior to rate measurements. The reactant partial pressures were fixed at 25 torr CO and 25 torr H₂O.

Of greater interest is the comparison of Pt@CeO₂/Si-Al₂O₃ and Pd@CeO₂/Si-Al₂O₃ stabilities in the WGS reaction, shown in Figure 7.3. As reported previously [62, 69], Pd@CeO₂/Si-Al₂O₃ catalysts calcined at 773 K deactivate rapidly in the WGS environment due to reduction of the ceria, which in turn causes a loss in the CO adsorption uptakes on Pd, probably due to the ceria shell closing up around the Pd [101]. This is shown in Figure 7.3 by the decrease in conversion from larger than 25% to less
than 15% over the period of only 1 h. The reduction of the ceria shell takes place even in
the relatively oxidizing environment of the WGS reaction [87]. By comparison, the CO
conversions during the WGS reaction over Pt@CeO₂/Si-Al₂O₃ were much higher and
more stable, consistent with the much smaller effect of reduction on CO adsorption
capacity, reported in Table 7.1.

Figure 7.3: CO conversion in the WGS reaction as a function of time at 623 K over the
Pt@CeO₂/Si-Al₂O₃-773 K (■) and Pd@CeO₂/Si-Al₂O₃-773 K (○) catalysts. The reactant
partial pressures were fixed at 25 torr CO and 25 torr H₂O.

It has been shown that high-temperature calcination of ceria dramatically changes
its reducibility [30] and that this in turn changes its ability to promote the WGS reaction
over ceria-supported Pt and Pd catalysts [89]. Because the reducibility of the catalyst
appears to be so important for the WGS reaction, we performed Coulometric Titration
experiments on the various catalysts to better understand their redox properties. Results
for conventional Pt and Pd catalysts are reported in Figure 7.4, with Figure 7.4A showing
data for alumina-supported Pt and Pd and Figure 7.4B data for Pd/CeO$_2$. All of the catalysts used for the data in this figure were prepared by impregnation of the metal salts, followed by calcination in flowing air at 773 K. As discussed in the Experimental section, the catalysts were then exposed to flowing mixture of 5% O$_2$, 11% H$_2$O and 84% Ar at 873 K prior to taking the coulometric titration data and the titration experiments themselves were performed at 873 K. Figure 7.4A demonstrates that very little (<10 µmol/g) oxygen could be removed from the 1-wt% Pt/Al$_2$O$_3$ catalyst, implying that the Pt remained in a reduced state in the flowing gas mixture. Results for the 1-wt% Pd/Al$_2$O$_3$ have been reported previously [166]. Approximately 95 µmol g$^{-1}$ of oxygen atoms are removed in a narrow range of O$_2$ pressures, between $10^{-3}$ and $10^{-5}$ atm. The amount of oxygen agrees well with reduction of PdO to Pd and the reduction occurs near the P(O$_2$) that would be predicted based on Pd-PdO equilibrium pressure at this temperature, 2.0x10$^{-3}$ atm [110]. With 1-wt% Pd/CeO$_2$, Figure 7.4B, one can again see removal of approximately 100 µmol g$^{-1}$ of oxygen near $10^{-3}$ atm corresponding to the Pd-PdO transition; however, additional reduction occurs at lower P(O$_2$) due to the removal of oxygen from the CeO$_2$ support. It is noteworthy that the PdO and CeO$_2$ reduce in distinctly different P(O$_2$) ranges.
Figure 7.4: Redox isotherms for (A) 1-wt% Pt/Al₂O₃ (■) and 1-wt% Pd/Al₂O₃ (◇), and (B) 1-wt% Pd/CeO₂ (◆). The samples were initially calcined in air at 773 K. Measurements were conducted at 873 K, starting from the oxidized state.
Data for the Pt@CeO$_2$/Si-Al$_2$O$_3$ and Pd@CeO$_2$/Si-Al$_2$O$_3$ core-shell catalysts are given in Figure 7.5, with Figure 7.5A showing results for the samples calcined at 773 K and Figure 7.5B showing results for the samples calcined at 1073 K. Considering first the Pd@CeO$_2$/Si-Al$_2$O$_3$ samples, the sample calcined at 773 K exhibits removal of $\sim$100 µmol g$^{-1}$ of oxygen near $10^{-5}$ atm, the expected amount and the expected P(O$_2$) for the PdO-Pd transition. An additional $\sim$220 µmol g$^{-1}$ of oxygen is removed from the CeO$_2$ at lower P(O$_2$). Considering that this sample had only 9-wt% CeO$_2$, the O:Ce ratio at this point is estimated to be approximately 1.6. It is interesting to note that this reduction of CeO$_2$ is much more extensive, and occurs at significantly higher P(O$_2$), than that found for the CeO$_2$ in the conventional Pd/CeO$_2$ catalyst. This is likely due to the fact that the redox properties of CeO$_2$ are strongly dependent on crystallite size and pretreatment conditions [87, 104].

The isotherm for the Pd@CeO$_2$/Si-Al$_2$O$_3$ calcined to 1073 K is significantly different. Similar to what some of us reported earlier for Pd@ZrO$_2$/Si-Al$_2$O$_3$ [166], there is no well-defined transition corresponding to a PdO-Pd transition. Reduction of the Pd@CeO$_2$/Si-Al$_2$O$_3$ occurred gradually with decreasing P(O$_2$). Since spectroscopic data showed that the Pd in these catalysts is easily oxidized to PdO [101], the results in Figure 7.4B imply that the PdO and CeO$_2$ reduction occur together. The high-temperature calcination, which has previously been demonstrated to enhance the catalytic properties of Pd@CeO$_2$/Si-Al$_2$O$_3$, is shown to promote a stronger interaction between PdO and CeO$_2$ even in the redox isotherm.
Interactions between Pt and CeO$_2$ in the Pt@CeO$_2$/Si-Al$_2$O$_3$ catalysts were less apparent. Although the redox isotherm for the Pt@CeO$_2$/Si-Al$_2$O$_3$ catalyst calcined at 773 K is very similar to that of the redox isotherm for Pd@CeO$_2$/Si-Al$_2$O$_3$ with the PdO-Pd transition removed, this only implies that reduction of CeO$_2$ is identical in both catalysts.
For both Pd@CeO$_2$/Si-Al$_2$O$_3$ and Pt@CeO$_2$/Si-Al$_2$O$_3$, when calcined at 773 K, the redox properties of the ceria component do not appear to be strongly affected by interactions with the precious metal. Following calcination to 1073 K, reduction of Pt@CeO$_2$/Si-Al$_2$O$_3$ is different from that of Pd@CeO$_2$/Si-Al$_2$O$_3$. Reduction of the Pt catalyst does not begin until $\sim 10^{-15}$ atm, a similar P(O$_2$) to that which would occur with normal ceria nanocrystals. There is no evidence for contact between the Pt and the CeO$_2$ phases.

What the isotherm data suggests about Pt@CeO$_2$/Si-Al$_2$O$_3$ is that interactions between the Pt and CeO$_2$ phases are relatively weak. This explains why the catalyst behaves similarly to what might be expected for a conventional, impregnated catalyst. For the catalyst calcined at 773 K, there remains contact between the Pt and the ceria that is responsible for enhanced WGS rates above that which are found for Pt/Al$_2$O$_3$. However, there is no special attraction which would cause CeO$_2$ to “cover” the Pt following reduction of the CeO$_2$, as was found with the Pd@CeO$_2$/Si-Al$_2$O$_3$ catalyst. There is also no stabilization of the catalyst after sintering at high temperatures. Calcination to higher temperatures in the Pt@CeO$_2$ catalyst simply causes sintering and segregation of the Pt and CeO$_2$ phases.

This does raise the question concerning why contact between Pd and CeO$_2$ is so different and the Pd@CeO$_2$ structures so much more stable. It has been reported that Pd reacts with specific sites on CeO$_2$ [74], which suggests some kind of chemical-bonding interaction between Pd and CeO$_2$. Furthermore, DFT studies have shown that Pt has the tendency to bind to both cerium and oxygen defect sites [171]. The differences between Pt-ceria and Pd-ceria interactions may be related to the ease with which Pd can be
oxidized. However, the reasons behind the differences are not completely understood and this is still an open area of investigation.

Even though CeO$_2$-supported metals have been applied to automotive, emissions-control catalysis for many years, there is clearly much to be learned about the nature of interactions between metals and reducible oxides. Given the importance of these materials to real applications, additional studies are required.

7.4 Summary

In this chapter, I have shown that the hierarchically structured, Pt@CeO$_2$/Si-Al$_2$O$_3$ and Pd@CeO$_2$/Si-Al$_2$O$_3$ catalysts have very different behaviors. Stronger interactions between CeO$_2$ and Pd help to stabilize a core-shell structure, but this structure is unstable for Pt. For catalysts calcined at 773 K, reduction of CeO$_2$ can lead to encapsulation of Pd for Pd@CeO$_2$/Si-Al$_2$O$_3$ catalysts but similar behavior is not observed with Pt@CeO$_2$/Si-Al$_2$O$_3$. Strong interactions also help to maintain the core-shell structure at high temperatures with Pd@CeO$_2$/Si-Al$_2$O$_3$, but this is again not observed with Pt.
Chapter 8. Conclusion

This thesis focused on characterization of a unique type of catalyst with Metal@Oxide core-shell nanostructures, for which the metal-oxide interface was maximized. Catalysts with different metal-oxide compositions were synthesized and examined to determine how the metal-oxide interactions influenced their morphology, redox properties, thermal stability and, subsequently, their catalytic activities. The results presented in this thesis make a significant contribution towards a better understanding of the nature of metal-oxide interactions.

In Chapter 3, the effect of varying the calcination temperature from 773 to 1073 K was examined on supported Pd@CeO$_2$ core-shell catalysts. It was found that calcining to higher temperatures increased rates for the methane-oxidation reaction significantly. The Pd@CeO$_2$/Si-Al$_2$O$_3$ catalysts calcined to 773 K were unstable for methane-steam-reforming (MSR) due to deep reduction of the catalyst while the catalysts calcined at 1073 K showed reasonably stable rates. CO adsorption and FTIR indicated adsorption on the Pd was suppressed following reduction at 673 K in H$_2$ when the catalyst had been calcined at only 773 K, but not after 1073 K. Transient-pulse measurements demonstrated that catalysts calcined at either 773 K or 1073 K were heavily reduced under MSR reaction conditions at 673 K; but the catalyst heated to 1073 K could be re-oxidized by H$_2$O at this temperature, while the 773 K sample could not be. It is suggested that
increasing calcination temperature modifies the structure of the ceria shell, which in turn changes the ceria redox properties.

In Chapter 4, the catalytic properties of Pd@ZrO\(_2\) core-shell catalysts supported on Si-modified alumina were studied for application to methane-oxidation and compared to the Pd@CeO\(_2\) catalysts. In the absence of water (dry conditions), both Pd@ZrO\(_2\) and Pd@CeO\(_2\) were highly active and showed nearly identical reaction rates and thermal stabilities. However, unlike catalysts based on Pd@CeO\(_2\), the Pd@ZrO\(_2\) catalysts were also very stable in the presence of high concentrations of water vapor. By means of coulometric titration and transient-pulse studies, it was demonstrated that ZrO\(_2\) in contact with Pd can be reduced. Additionally, coulometric titration showed that the Pd-PdO equilibrium at 873 K was shifted to much lower P(O\(_2\)) in the Pd@ZrO\(_2\) catalyst compared to conventional Pd/ZrO\(_2\) or Pd/Al\(_2\)O\(_3\) catalysts. Because PdO is more active for methane-oxidation, this observation provides a possible explanation for the superior performance of the Pd@ZrO\(_2\) catalyst.

In Chapter 5, a catalyst system consisting of core-shell nanostructures with Au cores and porous TiO\(_2\) shells was synthesized and characterized for room-temperature CO oxidation. The core-shell structures were prepared by colloidal methods starting from pre-formed 3 nm Au particles in solution and then adsorbed on to high-surface area, functionalized hydrophobic Al\(_2\)O\(_3\) supports. The resulting Au@TiO\(_2\)/Si-Al\(_2\)O\(_3\) catalyst showed higher activity and thermal stability when compared to a conventional Au/TiO\(_2\) sample prepared by impregnation of the same Au particles on to commercial titania P25. The core-shell catalyst was able to maintain its activity and 3 nm Au particles size upon
calcination up to 873 K, whereas the Au/TiO$_2$ sample was found to sinter. Furthermore, it was found that the crystallization of TiO$_2$ was suppressed in the core-shell structure, resulting in a thin layer of small TiO$_2$ particles, which is favorable for the dispersion and thermal stability of Au nanoparticles.

Chapter 6 focused on core-shell catalysts with ZnO shells and on alloy formation between ZnO shells and precious metal cores. Pt@ZnO and Pd@ZnO core-shell nanoparticles were successfully synthesized. *In-situ* TEM and coulometric titration experiments suggest that Pt-Zn alloys are formed upon reduction and that these are highly tunable in size. While methanol-steam-reforming (MSR) measurements on conventional Pt/Al$_2$O$_3$ and Pd/Al$_2$O$_3$ catalysts show poor CO$_2$ selectivities, a Pt@ZnO/Si-Al$_2$O$_3$ system showed comparable activity and selectivity for CO$_2$ as a conventional Pt/ZnO catalyst, providing further indication that Pt@ZnO forms a Pt-Zn alloy upon reduction due to the intimate contact between the two materials. This work also provides a general method to prepare alloyed particles of tunable size and composition starting with well-defined core-shell building blocks.

In Chapter 7, the catalytic and adsorption properties for Pt@CeO$_2$/Si-Al$_2$O$_3$ and Pd@CeO$_2$/Si-Al$_2$O$_3$ were compared. The results indicated that the CeO$_2$ shell was stable for Pd but not for Pt. Following calcination to 773 K, Pt@CeO$_2$/Si-Al$_2$O$_3$ exhibited water-gas shift (WGS) rates that are similar to rates found on conventional Pt/CeO$_2$, implying good contact between the Pt and CeO$_2$ phases, even at relatively low CeO$_2$ loading. WGS rates on Pt@CeO$_2$/Si-Al$_2$O$_3$ were also reasonably stable with time and unaffected by pre-reduction of the catalyst. By comparison, a very strong interaction
between Pd and CeO$_2$ in the core-shell particles caused the reduced ceria shell to encapsulate the Pd particles, resulting in rapid deactivation. After calcination to 1073 K, large metal particles were observed with Pt@CeO$_2$/Si-Al$_2$O$_3$, but not on Pd@CeO$_2$/Si-Al$_2$O$_3$. Coulometric titration measurements on these two materials suggested stronger interactions between CeO$_2$ and Pd that were likely responsible for the higher stability of the core-shell structure in Pd@CeO$_2$ compared to Pt@CeO$_2$.
BIBLIOGRAPHY


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