Investigation Of High-Surface-Area Titanate (atio3) Thin Films Prepared By Atomic Layer Deposition

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Investigation Of High-Surface-Area Titanate (ATiO3) Thin Films Prepared By Atomic Layer Deposition

Abstract
Heterogeneous catalysis is critically important in the chemical-processing and energy-related industries. Ideally, reaction sites on heterogeneous catalysts can be regenerated, and the catalysts should be active throughout the catalytic process. However, harsh reaction conditions and parallel side reactions can be harmful to the metal catalysts, making deactivation a common phenomenon. Finding a catalyst that is stable can be a challenging yet significant task. Metal-doped perovskite materials have been referred to as “intelligent catalysts” because of the ability to insert and remove metal cations from the support lattice under cyclic redox conditions. The concept of “intelligent catalysts” became interesting because the stability of the doped metals was found to be significantly improved. However, the concept was not entirely successful due to the low specific surface areas of these materials, the slow kinetics for ingress and egress from the lattice, and poor metal utilization. Reducing the length scale of the perovskite materials could potentially overcome these problems, and it can be achieved by coating a thin perovskite film with a thickness of around 1nm on a high-surface-area onto an inert support. Work in this thesis used Atomic Layer Deposition (ALD) to deposit titanates (ATiO3, A=Ca, Sr or Ba) that were roughly 1-nm thick onto high-surface-area substrates. When using these thin-film materials as supports for catalytically active metals, the thin-film samples showed properties similar to their bulk counterparts. Improved stabilities were found on the systems where strong interactions occur. However, the interactions between metals and the thin-film perovskite materials were found to be different from bulk “intelligent catalysts” in some ways. The differences between bulk and thin-film systems can lead to very different particle geometries and catalytic properties. Systematic comparisons of metal-perovskite interactions were performed for the titanate thin films with different A-site cations. Changing A-site cations can lead to changes in metal properties, including but not limited to the metal geometries, reducibilities, and the resulting catalytic performances. The role of A-site cations in determining the forms and degrees of metal-perovskite interactions were also discussed.

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DEDICATION

To my family and friends

To Ray, for his guidance, support and encouragement
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ABSTRACT

INVESTIGATION OF HIGH-SURFACE-AREA TITANATE (ATiO₃) THIN FILMS PREPARED BY ATOMIC LAYER DEPOSITION

Chao Lin
Raymond J. Gorte

Heterogeneous catalysis is critically important in the chemical-processing and energy-related industries. Ideally, reaction sites on heterogeneous catalysts can be regenerated, and the catalysts should be active throughout the catalytic process. However, harsh reaction conditions and parallel side reactions can be harmful to the metal catalysts, making deactivation a common phenomenon. Finding a catalyst that is stable can be a challenging yet significant task. Metal-doped perovskite materials have been referred to as “intelligent catalysts” because of the ability to insert and remove metal cations from the support lattice under cyclic redox conditions. The concept of “intelligent catalysts” became interesting because the stability of the doped metals was found to be significantly improved. However, the concept was not entirely successful due to the low specific surface areas of these materials, the slow kinetics for ingress and egress from the lattice, and poor metal utilization. Reducing the length scale of the perovskite materials could potentially overcome these problems, and it can be achieved by coating a thin perovskite film with a thickness of around 1 nm on a high-surface-area onto an inert support. Work in this thesis used Atomic Layer Deposition (ALD) to deposit titanates (ATiO₃, A=Ca, Sr or Ba) that were roughly 1-nm thick onto high-surface-area substrates. When using these thin-film materials as supports for catalytically active metals, the thin-film samples showed properties similar to their bulk counterparts. Improved stabilities were found on the systems where strong interactions occur. However, the interactions between metals and the thin-film perovskite materials were found to be different from bulk...
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CHAPTER 1. INTRODUCTION

1.1 Motivation

Heterogeneous catalysis is critically important in the chemical-processing and energy-related industries [1, 2]. Suitable catalysts can convert the raw reactants into more valuable or less harmful products in a benign manner [3]. For example, Platinum Group Metals (PGMs) can catalyze oxidation of CO and hydrocarbons at relatively low temperatures [4-6]. Ni-based catalysts can promote syngas production from methane and other light hydrocarbons [7, 8].

Ideally, reaction sites on heterogeneous catalysts can be regenerated, and the catalysts should be active throughout the catalytic process [9]. However, harsh reaction conditions and parallel side reactions can be harmful to the materials, making catalyst deactivation a common phenomenon. One important example would be the sintering behavior found on PGM particles in catalytic converters [4, 10]. The catalytic converter inside a passenger car can reach temperatures above 1273 K under some conditions and experience both oxidizing and reducing environments. This high-temperature environment can cause initially well-dispersed, small PGM particles on the monolith to agglomerate into large particles via either coalescence or Ostwald Ripening [11, 12]. The catalyst in the converter undergoes deactivation due to the smaller portion of metal atoms that are on the outer surface.

Another important example of deactivation is the coke formation that occurs when Ni catalysts are exposed to reforming processes [13]. At low H₂O:C ratios, carbon fibers can form on

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1 Part of this chapter was adapted from X. Mao, C. Lin, G.W. Graham, R.J. Gorte, A Perspective on Thin-Film Perovskites as Supports for Metal Catalysts, ACS Catalysis, 10 (2020) 8840-8849. Copyright 2020, American Chemical Society.
the Ni catalysts, with nucleation sites beneath the Ni particles. This can cause the Ni particles to be lifted from the support [14]. While periodic oxidations can burn off the accumulated carbon and regenerate the catalysts, the Ni particles would also be lost in the regeneration processes, leading to poor long-term stability. What is worse is that the mechanical strength of the carbon fibers can cause plugging of the reactors [15].

Maintaining stable catalytic performance has always been one of the biggest challenges in the field of heterogeneous catalysis. Research efforts towards stable catalyst design can be valuable. Among all the research efforts that have been investigated towards better catalyst stability, the so-called “intelligent catalysts” show promising properties and are investigated here to explore the potential of that concept.
1.2 Concept of Exsolution and “Intelligent Catalysts”

1.2.1 Brief History

Perovskite materials have the general formula ABO$_3$, with A$^{1+}$B$^{5+}$O$_3$, A$^{2+}$B$^{4+}$O$_3$ and A$^{3+}$B$^{3+}$O$_3$ being the three most common combinations to maintain electroneutrality [16, 17]. An important criterion to determine the perovskite stability is the Goldschmidt tolerance factor [18] given in Equation 1.1. Here $r_A$, $r_B$, and $r_O$ represent the ionic radii of the corresponding metal cations and of the oxygen anions, respectively. The ideal cubic crystal structure is observed for $t=1.0$. Rhombohedral and orthorhombic lattice symmetries are formed for 0.75 < $t$ < 1.0.

$$t = \frac{r_A + r_O}{\sqrt{2} \cdot (r_B + r_O)}$$  \hspace{1cm} \text{Equation 1.1}

Partial substitution of metal cations is possible if the tolerance factor can be met [19-21], and the ability to easily insert and remove precious metal cations under cyclic redox conditions forms the basis of self-regenerating, or “intelligent, catalysts” [22-27]. Upon oxidation, the dopant metal can become part of the perovskite structure; upon reduction, the dopant metal cation can be reduced to its zero-valent form and exit the lattice. In theory, this dynamic process should inhibit metal particle growth, thereby maintaining high metal dispersion.

Investigation of metal-doped perovskite materials can be dated back to the 1990s or even earlier [28, 29], but systematic studies about “Intelligent catalysts” and exsolution first came from Tanaka and his coworkers at Daihatsu Motor Company in the early 2000s [22-27]. After an initial study focusing on support effects for Pd on perovskite materials [30, 31], the group switched to synthesis and testing of this and other metal-doped perovskites. The first materials referred to as “intelligent catalyst” were Pd-based perovskites. It was found that upon high-temperature reduction, Pd could be reduced to its metallic form. The behavior was found to be reversible since
high-temperature oxidation was able to push the metallic Pd back into perovskite lattice. Similar behavior was later reported for Rh- and Pt-based perovskite materials [24].

Besides the reversibility claimed in those early studies, interesting properties were also reported for the “exsolved” particles. One of the most popular initial findings regarding “intelligent catalysts” is the ability of the perovskite host to maintain metal particle dispersion. For example, Pt that is doped into the host perovskite remained in the form of small particles during high-temperature redox cycles. After high-temperature redox treatments, Pt particles with size ranging from 1-3 nm can be found, whereas Pt/Al$_2$O$_3$ after the same treatments showed huge particles with diameters $> 100$ nm [24]. This interesting property has immediately drawn attention from researchers in the field of automobile emission control industry, since maintaining particle dispersion upon high temperature-redox cycles has always been a challenge [32, 33].

Later on, a wide range of metal-perovskite combinations allowed potential applications in many other sub-categories within the catalysis area, as well as studies in other fields such as fuel cell anode modifications [34-36] and reforming catalysts [37-39]. Most of these works focused on the metal particle formation process, known as exsolution, to form supported-metal catalysts in a well-controlled manner [40-42]. In the reforming processes investigated, the fact that Ni particles exsolved from the perovskite hosts do not coke draws a lot of attentions. Utilizing the “Intelligent catalysts” concept was viewed as a viable route for enhancing catalyst stability [37, 41, 42].

1.2.2 Issues with Bulk Intelligent Catalysts and Exsolution Behavior

Although “intelligent catalysts” do show promising properties, utilizing the concept has not been entirely successful. One of the issues is the low specific surface area of typical perovskite materials. Conventional synthesis methods for perovskite materials include the sol-gel method and
solid-state reactions of mixed oxides [43, 44]. Although the perovskite phase is thermodynamically favored, high-temperature calcination is usually required for both of these methods in order to achieve cation mixing at the atomic scale. As a result of that, typical perovskites have surface areas less than 10 m²/g, more than one order of magnitude lower than that of most commercial catalysts [45]. Even if perovskite materials with higher surface areas could be synthesized, environments for catalytic applications, such as the TWC (Three-Way Catalyst), involve redox cycles at temperatures as high as 1323 K [46]. Most high-surface-area materials cannot withstand those extreme environments, and the surface area of most perovskite materials drop to less than 2 m²/g [17].

Besides the low surface areas associated with large perovskite crystallites, there is a related yet even more important challenge to real applications. Careful mechanistic studies into the self-regeneration process have been carried out for the main TWC systems, and these have raised doubts about both the accessibility of reduced metal particles and the reversibility of the process [47-53]. In a study focusing on the Pt-CaTiO₃ system, for example, it was pointed out that the dopant metal cations can only travel a few nanometers under the provided redox conditions at 1073 K; and, as a result, most of the reduced metal particles remained in the bulk perovskite without having access to gas-phase reagents. In another study focusing on the La₀.₂Sr₀.₇Ti₀.₉Ni₀.₁O₃₋δ system, exsolved Ni particles were also found in the bulk after reduction [54]. Moreover, the process is usually not 100% reversible. A good example of irreversibility can be found in a study of the Rh-CaTiO₃ system. After accelerated aging of Rh-doped CaTiO₃ powder, ~90% of the Rh was found in the form of relatively large (10 nm) particles on the surface of the perovskite powder, while the rest of the Rh, in the form of small (1 nm) particles, remained trapped within the perovskite powder [50].

All the evidence clearly suggested that modification of the traditional “Intelligent catalysts” is needed to better utilize the properties [55-59]. One possible solution to increase the perovskite
surface area and decrease length scale for ingress and egress of metal particles is to make thin films of perovskite materials on an inert high-surface-area substrate. Details related to preparation of thin-film materials will be introduced in Section 2.1.2.

1.2.3 Unexplored Metal-Perovskite Interactions

Besides the limited applications of the concept due to the reasons mentioned in Section 1.2.2, there is another interesting area in the field that is yet fully explored, which is the specific interactions between metal and the perovskite materials. The interactions between metal and the hosts have been shown to be combination-specific. For example, Pt was reported to be interacting with the CaTiO$_3$ host while Pd did not [24]. Another example can be found on the Ni samples, when Ni was deposited onto ATiO$_3$ bulk perovskites and treated under the same condition, the amount of coke formed were found to be significantly different [60]. While researchers tried to understand the interactions and proposed some ideas such as the impact of lattice free volumes [61], systematic understanding regarding the interaction specificity is still required for better catalyst design.
1.3 Preparation of Thin-film Materials by Atomic Layer Deposition (ALD)

1.3.1 Estimation of Desired Film Thickness

As discussed previously, preparing high-surface-area, thermally stable perovskite materials will be the first step in fully realizing the potential brought by the exsolution process; and synthesizing thin-film perovskite materials coated onto porous supports that have high initial surface areas can be a potential route. Determination of the desired film thickness is an important first step. Considering a typical catalyst support with a surface area of 120 m$^2$/g, a simple calculation shows that a dense, 1-nm, conformal film of CaTiO$_3$ (assuming the thin-film perovskite material is dense and has a density of 3.98 g/cm$^3$) would have a weight loading of 32-wt% of the loaded material. This loading will also decrease the specific surface area (m$^2$/g) due to the mass changed in the sample, even if the added materials have no effect on the pore size and/or structure. Based on these criteria, it is apparent that the film thickness should be kept at ~1 nm. For the perovskite materials with a higher density, the same calculation would indicate that an even thinner film is required to achieve the initial goal of high specific surface areas.

1.3.2 ALD for Thin Film Preparations on Porous Materials

ALD is a technique for thin-film fabrication that has been widely used in the semiconductor industry. A schematic plot for a complete ALD cycle can be found in Figure 1-1. A complete ALD cycle consists of the following four steps: (a) adsorption of the gaseous precursor onto the surface of the substrate; (b) purging the excess precursor and its byproducts from the sample; (c) introduction of a gaseous reactant to remove ligands and regenerate sites; and (d) purging out the excess reactants and their byproducts.
Growth rates in ALD are slow, ~0.01 to 0.1 nm/cycle [62, 63]. To grow the thicker films required for semiconductor applications (e.g. 20 nm films might be typical for semiconductors [64]), rapid cycling is required in order to prepare the films in a reasonable amount of time. Therefore, when ALD is performed on flat substrates for these applications, the ALD processes would typically be performed in a flow system with inert gas to deliver the precursors to the substrate surface in a rapid manner. Unlike the commercial equipment for the ALD process in the semiconductor industry, the ALD system for my application needs to be redesigned to accommodate features of porous support materials [65]. It is important to notice that, based on the previous calculation, the number of ALD cycles required is relatively small compared to that

Figure 1-1 Schematic of one ALD cycle in a pore structure. (a) introduction of precursor molecules and adsorption on the surface; (b) purge of the unreacted precursor molecules and reaction products; (c) introduction of ligand removal reactants, which react with the chemisorbed precursor molecules; and (d) purge of the excess reactants and reaction products. This schematic is an example of an ideal ALD process for TiO$_2$ deposition using the TiCl$_4$/H$_2$O system. Reprinted with permission from reference [58], Copyright 2017, MDPI.
required for semiconductor ALD processes, making fast cycling less important. Second, rather than use a carrier-gas-assisted process, ALD under vacuum is desirable for porous materials since the carrier gas would hinder the precursor diffusion. Third, longer exposure times are required to avoid diffusion limitation and allow precursor penetration to the entire sample surface. Lastly, for catalysis applications, since the value added by the ALD thin films might not be as high compared to the semiconductor devices, the cost of the precursors should be controlled. Static systems can allow better precursor utilization since excess precursor is not lost with the carrier gas.

1.3.3 Opportunities for ALD

Thin films prepared by ALD have been demonstrated to have good thermal stability, thus allowing the investigation of related catalytic and thermodynamic properties. One example of good thermal stability for ALD thin films can be found in a study involving ALD of CeO$_2$ films coated onto Al$_2$O$_3$ [66]. The addition of 20 ALD cycles of CeO$_2$ was found to form a stable film on the support surface. The ALD-prepared catalyst showed improved thermal stability compared to bulk CeO$_2$, and Pd impregnated onto the ALD-modified support exhibited higher WGS and CO-oxidation rates due to the improved Pd-ceria contact. It is difficult to maintain functional oxides such as CeO$_2$ powders in a high-surface-area form. The fact that one can achieve similar promotion by CeO$_2$ in a thin-film catalyst opens up the possibility of using a more stable substrate for enhanced surface area, while still having the high catalytic activity of the functional oxide. For example, MgAl$_2$O$_4$ is a material that has been widely used as industrial catalyst supports [67]. The oxide has a stable spinel structure with a high specific surface area of > 100 m$^2$/g, even after high-temperature treatments, allowing it to be the substrate for the perovskite thin film deposition.
Alternating between different oxides during the ALD deposition process allows good mixing of the individual component of a mixed oxide, thus reducing the barrier for perovskite phase formation and the temperature required for phase formation. Recent studies in our laboratory have demonstrated successful preparation of oxide solid solutions, such as CeO$_2$-ZrO$_2$ solid solutions [68]. Additionally, the growth rates for the ALD process for the same element remained almost identical when alternating different oxides, allowing us to track stoichiometry while depositing the perovskite materials.

With the successful preparation of perovskite thin-film materials, the full potential of the concept of “Intelligent catalysts” is more likely to be realized. Catalytically active metals can be deposited onto the modified substrate surface. Given the reasonable specific surface areas of these ALD perovskite materials, catalytic performance can be probed and investigated. By minimizing diffusion limitations, it is possible to investigate and compare metal-perovskite interactions in a more systematic manner.
1.4 Thesis Scope

This dissertation consists of nine chapters including this introduction. **CHAPTER 2** provides a detailed description of the research apparatus that has been designed and utilized throughout my PhD research. Experimental methods for sample preparation and characterization are also included in **CHAPTER 2**.

In **CHAPTER 3**, results from a study in which ALD films of CeO₂ and ZrO₂ were used to modify ZrO₂ powders are presented. The addition of 20 ALD cycles of either CeO₂ or ZrO₂ was found to stabilize the surface area of the ZrO₂ powder following calcination to 1073 K and to suppress the tetragonal-to-monoclinic transition. Shrinkage of ZrO₂ wafers was also suppressed by the ALD films. While this work was not related to perovskite thin film preparation, the work demonstrated how powerful ALD can be for sample preparation and proved the thermal stability of the thin film materials.

**CHAPTER 4** demonstrates the successful preparation of CaTiO₃ thin films by ALD on MgAl₂O₄ supports. After the deposition of Ni, the reforming performance and the coke resistance were investigated and compared with that of a Ni/MgAl₂O₄ sample. It was found out that the ALD sample had comparable catalytic performance but much better coke resistance. Possible mechanisms for the high carbon tolerance of the perovskite-containing catalysts are discussed.

In **CHAPTER 5**, Pd-CaTiO₃ and Pt-CaTiO₃ interactions are reported and compared with bulk exsolution behaviors. While Pd/CaTiO₃/MgAl₂O₄ showed adsorption and CO-oxidation properties that were essentially the same as Pd/MgAl₂O₄, the Pt/CaTiO₃/MgAl₂O₄ catalyst exhibited evidence for strong support interactions. Pt/CaTiO₃/MgAl₂O₄ showed high activity for CO oxidation following reduction at 1073 K, even though CO adsorption was suppressed; but the
catalysts were dramatically less active after oxidation at 1073 K and reduction at 773 K. Both Pt/CaTiO$_3$/MgAl$_2$O$_4$ and a catalyst formed by exsolution of CaTi$_{0.95}$Pt$_{0.05}$O$_3$ exhibited very low rates for toluene hydrogenation in comparison to Pt/MgAl$_2$O$_4$. Pt particles on reduced Pt/CaTiO$_3$/MgAl$_2$O$_4$ exhibited an unusual rhombohedral shape and may be flat, a further indication of strong interactions between the metal and the support. Low Energy Ion Scattering (LEIS) indicated that high-temperature reduction caused a restructuring of the CaTiO$_3$.

In **CHAPTER 6**, the properties of Rh catalysts prepared from thin films of CaTiO$_3$, SrTiO$_3$, and BaTiO$_3$ are reported. Rh, added by ALD, interacted strongly with CaTiO$_3$, somewhat less strongly with SrTiO$_3$, and only weakly with BaTiO$_3$. The analogous bulk exsolution catalysts, synthesized by reduction of ATi$_{0.98}$Rh$_{0.02}$O$_3$ (A=Ca, Sr, and Ba), were also examined for comparison.

**CHAPTER 7** repeats the comparison of the effect of support with the various titanates for Ni catalysts. The effect of metal-perovskite interactions on the thermodynamics of Ni oxidation are also reported.

**CHAPTER 8** reports the results of the Pt-ATiO$_3$ systems. Detailed investigation of activities as a function of pretreatment conditions suggests that the temperature required to achieve ultimate performance of these samples were different.

Finally, in **CHAPTER 9**, the key findings in this thesis are summarized.
CHAPTER 2. EXPERIMENTAL METHODS

The goal of this chapter is to describe the techniques that have been utilized for the completion of my thesis work. The experimental techniques will be divided into four sub-categories: sample preparations, sample characterizations, catalytic measurements, and thermodynamic/reducibility investigations.

2.1 Sample Preparations

2.1.1 Synthesis of High-Surface-Area Support Material

The MgAl$_2$O$_4$ support was prepared by precipitation methods. Magnesium nitrate hexahydrate (Mg(NO$_3$)$_2$ · 6H$_2$O, Sigma Aldrich) and aluminum nitrate nonahydrate (Al(NO$_3$)$_3$, Sigma Aldrich) were dissolved together in 400 mL of distilled water to give a solution that was 0.15 M in Al$^{3+}$ and 0.075 M in Mg$^{2+}$. This mixed solution was titrated with 600 mL of a 1.5 M ammonium bicarbonate solution at 333 K, with the aim of keeping the solution pH near 11.5. The resulting precipitates were rinsed with distilled water three times, dried at 333 K, and then calcined in air at 1173 K in a muffle furnace for 12 h. To remove any excess MgO and Al$_2$O$_3$ that may have formed, the calcined samples were immersed in concentrated nitric acid (HNO$_3$, Fisher Scientific) for 1 h, filtered, and finally rinsed with water three times. After drying, the MgAl$_2$O$_4$ was again calcined to 773 K for 3 h to ensure removal of any remaining nitrates. The final MgAl$_2$O$_4$ powder had a BET surface area of ~120 m$^2$/g. The XRD pattern of the synthesized substrate material, which can be found in Figure 2-1, showed only the characteristic peaks for MgAl$_2$O$_4$. 

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CeO$_2$ and ZrO$_2$ powders were prepared by precipitating aqueous solutions of either Zirconium(IV) oxynitrate hydrate (ZrO(NO$_3$)$_2$ · xH$_2$O, Sigma Aldrich) or Cerium(III) nitrate hexahydrate (Ce(NO$_3$)$_3$·6H$_2$O, Sigma Aldrich) with excess ammonium hydroxide (NH$_4$OH, Fisher Scientific). The resulting precipitates were then dried overnight at 333 K and heated in air at 773 K for 3 h. After this pretreatment, the ZrO$_2$ powder had a BET surface area of 84 m$^2$/g and the CeO$_2$ powder had a surface area of 59 m$^2$/g.

### 2.1.2 Atomic Layer Deposition (ALD)

To prepare uniform coatings of oxides onto porous supports, the ALD systems commonly used in the semiconductor industry would not be useful. The oxide thin films in my work were prepared using a home-built, static system. ALD was also utilized for the deposition of catalytically active transition metals. The apparatus is basically a high-temperature adsorption system with VCR connections that can be evacuated by a mechanical pump. To avoid condensation of the precursors, all lines were heated. In addition to the heated vacuum lines, the system consists of two heated chambers, one for the support materials and one for the ALD precursors. The temperatures for each
of the heated chambers can be controlled separately to adjust for the suitable ALD temperature window. The chambers were separated from each other and from the vacuum pump, and the oxidant source could be introduced to the substrate chamber by adjusting the high-temperature valves. A schematic plot for the home-built-ALD system can be found in Figure 2-2.

![Figure 2-2 Schematic plot for home-built ALD setup](image)

As discussed previously, a complete ALD cycle consists of the following four steps: (a) adsorption of the gaseous precursor onto the surface of the substrate; (b) purging the excess precursor and its byproducts from the sample; (c) introduction of a gaseous reactant to remove ligands and regenerate sites; and (d) purging out the excess reactants and their byproducts. Here the first two steps will be referred to as precursor deposition step and the steps (c) and (d) will be referred to as the oxidation step.

Procedures for doing one complete ALD cycle using the static system are as follows. Suitable amounts of substrate (~500 mg/batch) and precursor (amount varies, depending on
precursor vapor pressure) were first loaded into borosilicate tubes. The tubes were then connected to the ALD vacuum system using Cajon-type fittings. Prior to the deposition step, all lines and tubes were evacuated to a pressure of \( \sim 10^{-3} \) Torr using the mechanical pump. The entire system was then heated to the desired temperature for the deposition processes. Criteria for selecting suitable temperatures for the substrate chamber and the precursor chambers depended on the precursor. For the substrate chamber, it is important for the temperature to be within the “ALD window” for a given precursor, since a temperature that is too high will lead to chemical vapor deposition and a temperature that is too low can lead to precursor condensation on substrate surface and system walls [69]. For the precursor chamber, the temperature was selected in order that there be a suitable vapor pressure (usually \( > 5 \) Torr) for exposing the sample. In all cases, the temperature of the precursor chamber must be the lowest temperature of the system so as to avoid condensation. After reaching the desired temperatures for both chambers, the valve to the vacuum pump (V1 in the schematic plot) was closed and the valve separating substrate and the precursor opened, allowing the high-surface-area substrate to be exposed to the precursor vapor. Exposure times varied, with the requirement that the time be sufficient to allow reaction between precursor vapor and surface functional groups to go to completion. After completing the surface reaction, the precursor was isolated by closing the valve and the sample chamber was evacuated to allow purging of reaction byproducts. Since the deposition could lead to formation of some unexpected side-products and create diffusion limitation for precursor vapors, some ALD processes require multiple “dose-purge” processes being performed.

Oxidation process would then take place. The oxidation step depends strongly on the precursor. For some precursors (e.g. TiCl<sub>4</sub>), the sample chamber was simply isolated from the precursor chamber and the oxidant, H<sub>2</sub>O vapor in the case of TiCl<sub>4</sub>, was allowed to flow into the
sample chamber for suitable amount of time to allow complete oxidation of the precursors. The sample could then be evacuated to complete the cycle. However, some precursors could not be oxidized at the relatively low temperatures used for precursor exposure. For example, for precursors with TMHD (2,2,6,6-tetramethyl-3,5-heptanedionato) ligands, complete oxidation required temperatures higher than the “ALD window.” This is shown by the Temperature Programmed Oxidation (TPO) results in Figure 2-3, performed on a ZrO₂ powder following exposure to Ce(TMHD)₄. The data show that temperatures in excess of 600 K are required to completely remove the ligands, and this is above the ALD temperature window [70]. For these precursors, samples were simply removed from the system and heated in a muffle furnace to oxidize the ligands before the next ALD cycle. After the oxidation step, the sample tube would be attached back to the ALD system. The sample would be purged to vacuum before the next ALD cycle. Table 2-1 summarized the parameters for the ALD processes performed in this thesis.

![Figure 2-3](image)

**Figure 2-3** Temperature Programmed Oxidation performed on the ZrO₂ after exposure to the Ce(TMHD)₄ precursor. The heating rate for the sample was 20 K·min⁻¹. This experiment was performed in flowing air with 100 mg of sample, an air flowrate of 50 mL·min⁻¹. Reprinted with permission from reference [62], Copyright 2017, MDPI.
### 2.1.3 Incipient Wetness Impregnation

In the early stages of my work, catalytically active metals, including Ni and Pd, were deposited onto support surface by Incipient Wetness Impregnation. For example, 1-wt% Pd was added to selected samples allowing aqueous solutions of Tetraamminepalladium nitrate (Pd(NH$_3$)$_4$(NO$_3$)$_2$, Alfa Aesar) to come in contact with the support powders. After impregnation of the metal salt, the samples were dried overnight at 333 K and calcined in air at 773 K for 1 h. A similar procedure was used to prepare the Ni catalysts. In that case, the metal salt Nickel (II) nitrate hexahydrate (Ni(NO$_3$)$_2$·6H$_2$O, Alfa Aesar).

#### Table 2-1 Summarization of key parameters for various ALD processes

<table>
<thead>
<tr>
<th>ALD process</th>
<th>Precursor</th>
<th>Deposition temperature and time</th>
<th>Oxidant</th>
<th>Oxidation temperature and time</th>
<th>Growth rate (atoms/m$^2$/cycle)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca-ALD</td>
<td>Ca(TMHD)$_2$</td>
<td>573K, 10 min</td>
<td>air</td>
<td>773K, 5 min</td>
<td>6.9×10$^{17}$</td>
</tr>
<tr>
<td>Sr-ALD</td>
<td>Sr(TMHD)$_2$</td>
<td>573K, 10 min</td>
<td>air</td>
<td>773K, 5 min</td>
<td>3.6×10$^{17a}$</td>
</tr>
<tr>
<td>Ba-ALD</td>
<td>Ba(TMHD)$_2$</td>
<td>573K, 10 min</td>
<td>air</td>
<td>773K, 5 min</td>
<td>3.7×10$^{17a}$</td>
</tr>
<tr>
<td>Ti-ALD</td>
<td>TiCl$_4$</td>
<td>423K, 1 min*3</td>
<td>Humidified air</td>
<td>423K, 3 min</td>
<td>9.9×10$^{17}$</td>
</tr>
<tr>
<td>Pt-ALD</td>
<td>Pt(acac)$_2$</td>
<td>423K, 5 min</td>
<td>air</td>
<td>573K, 5 min</td>
<td>7.7-11.5×10$^{17}$</td>
</tr>
<tr>
<td>Pd-ALD</td>
<td>Pd(TMHD)$_2$</td>
<td>573 K, 5 min</td>
<td>air</td>
<td>773K, 5 min</td>
<td>5.9-8.8×10$^{17}$</td>
</tr>
<tr>
<td>Rh-ALD</td>
<td>Rh(acac)$_3$</td>
<td>523K, 5min</td>
<td>air</td>
<td>573K, 5 min</td>
<td>13×10$^{17}$</td>
</tr>
<tr>
<td>Ce-ALD</td>
<td>Ce(TMHD)$_2$</td>
<td>503K, 5min</td>
<td>air</td>
<td>773K, 5 min</td>
<td>8.7×10$^{17}$</td>
</tr>
<tr>
<td>Zr-ALD</td>
<td>Zr(TMHD)$_2$</td>
<td>503K, 5min</td>
<td>air</td>
<td>773K, 5 min</td>
<td>4.2×10$^{17}$</td>
</tr>
</tbody>
</table>

*a: In order to reconcile the weight changes with the compositions obtained from ICP-OES, it was necessary to assume that SrCO$_3$ and BaCO$_3$ were formed initially.*
2.1.4 Bulk Perovskite Synthesis

Bulk perovskites, ATi$_x$M$_{1-x}$O$_3$ (A=Ca, Sr, or Ba, M=Rh or Pt), were synthesized using sol-gel procedures. The corresponding A-site cation (either Ca(NO$_3$)$_2$·(H$_2$O)$_4$, (Sigma-Aldrich), Sr(NO$_3$)$_2$, (Sigma-Aldrich), or Ba(NO$_3$)$_2$, (Alfa Aesar)) was dissolved in an aqueous solution containing suitable amounts of Dihydroxybis (ammonium lactato) titanium solution ([CH$_3$CH(O-)CO$_2$NH$_4$]$_2$Ti(OH)$_2$, Alfa Aesar) and Rhodium(III) nitrate hydrate (Rh(NO$_3$)$_4$·xH$_2$O, Alfa Aesar) or Tetraammineplatinum(II) nitrate (Pt(NH$_3$)$_4$(NO$_3$)$_2$, Alfa Aesar). After adding stoichiometric amounts of citric acid (Fisher Scientific), the solution was heated to form a viscous gel. After drying, the resulting powder was crushed and placed in a muffle furnace at 1173 K for either 6 h or 24 h to form the perovskite phases.

2.2 Sample Characterizations

2.2.1 Surface Area Measurements

Surface areas were measured using BET isotherms in a homemade adsorption apparatus at 78 K. The detailed principles behind multilayer adsorption and the equations used to calculate surface area can be found in the literature [71]. To measure the isotherms, the samples were first heated to 423 K for 10 min under vacuum to remove any moisture from the sample. After cooling the sample to 78 K, the volumes of adsorbed gas were measured.

2.2.2 X-Ray Diffraction (XRD)

XRD is utilized to determine the phase formation upon different treatments for various samples. Patterns were recorded on a Rigaku Smartlab diffractometer or a Rigaku MiniFlex diffractometer, both diffractometers were equipped with a Cu K$_\alpha$ source ($\lambda = 0.15416$ nm). Samples
were grinded into powders before XRD measurements. The scanning rate were controlled at 10°·min⁻¹ and the patterns between 20 of 20° and 60° were collected.

2.2.3 Temperature-Programmed Desorption/Thermogravimetric Analysis (TPD-TGA)

TPD-TGA was utilized in my thesis work for surface characterization and was carried out in a system that has been described in detail elsewhere [72]. The system is built around a CAHN 2000 microbalance and a quadrupole mass spectrometer (SRI RGA-100) and could be evacuated to 10⁻⁸ Torr with a turbomolecular pump. In a typical measurement, 50-mg samples were heated in a vacuum to 823 K, then exposed to the vapor of 2-propanol (99.9%, Fisher, USA) at room temperature. After 1-h evacuation, TPD-TGA measurements were performed using a temperature ramp of 10 K·min⁻¹.

2.2.4 Dispersion Measurements

Dispersion measurements can give us estimations on metal particle sizes. For most of the procedures involving precious metals in my thesis work, metal dispersions were estimated using CO chemisorption at room temperature, assuming a stoichiometry of one CO per metal. For these measurements, the samples were first pretreated in a flow reactor at the desired conditions before being transferred to the adsorption apparatus. Within the adsorption system, the samples were reduced in 400 Torr H₂ for 30 min at 473 K to remove any oxide formed in transferring the sample from the flow reactor to the adsorption system. It is worth mentioning that the assumption of one CO per metal atom was utilized throughout my thesis work, even though the CO: metal stoichiometry is known to depend on particle sizes.
However, CO does not bind to Ni surface as strong as what it does on those precious metal surfaces. Ni dispersions were estimated using H$_2$ chemisorption. 200 mg of samples were placed in a quartz tube connected to the chemisorption setup and reduced at the desired temperature by 400 Torr H$_2$ for 30 min. After 1-h evacuation at elevated temperatures, H$_2$ adsorption was measured by pulsing gas onto the sample at 308 K. The dispersion value was calculated by assuming an adsorption stoichiometry of one hydrogen atom per surface Ni. Dispersion values for different samples were measured in triplicate for each sample with a Ni dispersion standard deviation of 10%.

2.3 Catalytic Measurements

Most of the catalytic measurements were performed on two of the home-built reactor setups, connecting to either a gas chromatograph (GC, SRI 8610C) equipped with a TCD detector or a quadrupole mass spectrometer (SRS RGA-100). The reactor sections of the setups are essentially the same. Desired flows of different gases were controlled by sets of valves and flow controllers. All gases were mixed together before being introduced to catalysts samples. The effluent gases would be introduced to either GC or Masspec system. For the GC system, a six-way-valve is applied to allow fixed volume injection into GC. For the Masspec system that needs to work under Ultra-High-Vacuum (UHV) conditions, a leak valve is implemented to allow control of the amount of gas introduced to the UHV chamber. A mechanical pump and a turbomolecular pump in series were connected to the UHV chamber to keep the pressure at the desired vacuum level. Schematic demonstration for the reactors and the connected GC or Masspec can be found in Figure 2-4.
Most of the catalytic properties for the catalysts prepared were probed using the GC or Masspec systems described in Section 2.3. These would include reaction rates for CO oxidation, toluene hydrogenation, methane steam reforming, methane dry reforming, coke quantification, etc. Detailed description of the procedures would be implemented in the following chapters where the specific reactions were used.
2.4 Reducibility Measurements

2.4.1 Oxygen Titration

Sample reducibilities were determined by flow titration or oxygen titration, using the reaction system with a mass spectrometer that has been described in Section 2.3. These experiments were performed at 1 atm. Desired amount of samples were first reduced in pure H₂ at the chosen temperature. After purging a sample with He, it was exposed to dry air at 1073 K. The O₂ uptake was then determined by integrating the difference between the N₂ and O₂ signals in the mass spectrometer.

2.4.2 Coulometric Titration (CT)

The metal oxidation reaction proceeds according to the following formula:

\[ M + \frac{x}{2}O₂ = MO_x \]  

Equation 2.1

The equilibrium between the metal and metal oxides are then determined by the Gibbs free energy of metal, metal oxide and oxygen. Since both M and MOₓ are solids with activity value of unity, the equilibrium constant, K, can be directly related to oxygen partial pressure in equilibrium with the two solids according to the following equation:

\[ K = \exp\left(-\frac{\Delta G}{RT}\right) = P(O₂)^{\frac{x}{2}} \]

Equation 2.2

Therefore, measurement of the oxygen partial pressure determines the equilibrium constant and the Gibbs free energy.

Coulometric titration (CT) was used to determine equilibrium P₀₂ values. A schematic plot for the CT system can be found in Figure 2-5. In Coulometric titration, a 500-mg sample is inserted into a YSZ (yttria-stabilized zirconia) tube that has a Pt electrode painted on the inside and a Ag
The YSZ tube was then placed in a horizontal tube furnace and heated to the temperature of interest using a heating rate of 1.0 K·min⁻¹. After the temperature ramp, a mixture of 10% H₂, 10% H₂O, and 80% He was allowed to flow over the sample at a flow rate of 110 mL·min⁻¹ in order to ensure that the sample was completely reduced at the start of the measurements. After 1 h at the temperature of interest, the flow was stopped and the ends of the YSZ tube were sealed. Specified amounts of oxygen were then electrochemically pumped from the inside of the YSZ tube by applying a current across the electrodes using a Gamry instrument potential stat. After allowing the system to come to equilibrium with the electrodes at open circuit, the equilibrium Pₒ₂ was calculated from the Nernst equation and the open circuit potential. To demonstrate equilibrium, oxidation isotherms were also measured starting with the oxidized sample and the results were found to be the same.

\[
E = -\frac{RT}{nF} \ln \frac{P_{O₂,\text{inside}}}{P_{O₂,\text{outside}}}
\]

Figure 2-5 Schematic plot for Coulometric Titration (CT) setup.
2.4.3 Temperature-Programmed Reduction (TPR)

TPR measurements were performed in the reactor/mass-spectrometer system described in Section 2.3. Prior to these experiments, 500-mg samples were oxidized in dry air for 1 h at 1073 K. The TPR measurements were then performed using 10% CO:He mixtures with a total flow rate of 20 mL·min$^{-1}$ and a heating rate of 10 K·min$^{-1}$ from 298 to 1073 K. It should be noted that the results from TPR cannot be related to the thermodynamic reducibilities of different samples, since other factors such as geometries of the samples and diffusion barriers can also have an impact on the TPR profile.
CHAPTER 3. DEMONSTRATION OF ALD: STABILIZATION OF ZrO₂ POWDERS BY ALD OF CeO₂ AND ZrO₂²

Summary

This chapter aims at demonstrating how powerful ALD can be for sample preparation and proving the thermal stability of thin film materials. ZrO₂ powders were modified by ALD with CeO₂ and ZrO₂, using Ce(TMHD)₄ and Zr(TMHD)₄ as the precursors, in order to determine the effect of ALD films on the structure, surface area, and catalytic properties of the ZrO₂. Growth rates were measured gravimetrically and found to be 0.017 nm/cycle for CeO₂ and 0.031 nm/cycle for ZrO₂. Addition of 20 ALD cycles of either CeO₂ or ZrO₂ was found to stabilize the surface area of the ZrO₂ powder following calcination to 1073 K and to suppress the tetragonal-to-monoclinic transition. Shrinkage of ZrO₂ wafers was also suppressed by the ALD films. When used as a support for Pd in CO oxidation, the CeO₂-modified materials significantly enhanced rates due to interactions between the Pd and the CeO₂.

² This chapter was published as C. Lin, X. Mao, T.M. Onn, J. Jang, R.J. Gorte, Stabilization of ZrO₂ Powders via ALD of CeO₂ and ZrO₂, Inorganics, 5 (2017) 65. Copyright 2017, MDPI.
3.1 Introduction

Ceria is an important catalytic material, both as an oxidation catalyst by itself and as a promoter when it is in contact with transition metals [73-78]. Because pure ceria loses its reducibility after high-temperature treatments or redox cycling [79-81], it is often used in the form of a mixed oxide with zirconia, especially in Three-Way Catalysts (TWC) employed in automotive emissions-control applications [82, 83]. It is sometimes assumed that the role of zirconia in Oxygen Storage Capacitance (OSC) is to maintain surface area but ceria-zirconia phases maintain their reducibility upon redox cycling, even though they do not have substantially higher surface areas than would pure ceria under these conditions [83, 84]. Indeed, oxygen binding in ceria-zirconia solid solutions has been shown to be weaker than oxygen binding in pure ceria [85-87].

There is evidence that interfacial contact between ceria and zirconia can influence properties of ceria even when the two oxides exist as separate phases. For example, it has been reported that most Ce ions at the interface of epitaxial ceria films on yttria-stabilized zirconia (YSZ) substrates exist as Ce$^{3+}$ and that the average oxidation state is affected several nanometers from that interface [88]. In another report, ceria films on polycrystalline zirconia were shown to be much more reducible than ceria films on alumina [87]. Still another study of ceria films on YSZ single crystals found that the ceria particles tend to orient along specific crystallographic directions, suggesting strong interactions between the two phases [89].

In an attempt to take advantage of these interactions on high-surface-area catalysts, our laboratory investigated 0.4-nm, conformal zirconia films on ceria powders using Atomic Layer Deposition (ALD) [90]. In ALD, a substrate powder is first allowed to react with an organometallic precursor to a monolayer coverage, after which the adsorbed precursor is oxidized in a separate
step. Conformal films of varying thickness are formed by repeating this cycle the desired number of times. The zirconia-on-ceria ALD study found that the surface areas and crystallite sizes of ALD-modified ceria powders were dramatically stabilized against sintering to temperatures up to 1073 K [90]. Whereas the crystallite size of an unmodified ceria powder increased from 18 nm to 32 nm when the calcination temperature increased from 673 to 1073 K, the crystallite size of the ALD-modified ceria was unchanged by this treatment. The modified ceria also maintained its promotional effects for the water-gas-shift reaction when used as a support for Pd and showed improved tolerance to SO₂ poisoning.

Because the ALD film thicknesses in this previous study were much less than the crystallite sizes of the ceria powders that were stabilized, it is surprising that the zirconia film could have such a strong impact on crystallite stability. That, in turn, leads to questions about the mechanism of the stabilization and what effect film thickness and composition have on the results. Therefore, the properties of ceria and zirconia powders following ALD of ceria and zirconia films were investigated. The presented results show that both ceria and zirconia powders can be stabilized by zirconia ALD films, implying that there must be a physical aspect to the stabilization. ALD films appear to prevent surface diffusion of oxide cations, thus preventing sintering and crystallite growth. This could have important implications for stabilization of catalysts.
3.2 Experimental Methods

CeO$_2$ and ZrO$_2$ powders were prepared by precipitation following the procedures described in Section 2.1.1. The ZrO$_2$ powder had a BET surface area of 84 m$^2$/g and the CeO$_2$ powder had a surface area of 59 m$^2$/g.

ALD modification was performed using procedures and equipment that have been described in Section 2.1.2. To ensure that the substrate surface was saturated with adsorbed precursor, the substrate was exposed to the precursors multiple times before evacuation. As shown in Figure 2-3, temperatures in excess of 600 K are required to completely remove the ligands. The samples in this study were removed from the ALD system after each precursor exposure and heated to 773 K for 300 s in a muffle furnace. The samples were then replaced into the ALD system and the cycle repeated. The total time for one cycle, including exposure, evacuation, and oxidation cycles, was approximately 12 min. ZrO$_2$ samples modified by ALD will be referred to by the species deposited and the number of ALD cycles (e.g. A sample with 20 ALD cycles of CeO$_2$ is referred to as 20CeO$_2$/ZrO$_2$).

Surface areas were measured using BET isotherms in a homebuilt adsorption apparatus described in Section 2.2.1. For each sample, the surface area was measured 3 times and the surface areas were found to vary by no more than 2 m$^2$/g. X-Ray Diffraction (XRD) patterns were recorded on a Rigaku Smartlab diffractometer equipped with a Cu-K$\alpha$ source ($\lambda = 0.15416$ nm).

1-wt% Pd was added to selected samples using incipient wetness of aqueous solutions of Tetraamminepalladium nitrate (5.0% Pd(NH$_3$)$_4$(NO$_3$)$_2$, Alfa Aesar) following the description in Section 2.1.3. Pd dispersions were measured volumetrically using CO adsorption uptakes at room temperature.
CO oxidation rates were measured at differential conversions using the reactor setup described in Section 2.3. The total gas flow rate through the reactor was 120 mL·min⁻¹ and sample size was 100 mg in all experiments. The partial pressures of CO and O₂ were fixed at 25 and 12.5 Torr, respectively, by adjusting the flow rates of CO, O₂, and He.

The sintering character of the powders was examined by measuring the diameters of pressed wafers that had been heated to various temperatures. In these experiments, 160.0 mg of each sample were pressed into a wafer that had an initial diameter of 1.495 cm. The samples were then calcined for 30 min to various temperatures. The diameters of the pellets were then measured by Vernier caliper with the precision of 0.005 cm.
3.3 Results

The initial characterization of the deposition process for CeO$_2$ and ZrO$_2$ films on the ZrO$_2$ substrate involved measuring the sample mass as a function of the number of ALD cycles, as shown in Figure 3-1. For both CeO$_2$ and ZrO$_2$ deposition, the data demonstrate that the sample mass increased almost linearly with the number of ALD cycles. For CeO$_2$ deposition on ZrO$_2$, the mass increase after 20 cycles was 0.20 g/g ZrO$_2$. Assuming that the film grew uniformly over the 84-m$^2$/g ZrO$_2$ surface and had the bulk properties of CeO$_2$, this mass change corresponds to a growth rate of 0.017 nm/cycle. The deposition rate for ZrO$_2$ on ZrO$_2$ was higher, with the sample mass increasing by 0.30 g/g ZrO$_2$ after 20 cycles, corresponding to a deposition rate of 0.031 nm/cycle.

One of the most interesting observations from the previous ALD study of ZrO$_2$ on CeO$_2$ was that a 0.4-nm film, a thickness less than the 0.52-nm lattice parameter of cubic zirconia, was able to stabilize the surface area and crystallite size of CeO$_2$ to high temperatures [90]. To better understand the effect of ALD films, I investigated the influence of CeO$_2$ and ZrO$_2$ films on a ZrO$_2$ substrate as a function of film thickness. BET surface areas are reported as a function of calcination...
temperature in Table 3-1 for ZrO$_2$ samples that had been treated with 2, 10, or 20 ALD cycles of either CeO$_2$ or ZrO$_2$. The unmodified ZrO$_2$ sintered dramatically with temperature, with the surface area decreasing from 84 m$^2$/g after calcination at 773 K to only 20 m$^2$/g after heating to 1073 K.

Table 3-1 BET surface areas as a function of calcination temperature

<table>
<thead>
<tr>
<th>Calcination Temperature (K)</th>
<th>ZrO$_2$</th>
<th>2CeO$_2$/ZrO$_2$</th>
<th>10CeO$_2$/ZrO$_2$</th>
<th>20CeO$_2$/ZrO$_2$</th>
<th>2ZrO$_2$/ZrO$_2$</th>
<th>10ZrO$_2$/ZrO$_2$</th>
<th>20ZrO$_2$/ZrO$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>773</td>
<td>84</td>
<td>80</td>
<td>73</td>
<td>62</td>
<td>78</td>
<td>72</td>
<td>65</td>
</tr>
<tr>
<td>873</td>
<td>70</td>
<td>60</td>
<td>66</td>
<td>54</td>
<td>66</td>
<td>70</td>
<td>63</td>
</tr>
<tr>
<td>973</td>
<td>48</td>
<td>56</td>
<td>63</td>
<td>52</td>
<td>55</td>
<td>68</td>
<td>62</td>
</tr>
<tr>
<td>1073</td>
<td>20</td>
<td>33</td>
<td>40</td>
<td>51</td>
<td>35</td>
<td>32</td>
<td>47</td>
</tr>
</tbody>
</table>

The fresh 20CeO$_2$/ZrO$_2$ and 20ZrO$_2$/ZrO$_2$ samples, calcined at only 773 K, had lower surface areas, 62 m$^2$/g and 65 m$^2$/g respectively, primarily because of the added mass of the films. For example, addition of 0.3 g ZrO$_2$/g ZrO$_2$ would decrease the specific surface area by a factor of 1.3 (84 m$^2$/1.30 g = 63 m$^2$/g), even if the film had no influence on the pore sizes or distribution. Similar to what was reported for ZrO$_2$ ALD films on CeO$_2$, the decrease in surface areas with calcination temperature was much less severe for both the 20CeO$_2$/ZrO$_2$ and 20ZrO$_2$/ZrO$_2$ samples compared to pure ZrO$_2$. Following calcination to 1073 K, the surface areas of these two samples were 51 and 47 m$^2$/g, respectively, more than double that of the unmodified sample that had been heated to this temperature. The effects of ALD modification were also observed, to a less extent, with 10 and 2 ALD cycles of both CeO$_2$ and ZrO$_2$. 

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Another indication of the stabilizing effect of the ALD films comes from the XRD patterns shown in Figure 3-2. The patterns in Figure 3-2(a) are of the pure ZrO$_2$, 20CeO$_2$/ZrO$_2$ and 20ZrO$_2$/ZrO$_2$ samples after calcination at 773 K. The pattern for pure ZrO$_2$ indicates that the material is primarily in the tetragonal form, as shown by the large peak at 30 degrees 20, but with a small amount of monoclinic phase, shown by the small peak near 28 degrees 20. The deposition of 20 ALD cycles of either CeO$_2$ or ZrO$_2$, with calcination at 773 K, did not change the patterns.

While peaks associated with crystalline CeO$_2$ would be difficult to distinguish from the mixture of tetragonal and monoclinic ZrO$_2$, previous work has shown that ALD films this thin (The film on the 20CeO$_2$/ZrO$_2$ sample is only 0.33 nm thick.) are invisible to XRD [91]. The effects of calcining the same three samples to 1073 K is shown in Figure 3-2(b). The pure ZrO$_2$ is almost completely converted to its monoclinic form. By contrast, the 20CeO$_2$/ZrO$_2$ remains primarily in the tetragonal form and the 20ZrO$_2$/ZrO$_2$ sample is a mixture of the two phases.

![Figure 3-2 XRD patterns for (I) Unmodified ZrO$_2$, (II) 20CeO$_2$/ZrO$_2$, and (III) 20ZrO$_2$/ZrO$_2$. Patterns shown in a) were from samples calcined at 773 K and patterns in b) at 1073 K. Peaks marked with asterisks stand for tetragonal phase ZrO$_2$ and open circles stand for monoclinic phase ZrO$_2$.](image-url)
The sintering character of powders is critically important in ceramics processing [92] and the BET and XRD results suggested that ALD modification should significantly affect the properties of the ZrO$_2$ powder. That this is the case is demonstrated by Figure 3-3, which plots the percent change in the diameters of ZrO$_2$, 20CeO$_2$/ZrO$_2$ and 20ZrO$_2$/ZrO$_2$ wafers as a function of calcination temperature. Not surprisingly, the ultimate shrinkage after calcination to 1573 K was the same for each of the materials, ~16%; however, pure ZrO$_2$ had sintered to this value by 1273 K. The sintering curves for the ALD-modified samples, especially 20CeO$_2$/ZrO$_2$, were shifted upward by approximately 100 K, which means that the ALD-prepared samples would only have the same shrinkage if heated an additional 100 K, again consistent with the fact that the ALD films had increased the stability of the powders.

![Figure 3-3 Shrinkage of ceramic wafers as a function of calcination temperature: (○) Unmodified ZrO$_2$; (■) 20CeO$_2$/ZrO$_2$; (●) 20ZrO$_2$/ZrO$_2$. The original diameters for all the pellets were 1.495 cm.](image)

It has been previously demonstrated that rates for CO oxidation at interfacial sites between Pd and CeO$_2$ are much higher than rates on either Pd or CeO$_2$ individually [93]. There is no similar enhancement of CO-oxidation rates at Pd and zirconia interfaces [80]. Therefore, to determine how the ALD-modified catalysts would perform as catalyst supports and obtain a measure of how good
is the contact between Pd and the ceria in the samples, CO-oxidation rates were measured on selected samples after adding 1-wt% Pd. Measurements were performed on the ZrO$_2$, CeO$_2$, 20CeO$_2$/ZrO$_2$, and 20ZrO$_2$/ZrO$_2$ samples after the supports had been calcined to either 773 K or 1073 K. In all cases, the Pd was added after calcination of the support. After addition of Pd, the catalysts were calcined to 773 K. Pd dispersions for each of the catalysts are reported in Table 3-2. It is interesting to notice that the dispersions measured for Pd/CeO$_2$ and Pd/20CeO$_2$/ZrO$_2$ were similar and significantly higher than those on the Pd/ZrO$_2$ and Pd/20ZrO$_2$/ZrO$_2$ samples, which implies that there is a more favorable interaction between the Pd and the CeO$_2$.

Table 3-2 Pd dispersions as a function of support calcination temperature

<table>
<thead>
<tr>
<th>Calcination Temperature (K)</th>
<th>Pd Dispersion (%)</th>
<th>ZrO$_2$</th>
<th>20 ZrO$_2$/ZrO$_2$</th>
<th>CeO$_2$</th>
<th>20 CeO$_2$/ZrO$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>773 K</td>
<td></td>
<td>6.3</td>
<td>13.2</td>
<td>39.6</td>
<td>38.4</td>
</tr>
<tr>
<td>1073 K</td>
<td></td>
<td>4.7</td>
<td>11.2</td>
<td>30.1</td>
<td>32.3</td>
</tr>
</tbody>
</table>

Figure 3-4(a) shows differential reaction rates for the catalysts after the supports had been calcined to 773 K. Rates on the Pd/ZrO$_2$ and Pd/20ZrO$_2$/ZrO$_2$ catalysts were essentially identical and rates on the Pd/CeO$_2$ and Pd/20CeO$_2$/ZrO$_2$ were essentially identical. Extrapolating the rates to the same temperature, rates on the two ceria-containing samples were more than a factor of ten higher, which is more than can be explained by the higher dispersions. This agrees with the previous observations of enhanced rates at the Pd-ceria interface. Figure 3-4(b) shows differential rates for the same materials after the supports had been calcined to 1073 K. The only catalyst affected by this treatment was the Pd/CeO$_2$ sample. The loss of activity in this sample is likely due to loss of CeO$_2$ surface area, as reported previously for a similar Pd/CeO$_2$ catalyst used for the WGS reaction [66]. The Pd/ZrO$_2$ and Pd/20ZrO$_2$/ZrO$_2$ catalysts were not affected because reaction occurs only
on the Pd phase. The Pd/20CeO$_2$/ZrO$_2$ catalyst was not affected because the surface area did not significantly change.

Figure 3-4 Differential CO oxidation for various samples after addition of 1-wt% Pd. The samples in a) were calcined to 773 K and the samples in b) to 1073 K. Pd was added after calcination. The samples are as follows: (■) 20CeO$_2$/ZrO$_2$; (●) 20ZrO$_2$/ZrO$_2$; (○) unmodified ZrO$_2$; (□) unmodified CeO$_2$. 
3.4 Discussion

This chapter shows that ALD of very thin films of ZrO$_2$ on CeO$_2$ are able to stabilize the surface area and structure of the ZrO$_2$ substrate. It is shown here that substrate stabilization by ALD is not unique to ZrO$_2$ films on CeO$_2$. In particular, the fact that ZrO$_2$ films are able to stabilize ZrO$_2$ substrates implies that the effect must be structural and not due to any chemical bonding effects between different species. Finally, it is noteworthy that there is a noticeable change in the sintering characteristics following only two ALD cycles, corresponding to a coverage that is much less than a monolayer.

Since cation surface diffusion is a major contributor to the sintering process in ceramic materials [94], it would appear that ALD films act by suppressing surface diffusion. The mechanism behind this suppression may be different depending on the system. In the case of CeO$_2$ films on ZrO$_2$, there may be bonding between the dissimilar atoms that stabilize the surface cations. With ZrO$_2$ films on ZrO$_2$, the role of the ALD film may be to remove hydroxyls or fill in vacancies, thus stabilizing the metal cations.

In addition to stabilizing surface area, the ALD films influenced the structure of the zirconia substrate (e.g. preventing formation of the monoclinic phase upon heating). This can be important in some catalytic applications. For example, the acid-base properties of zirconia are reported to change with the different polymorphs [95]. The ability to stabilize a particular phase without significantly changing the surface area and without the addition of dopants could be very useful.

ALD thin films can also be useful in making high-surface-area, functional supports. The present CO-oxidation results indicate that a CeO$_2$ ALD film as thin as 0.34 nm can increase rates
for CO oxidation on supported-Pd catalysts to the same level observed for Pd supported on CeO$_2$. It is difficult to maintain CeO$_2$ powders in a high-surface-area form. The fact that one can achieve similar properties in a thin-film catalyst opens up the possibility of using a more stable substrate for enhanced surface area, while still having the high catalytic activity of the functional oxide. The use of thin-film supports could also be very important if the functional oxide is expensive. Besides, for concepts such as “intelligent catalysts” where the oxide geometry might play a role in determining metal-perovskite interactions, ALD provides opportunities to understand the systems better as very thin films can now be prepared. The thermal stability demonstrated in this chapter make this thin-film preparation technique promising for the perovskite thin-film preparation, since perovskite phase formation is favored at elevated temperature.
3.5 Conclusions

ALD films of CeO$_2$ and ZrO$_2$ on ZrO$_2$ powders are able to significantly stabilize the surface area and zirconia phase by suppressing surface diffusion of cations. CeO$_2$ films can also enhance the catalytic properties of the ZrO$_2$ when the material is used as a support for Pd in CO oxidation. This ability to modify oxides by ALD could be important for applications involving functional oxides. The chapter demonstrated the capability of ALD for thin film preparation, and the technique will be applied in later chapters for the synthesis of perovskite materials.
CHAPTER 4. IMPROVED COKING RESISTANCE OF “INTELLIGENT” Ni CATALYSTS PREPARED BY ATOMIC LAYER DEPOSITION

Summary

This chapter demonstrates the successful preparation of the thin-film perovskite, CaTiO$_3$, on a MgAl$_2$O$_4$ support by Atomic Layer Deposition (ALD). This composite support was then examined as a support for Ni in the steam and CO$_2$ reforming of methane. 1-nm CaTiO$_3$ films were characterized by Scanning Transmission Electron Microscopy (STEM) and X-Ray Diffraction (XRD) and shown to be stable to at least 1073 K. Catalysts with 1- and 20-wt% Ni were studied. Following calcination at 1073 K, the Ni/CaTiO$_3$/MgAl$_2$O$_4$ catalysts required high-temperature reduction to achieve activities comparable to that of their Ni/MgAl$_2$O$_4$ counterparts. However, the Ni catalysts on perovskite thin films exhibited dramatically improved tolerance towards carbon-whisker formation. The carbon content on the 1-wt% Ni catalyst on CaTiO$_3$/MgAl$_2$O$_4$ was small even after heating the catalyst in a dry, 10% CH$_4$-He mixture at 1073 K for 12 h.

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4.1 Introduction

Dry reforming of methane-rich natural gas, also known as CO₂ reforming, is receiving increasing attention as a means for producing syngas from feedstocks that contain high levels of CO₂ and for producing syngas for applications requiring a low H₂:CO ratio [96]. As discussed in Section 1.1, the primary problem encountered in dry reforming is the tendency of these materials to form carbon deposits, which in turn has led to a search for materials that do not coke under these conditions. Among the various materials examined for this application are alloy catalysts [97], metal catalysts with redox-active or oxygen-conducting supports [98-100] and precious-metal catalysts [101]. While these materials have demonstrated improvements in activity and/or stability, there is still a need for new catalysts that are active, stable, and relatively inexpensive.

As mentioned in CHAPTER 1, the exsolved Ni particles from a perovskite host can be anti-coking. Because the exsolved Ni particles differed from those formed by infiltration in that they remained partially embedded in the support [41], it was argued that carbon tolerance in the exsolved catalysts resulted from anchoring of the Ni to the support, which in turn suppressed Ni particles from “lifting off” the support to form carbon whiskers [14]. However, there are problems with implementing catalysts made using the exsolution process due to the low surface areas and slow diffusion. As discussed in CHAPTER 3, it should be possible to prepare thin films of the perovskite on a more stable support by Atomic Layer Deposition (ALD), thus avoiding the problems associated with bulk perovskites.

Several additional factors were considered in the present work. First, CaTiO₃ would have similar properties to SrTiO₃. The lower density of CaTiO₃ contributes to having a higher specific surface area for the final material. Second, because ALD growth rates for all but the smallest
precursors tend to be in the range from 0.01 to 0.04 nm/cycle [65], reasonable control over the stoichiometry of the films can be achieved by alternating the precursors for the A- and B-site cations of the perovskite. Third, even very thin films lead to significant perovskite loadings. As discussed previously, a simple calculation using the bulk properties of CaTiO$_3$ shows that a 1-nm thick film on a high-surface area support can lead to significant weight gain. It is clearly not practical to have perovskite films that are much thicker than 1 nm. Furthermore, because the weight changes are significant, ALD growth rates can be measured gravimetrically.

This chapter demonstrates my first successful attempt in synthesizing titanate thin films. CaTiO$_3$ films were prepared on MgAl$_2$O$_4$ and shown to exhibit reasonable stability to high temperatures. Ni catalysts prepared from these CaTiO$_3$/MgAl$_2$O$_4$ supports exhibit similar initial catalytic activities for Steam Methane Reforming (SMR) and Dry Methane Reforming (DMR) as Ni/MgAl$_2$O$_4$ but with much better tolerance against carbon formation.
4.2 Experimental Methods

The MgAl$_2$O$_4$ support was prepared using the method described in Section 2.1.1. The final MgAl$_2$O$_4$ powder had a BET surface area of 118 m$^2$/g. XRD showed only the characteristic peaks for MgAl$_2$O$_4$.

The CaTiO$_3$ films were prepared by ALD using a home-built, static system that has been described in detail in Section 2.1.2. The calcium precursor used in this study was Bis(2,2,6,6-tetramethyl-3,5-heptanedionato) calcium, (Ca(TMHD)$_2$, Strem, USA) and the titanium precursor was titanium chloride (TiCl$_4$, Sigma-Aldrich, USA). Although the TMHD ligands can be oxidized by NO$_2$ at this temperature [102], samples in the present study were simply removed from the system and heated in a muffle furnace at 773 K for 5 min. The elemental composition and concentration for ALD samples were determined by InductivelyCoupled Plasma-Optical Emission Spectrometry (ICP-OES) performed on a Spectro Genesis spectrometer with a concentric nebulizer. For the ICP-OES measurement, the sample (~25 mg) was dissolved in a 5-ml solution of Aqua Regia overnight. The solution was then diluted with a 10-wt% HNO$_3$ solution to an appropriate concentration before ICP analysis.

Catalysts with Ni were prepared by incipient wetness with aqueous solutions of Nickel(II) nitrate hexahydrate (98% Ni(NO$_3$)$_2$·6H$_2$O, Alfa Aesar). Detailed preparation method can be found in Section 2.1.3. Surface areas were measured using BET isotherms in a homemade adsorption apparatus. X-ray diffraction (XRD) patterns were recorded on a Rigaku Smartlab diffractometer equipped with a Cu K$_\alpha$ source ($\lambda = 0.15416$ nm).

Ex-situ scanning transmission electron microscopy (STEM) was performed on powder specimens. Elemental mapping via Energy Dispersive X-ray Spectroscopy (EDS) was performed
with a FEI Talos F200X or JEOL 2800 operated at 200 kV, equipped with four large angle dual
dry solid-state 100 mm$^2$ detectors (Super-X G2™ system). SEM images were taken with a JEOL
JSM-6700 field emission SEM equipped with secondary and backscattered electron detectors for
investigating the surface morphology and phase homogeneity, respectively.

Ni dispersions were estimated using H$_2$ chemisorption described in Section 2.2.4. The
oxidation state of the Ni following various pretreatments was determined by flow titration using
procedures described in Section 2.4.1.

SMR and DMR activities were measured under differential conversions using the reactor
setup described in Section 2.3. The total gas flow rate through the reactor was maintained at 100
mL·min$^{-1}$, and the catalyst sample size was 100 mg. For SMR, the H$_2$O, CH$_4$, and He ratios were
2:1:7, while the CO$_2$, CH$_4$, and He ratios were 1:1:8 in DMR. The samples were oxidized at 1073
K in air, then reduced in flowing diluted H$_2$ (5% with balancing He at a total flow rate of 100
mL·min$^{-1}$) at specified temperatures for 1 h before measuring activities.

To quantify the tendency of catalysts to form carbon, 100-mg samples were exposed to 100
mL·min$^{-1}$ of 10% CH$_4$ in He at 1073 K for fixed periods of 3 h, 6 h, 9 h and 12 h. The amount of
carbon formed was then determined in a flow reactor by passing 20% O$_2$ in He over the catalyst at
50 mL·min$^{-1}$ and 1073 K while a mass spectrometer was used to detect the CO$_2$ produced. Multiple
experiments were performed for each exposure time but the results were always within ~10%.
4.3 Results

Film growth rates for CaO, TiO$_2$, and CaTiO$_3$ were determined gravimetrically and the data are shown in Figure 4-1. In all cases, the sample weight increased almost linearly with the number of cycles in this coverage range. For TiO$_2$ and CaO, the weight changes after 40 cycles were 0.62 g TiO$_2$/g MgAl$_2$O$_4$ and 0.31 g CaO/g MgAl$_2$O$_4$, respectively. The lower growth rate for CaO is primarily due to the very large TMHD ligands on the Ca(TMHD)$_2$ precursor. Assuming the films are formed at their bulk densities over the entire 118 m$^2$/g MgAl$_2$O$_4$ surface, these weight changes correspond to growth rates of 0.016 nm/cycle for CaO and 0.032 nm/cycle for TiO$_2$, in reasonable agreement with literature values for ALD on flat surfaces [103, 104]. On an atom basis, the deposition rates were 6.9×10$^{17}$ Ca/m$^2$ per cycle and 9.9×10$^{17}$ Ti/m$^2$ per cycle. Therefore, to achieve the correct stoichiometry for CaTiO$_3$, a strategy in which I deposited 6 cycles of CaO, followed by 4 cycles of TiO$_2$ was implemented. After 40 total cycles, the weight gain was 0.43 g CaTiO$_3$/g MgAl$_2$O$_4$, or 30-wt%, corresponding to a film thickness slightly less than 1 nm, assuming uniform growth of a CaTiO$_3$ film with bulk properties. After calcination at 773 K, the surface area of the CaTiO$_3$/MgAl$_2$O$_4$ sample was 87 m$^2$/g, with most of the decrease in the specific surface area being due to the increased sample mass (118 m$^2$/1.43 g = 84 m$^2$/g). The Ca: Ti ratio for the ALD-prepared samples were verified to be around 0.9:1 from ICP-OES analysis.
The 30-wt% CaTiO$_3$/MgAl$_2$O$_4$ sample was examined by electron microscopy, with Figure 4-2 showing images after calcination at 1073 K. The High-Angle Annular Dark-Field Scanning Transmission Electron Microscope (HAADF-STEM) images indicate that the sample is made up of features that are roughly 5 to 10 nm in size. There are no clear image features that correlate specifically to the CaTiO$_3$. The elemental maps obtained from EDS show that the Ca and Ti have deposited uniformly over the substrates and forming brighter rings on the edges.
The structure of the film was investigated using XRD, with results in Figure 4-3 displaying the patterns on the 30-wt% CaTiO$_3$/MgAl$_2$O$_4$ sample as a function of calcination temperature. The pattern in Figure 4-3(a), measured after calcination at 773 K, is identical to that of pure MgAl$_2$O$_4$, implying that the ALD film was X-ray amorphous. There are no peaks that could be assigned to any other compositions. When the sample was calcined at 1073 K, Figure 4-3(b), the characteristic peaks for CaTiO$_3$ begin to appear. The peaks associated with the perovskite phase increased in intensity after calcination at 1173 K, without showing any evidence for solid-state reactions with the MgAl$_2$O$_4$. One surprising aspect to these results is that the perovskite peaks are relatively narrow, indicative of a coherence length of approximately 40 nm. Since there is no evidence for features this size in electron microscopy, the coherence length may be associated with two dimensional, planar crystallites. It is noteworthy that the XRD patterns reported previously for LaFeO$_3$ films on MgAl$_2$O$_4$ also exhibited narrow lines for perovskite films that were thin and uniform [58].

**Figure 4-2** Representative HAADF-STEM results for CaTiO$_3$ films deposited by ALD on MgAl$_2$O$_4$, after calcination at 1073 K, with EDS mapping of Mg, Al, Ca, and Ti.
Catalysts with 1- and 20-wt% Ni were prepared with the 30-wt% CaTiO$_3$/MgAl$_2$O$_4$ supports and were tested for SMR and DMR rates. Figure 4-4(a) compares SMR rates with 1-wt% Ni loadings (1Ni/CaTiO$_3$/MgAl$_2$O$_4$ and 1Ni/MgAl$_2$O$_4$) following reduction at either 773 or 1073 K. For the 1Ni/MgAl$_2$O$_4$ catalyst, the reduction temperature did not significantly change the catalytic activity. However, the reduction temperature had a fairly dramatic effect on rates over the 1Ni/CaTiO$_3$/MgAl$_2$O$_4$ catalyst, increasing by an order of magnitude after reduction at 1073 K. Rates on the two catalysts were nearly the same after reduction at the higher temperature. The requirement for high reduction temperatures on the 1Ni/CaTiO$_3$/MgAl$_2$O$_4$ catalyst is consistent with observations on other exsolution catalysts for which high reduction temperatures are necessary.
temperatures are required to pull the metal out of the perovskite lattice [22, 58]. The results therefore suggest that Ni is being incorporated into the perovskite lattice during calcination. To further test the idea that Ni may reversibly enter and exit the perovskite lattice, SMR rates on the 1Ni/CaTiO$_3$/MgAl$_2$O$_4$ catalyst were measured after cycling between oxidation at 1073 K/reduction at 773 K and oxidation at 1073 K/reduction at 1073 K. As shown in Figure 4-4(b), the sample showed low activity whenever reduction was at the lower temperature and high activity when the reduction was at 1073 K.

Figure 4-4 Steady-state, differential reaction rates for SMR with 38 Torr CH$_4$ and 76 Torr H$_2$O. (a) Rates for (∆) 1Ni/CaTiO$_3$/MgAl$_2$O$_4$ reduced at 773 K; (▲) 1Ni/CaTiO$_3$/MgAl$_2$O$_4$ reduced at 1073 K; (◊) 1Ni/MgAl$_2$O$_4$ reduced at 773 K; (♦) 1Ni/MgAl$_2$O$_4$ reduced at 1073 K. (b) Rates for 1Ni/CaTiO$_3$/MgAl$_2$O$_4$ after the following pretreatments: (∆) Oxidation at 1073 K, followed by reduction at 773 K; (▲) Oxidation at 1073 K, followed by reduction at 1073 K. Black symbols denote the first redox cycle and the red symbols the second cycle.

To get information on the state of the Ni in the CaTiO$_3$-containing samples, HAADF-STEM/EDS measurements were performed on the 1Ni/CaTiO$_3$/MgAl$_2$O$_4$ sample before and after reduction at 1073 K, with results reported in Figure 4-5 and Figure 4-6. As discussed previously, the HAADF-STEM images show that sample consists of poorly defined features that are roughly 5 to 10 nm in size. EDS mapping of the oxidized sample indicates that, except for a Ti-rich region at the top-left side of this particular image, the distributions of Ca and Ti remain uniform over the
samples. Ni is present over most of the surface, although there are 10-nm-sized regions that are rich in Ni in some parts of the sample. The images in Figure 4-6 were obtained on the same sample after reduction at 1073 K. What is most surprising is that the images did not change dramatically. The Ca and Ti remain well distributed; there is also evidence of some coalescence of the Ni-rich regions into particles, but the Ni still appears to be spread over much of the surface.

Figure 4-5 HAADF-STEM and EDS maps for 1Ni/CaTiO₃/MgAl₂O₄ after oxidation at 1073 K.
To gain further insights into the state of the Ni on these catalysts, oxygen-titration was performed as a function of reduction temperature, with the results shown in Table 4-1. These values did not change with repeated reduction-oxidation cycles and the standard deviation for multiple measurements were ~10%. For the 1Ni/MgAl₂O₄ sample, the titration data indicate that the Ni was 40% reduced after reduction at 773 K and 100% reduced after reduction at 1073 K. The incomplete reduction of Ni after heating in H₂ at 773 K may imply partial reaction of Ni with the support that could only be reversed at the higher temperature. The extents of Ni reduction on the 1Ni/CaTiO₃/MgAl₂O₄ sample were much lower, only 6% at 773 K and 50% at 1073 K. This is consistent with the reaction data which showed that 773-K reduction is insufficient to activate the catalyst. Even high-temperature reduction was insufficient to completely reduce the Ni on the CaTiO₃-containing sample, possibly because some Ni remains in the CaTiO₃ lattice.

Figure 4-6 HAADF-STEM and EDS maps for 1Ni/CaTiO₃/MgAl₂O₄ after reduction at 1073 K.
**Table 4-1** O$_2$ uptakes for samples after reduction at specified temperature

<table>
<thead>
<tr>
<th>Sample</th>
<th>O$_2$ uptake (μmol/g catalyst)</th>
<th>773 K reduction</th>
<th>1073 K reduction</th>
</tr>
</thead>
<tbody>
<tr>
<td>1Ni/CaTiO$_3$/MgAl$_2$O$_4$</td>
<td>5</td>
<td>43</td>
<td></td>
</tr>
<tr>
<td>1Ni/MgAl$_2$O$_4$</td>
<td>35</td>
<td></td>
<td>90</td>
</tr>
</tbody>
</table>

Results for DMR on 1Ni/CaTiO$_3$/MgAl$_2$O$_4$ and 1Ni/MgAl$_2$O$_4$ are shown in Figure 4-7 and were very similar to that for SMR, except that the rates for methane conversion were approximately an order-of-magnitude lower for the conditions of our experiments. In order to examine the effect of Ni loading, DMR rates were also measured on catalysts with 20-wt% Ni, 20Ni/CaTiO$_3$/MgAl$_2$O$_4$ and 20Ni/MgAl$_2$O$_4$. The comparison of the two samples in Figure 4-8(a) shows that rates on the 20Ni/CaTiO$_3$/MgAl$_2$O$_4$ catalyst were again affected by the higher reduction temperature while rates on the 20Ni/MgAl$_2$O$_4$ catalyst were not. DMR rates on the 20Ni/CaTiO$_3$/MgAl$_2$O$_4$ catalyst reduced at 773 K were low but rates were similar for the two catalysts after reduction at 1073 K. Figure 4-8(b) demonstrates that the 20Ni/CaTiO$_3$/MgAl$_2$O$_4$ catalyst also required high-temperature reduction to fully restore activity after oxidation at 1073 K. However, the effect of reduction temperature on the 20Ni/CaTiO$_3$/MgAl$_2$O$_4$ catalyst was not as strong as on the 1Ni/CaTiO$_3$/MgAl$_2$O$_4$, likely due to the higher Ni loading. Indeed, the surprising result in Figure 4-8 is that the 20Ni/CaTiO$_3$/MgAl$_2$O$_4$ catalyst was affected by high-temperature redox cycling at all. At this high Ni loading (the atomic ratios in this sample were Ni:Ca:Ti of 3:2:2), it is not possible for a majority of the Ni to enter the perovskite lattice. The strong interactions between Ni and the CaTiO$_3$ must involve more than exsolution.
**Figure 4-7** Steady-state, differential reaction rates for DMR with 38 Torr of CH$_4$ and CO$_2$. (a) Rates reported for: (○) 1Ni/CaTiO$_3$/MgAl$_2$O$_4$ reduced at 773 K; (●) 1Ni/CaTiO$_3$/MgAl$_2$O$_4$ reduced at 1073 K; (□) 1Ni/MgAl$_2$O$_4$ reduced at 773 K; (■) 1Ni/MgAl$_2$O$_4$ reduced at 1073 K. (b) Rates for 1Ni/CaTiO$_3$/MgAl$_2$O$_4$ after the following pretreatments: (○) Oxidation at 1073 K, followed by reduction at 773 K; (●) Oxidation at 1073 K, followed by reduction at 1073 K. Black symbols denote the first redox cycle, while red symbols the second cycle.

**Figure 4-8** Steady-state, differential reaction rates for DMR with 38 Torr of CH$_4$ and CO$_2$. (a) Rates reported for: (○) 20Ni/CaTiO$_3$/MgAl$_2$O$_4$ reduced at 773 K; (●) 20Ni/CaTiO$_3$/MgAl$_2$O$_4$ reduced at 1073 K; (□) 20Ni/MgAl$_2$O$_4$ reduced at 773 K; (■) 20Ni/MgAl$_2$O$_4$ reduced at 1073 K. (b) Rates for 20Ni/CaTiO$_3$/MgAl$_2$O$_4$ after the following pretreatments: (○) Oxidation at 1073 K, followed by reduction at 773 K; (●) Oxidation at 1073 K, followed by reduction at 1073 K. Black symbols denote the first redox cycle, while red symbols the second cycle.
To better understand the SMR and DMR rates, Ni dispersions were measured using H₂ adsorption, with results shown in Table 4-2. On the MgAl₂O₄-supported catalysts, the dispersions were essentially independent of reduction temperature with roughly 8% on the 1-wt% Ni catalyst and 5% on the 20-wt% Ni catalyst. In contrast to this, the measured dispersions on the 1Ni/CaTiO₃/MgAl₂O₄ and 20Ni/CaTiO₃/MgAl₂O₄ samples were strongly dependent on the reduction temperature. After reduction at 773 K, the dispersion on the 1Ni/CaTiO₃/MgAl₂O₄ was very low, only 1%, but increased to 7% after reduction at 1073 K. The dispersion was again low when this sample was oxidized at 1073 K followed by reduction at 773 K, with dispersion restored by a second reduction at 1073 K. This is consistent with the reaction measurements and a possible exsolution process. For the 20Ni/CaTiO₃/MgAl₂O₄ sample, the effects of oxidation and reduction were not as dramatic, again consistent with the reaction data.

<table>
<thead>
<tr>
<th>Sample</th>
<th>1(^{\text{st}}) cycle</th>
<th>2(^{\text{nd}}) cycle</th>
</tr>
</thead>
<tbody>
<tr>
<td>1Ni/MgAl₂O₄</td>
<td>8</td>
<td>7</td>
</tr>
<tr>
<td>20Ni/MgAl₂O₄</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>1Ni/CaTiO₃/MgAl₂O₄</td>
<td>1</td>
<td>7</td>
</tr>
<tr>
<td>20Ni/CaTiO₃/MgAl₂O₄</td>
<td>1</td>
<td>4</td>
</tr>
</tbody>
</table>

Significantly, the coking characteristics of the catalysts containing CaTiO₃ were dramatically better. This is demonstrated most clearly by the photographs in Figure 4-9. The two photographs on the left are of the 1Ni/CaTiO₃/MgAl₂O₄ and 1Ni/MgAl₂O₄ catalysts after reduction at 1073 K. The catalyst powders are present as short beds with white glass-wool packing on both
sides. The photographs on the right were obtained from the same catalysts after exposure to flowing 10% CH₄ in He at 1073 K for 12 h. The 1Ni/CaTiO₃/MgAl₂O₄ catalyst was essentially unchanged in appearance by this harsh treatment, whereas the entire tube containing the 1Ni/MgAl₂O₄ catalyst became filled with carbon whiskers. SEM images of these same two samples are shown **Figure 4-10**. As expected, the 1Ni/MgAl₂O₄ sample was filled with carbon whiskers; but there was no evidence for such fibers in the 1Ni/CaTiO₃/MgAl₂O₄ sample.

**Figure 4-9** Photographs of samples before (left) and after (right) exposure to dry CH₄ at 1073 K for 12 h. (a) 1Ni/CaTiO₃/MgAl₂O₄; (b) 1Ni/MgAl₂O₄
To quantify the tendency of the various catalysts to deactivate by coking, 100-mg samples of the 1073-K reduced catalysts were exposed to 100 mL·min⁻¹ of 10% CH₄ in He at 1073 K for 12 h. The amounts of carbon that deposited on the various samples were then determined from the quantities of CO₂ that were formed when 50 mL·min⁻¹ of a 20% O₂-He mixture was passed over the samples in a flow reactor at 1073 K. The results are shown in Table 4-3. The amounts of carbon formed on the 1Ni/MgAl₂O₄ and 20Ni/MgAl₂O₄ catalysts were very large, much greater than the amounts of Ni present in the catalysts. For example, 1-wt% Ni is 0.17 mmol/g, so that 6 mmol C/g corresponds to more than 35 carbons per Ni. This is consistent with formation of carbon whiskers. By comparison, carbon formation on the 1Ni/CaTiO₃/MgAl₂O₄ catalyst was almost negligible at 0.33 mmol/g. This catalyst also retained its SMR activity following the 12-h pretreatment in dry methane. Significantly more carbon formed on the 20Ni/CaTiO₃/MgAl₂O₄ catalyst but the carbon content after methane pretreatment was still significantly reduced compared to the 20Ni/MgAl₂O₄ catalyst.

**Figure 4-10** SEM images of the samples after exposure to dry CH₄ at 1073 K for 12 h: (a) 1Ni/CaTiO₃/MgAl₂O₄; (b) 1Ni/MgAl₂O₄.
Table 4-3 Total carbon content comparison for various samples

<table>
<thead>
<tr>
<th></th>
<th>Total Carbon Content (mmol carbon/g catalyst)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1Ni/MgAl₂O₄</td>
<td>6</td>
</tr>
<tr>
<td>1Ni/CaTiO₃/MgAl₂O₄</td>
<td>0.33</td>
</tr>
<tr>
<td>20Ni/MgAl₂O₄</td>
<td>180</td>
</tr>
<tr>
<td>20Ni/CaTiO₃/MgAl₂O₄</td>
<td>11</td>
</tr>
<tr>
<td>1Ni/CaO/MgAl₂O₄</td>
<td>5.12</td>
</tr>
<tr>
<td>1Ni/TiO₂/MgAl₂O₄</td>
<td>0.18</td>
</tr>
</tbody>
</table>

The amount of carbon formation on 1Ni/MgAl₂O₄ and 1Ni/CaTiO₃/MgAl₂O₄ samples was measured as a function of time, with results shown in Figure 4-11. Since different catalyst batches were used for this experiment, there is a small variation in the amount of carbon formed. However, different trends for carbon accumulation with or without ALD coating were obviously observed. A linear relation between carbon accumulation and time of exposure was observed for the 1Ni/MgAl₂O₄ sample, possibly due to the whisker carbon formation. For the ALD-modified catalysts, the amount of additional carbon formed after the initial period of around 3 h is negligible.

![Figure 4-11](image)

Figure 4-11 Coke formation as a function of time for (♦)1Ni/MgAl₂O₄; (▲) 1Ni/CaTiO₃/MgAl₂O₄
To eliminate the possibility that the changes in activities and coking resistance are from addition of a single component to the support, similar experiments were carried out for 1Ni/CaO/MgAl$_2$O$_4$ and 1Ni/TiO$_2$/MgAl$_2$O$_4$ (both with 30 wt% ALD loadings, 50 cycles and 25 cycles for CaO and TiO$_2$, respectively) with results shown in Figure 4-12 and Table 4-3. These show that the addition of CaO has very little effect on the reforming activities and coking resistance of the Ni/MgAl$_2$O$_4$ catalyst. The titania-containing sample exhibited very poor catalytic performance in both low-temperature and high-temperature reducing conditions. However, no significant coke was found for the titania-containing catalysts. The data for the CaO- and TiO$_2$-containing samples demonstrate that the properties of the CaTiO$_3$-containing catalyst cannot be explained by the presence of the individual oxides.

\[ \text{Figure 4-12} \] Steady-state, differential reaction rates for SMR with 38 Torr of CH$_4$ and 76 Torr H$_2$O. (a) Rates reported for: (◊) 1Ni/CaO/MgAl$_2$O$_4$ reduced at 773 K; (♦) 1Ni/CaO/MgAl$_2$O$_4$ reduced at 1073 K; (b) Rates reported for: (○) 1Ni/TiO$_2$/MgAl$_2$O$_4$ reduced at 773 K; (●) 1Ni/TiO$_2$/MgAl$_2$O$_4$ reduced at 1073 K;
4.4 Discussion

The results here confirm the earlier reports that Ni particles exsolved from perovskites exhibit a dramatically reduced tendency to form carbon whiskers when exposed to dry methane at elevated temperatures [37, 105]. The earlier studies used La$_x$Sr$_{1-x}$TiO$_3$ as the perovskite support; the fact that CaTiO$_3$ gave similar results implies that the conclusions apply to titania-based perovskites more generally. Another difference from past work is that the previous supports were bulk crystallites while the present work used very thin perovskite films. The high surface areas achievable with the thin-film supports also allowed us to show that the steam-reforming activities of the perovskite-supported catalysts are similar to that observed with conventional Ni catalysts.

The work with bulk-perovskite supports hypothesized that coke tolerance of the exsolved Ni results from the particles remaining partially embedded in the oxide support [37]. It was thought that embedding prevented the Ni particles from “lifting off” the surface with the growing carbon whisker. However, it seems unlikely that this mechanism can completely explain results with the thin-film support. The fact that high reduction temperatures were required to activate these catalysts does suggest that there are strong interactions between the metal and the perovskite thin-film support. These interactions may anchor the metal to the surface, even if the mechanism behind this anchoring is not due to “socketing” of the metal into the surface. The differences in the carbon accumulation rates, together with the SEM images for samples after methane exposure also suggested different metal-support interactions when the MgAl$_2$O$_4$ is modified by a perovskite sub-layer. The TEM images of the catalysts here also suggested that the oxidized Ni had spread out over the perovskite substrate. If a strong-metal-support interaction is indeed responsible for the present catalyst properties, it is interesting to notice that these are induced by oxidizing conditions.
and removed by high-temperature reduction, exactly the opposite of what is observed with the so-called SMSI effect commonly reported with titania-supported catalysts [106].

The ability to form thin films of the perovskite is essential for making practical catalysts that have high surface areas, and ALD may be uniquely capable of preparing these. With conventional co-precipitation, each individual oxide will precipitate under different conditions and very high temperatures are usually required to achieve cation mixing that results in the thermodynamically stable perovskite phase. The slow growth rates in ALD ensure that the oxide films are reasonably well mixed immediately after deposition, so that relatively mild heating is sufficient to form the mixed-oxide phase.

There are still questions about what factors are most important in determining the properties of the CaTiO$_3$-supported Ni and how to take advantage of those properties. For example, would perovskites that are not titania-based show the same carbon tolerance that was observed here? There is some indication that Ni supported on BaZrO$_3$ is also carbon tolerant implying that the titanates are not unique [107]. What changes are occurring in the state of the Ni upon high-temperature reduction? Is the high coke tolerance observed here for reactions of methane found with other hydrocarbons? Given the potential importance of coke tolerance, it will be very interesting to pursue these questions. We will be revisiting the Ni systems in CHAPTER 7 for better understanding of the Ni-perovskite interactions from a thermodynamic perspective.
4.5 Conclusions

In this chapter, I have demonstrated that thin, conformal CaTiO$_3$ films can be prepared on a MgAl$_2$O$_4$ support. Ni reforming catalysts based on these composite supports require high-temperature reduction in order to be as catalytically active as a conventional Ni/MgAl$_2$O$_4$; however, the CaTiO$_3$-containing catalysts exhibit dramatically improved tolerance against whisker formation when heated in dry methane just like its bulk counterparts. Since the anti-coking properties are observed, even with high Ni loadings, the explanation for the high carbon tolerance must involve strong bonding interactions between the Ni and the support.
CHAPTER 5. “INTELLIGENT” Pt CATALYSTS STUDIED ON HIGH-SURFACE-AREA CaTiO$_3$ FILMS

Summary

In this chapter, the same CaTiO$_3$ films studied in CHAPTER 4 were examined as catalyst supports for Pt and Pd. The results reported here clearly suggest a connection between bulk and thin-film perovskites, since the specificity that was found with the bulk systems can be reproduced for these thin-film materials. Pd does not interact with CaTiO$_3$/MgAl$_2$O$_4$, while the Pt/CaTiO$_3$/MgAl$_2$O$_4$ catalyst exhibited evidence for strong support interactions. Both Pt/CaTiO$_3$/MgAl$_2$O$_4$ and a catalyst formed by exsolution of CaTi$_{0.95}$Pt$_{0.05}$O$_3$ exhibited very low rates for toluene hydrogenation in comparison to Pt/MgAl$_2$O$_4$. Differences between the thin-film and bulk perovskites were also identified. Scanning Transmission Electron Microscope Energy/Dispersive X-ray Spectroscopy (STEM/EDS) showed that the CaTiO$_3$ films uniformly covered the MgAl$_2$O$_4$ surface after both reduction and oxidation at 1073 K. Pt particles on reduced Pt/CaTiO$_3$/MgAl$_2$O$_4$ exhibited an unusual rhombohedral shape and may be flat, a further indication of strong interactions between the metal and the support. Low Energy Ion Scattering (LEIS) indicated that high-temperature reduction caused a reconstruction of the CaTiO$_3$.

5.1 Introduction

As discussed in CHAPTER 1, maintaining the dispersion of supported metals is extremely important for catalysts that must maintain their activity in very harsh environments. The conditions experienced by three-way, automotive, emissions-control catalysts are especially challenging because the temperatures can be high, there is a significant partial pressure of water, and the environment cycles between oxidizing and reducing conditions. Self-regenerating, “intelligent” catalysts could potentially be a route for synthesizing anti-sintering catalysts [22, 23, 26]. Unfortunately, the concept has not been entirely successful, because of the large crystallite size, slow kinetics of the exsolution process, and the poor metal utilization [37, 48].

In CHAPTER 4, I demonstrated the successful preparation of CaTiO₃ thin films on high-surface-area substrates. Ni catalysts supported on these thin-film perovskites displayed at least some characteristics that were the same as those found with bulk-perovskite supports. When Ni/CaTiO₃/MgAl₂O₄ was oxidized at 1073 K and reduced at 773 K, it was inactive for steam reforming; following reduction at 1073 K, it became active and remained active unless calcined to 1073 K. The Ni/CaTiO₃/MgAl₂O₄ catalyst was found to exhibit greatly increased tolerance against coking when exposed to dry methane at 1073 K.

Although the thin-film supports show some characteristics similar to those observed in the bulk catalysts, there are a number of important questions concerning the nature of metal-perovskite interactions, both with bulk perovskites and with these thin-film, perovskite supports. First, even 30 wt% CaTiO₃ on a 120-m²/g support corresponds to films that are only about 1-nm thick, which is less than a typical metal-particle size. (The film thickness here is calculated from the mass of the film, assuming the film has the bulk density, as discussed in Section 1.3.1.) When the thickness of
the perovskite film is less than the metal-particle size, it is not obvious that the concept of “exsolution” should apply. Second, interactions between a metal catalyst and its perovskite support should be composition specific. For example, Pt was reported to reversibly enter the CaTiO$_3$ lattice, while Pd did not [24]. That leads to the question whether similar specificity will be observed with thin-film perovskites. Third, the fact that Ni particles exsolved from LSTN and Ni particles supported on CaTiO$_3$/MgAl$_2$O$_4$ both showed tolerance against carbon formation suggests that there are differences in the catalytic properties of these materials that go beyond improved thermal stability. It is therefore interesting to ask whether other exsolved metals would also show unique catalytic properties.

In this chapter, support effects with CaTiO$_3$ for both Pt and Pd catalysts were investigated. Similar to what has been reported with bulk CaTiO$_3$ [24], Pt interacts strongly with the thin-film CaTiO$_3$/MgAl$_2$O$_4$ supports while Pd does not. Similar to what was observed with Ni/CaTiO$_3$/MgAl$_2$O$_4$, high-temperature oxidation of the Pt/CaTiO$_3$/MgAl$_2$O$_4$ catalyst is required to induce the interactions and high-temperature reduction is required to re-activate the catalyst. Furthermore, although the reduced forms of Pt/CaTiO$_3$/MgAl$_2$O$_4$ and of bulk Pt/CaTiO$_3$ catalysts are active for CO oxidation, it was found out that the adsorption and reaction properties of these catalysts are significantly different from that found with Pt on non-interacting supports, implying that the perovskite plays a role beyond simple exsolution.
5.2 Experimental Methods

A detailed description of the preparation methods used to make the MgAl₂O₄-supported films is given in Section 2.1.1. CaO, TiO₂, and CaTiO₃ films were grown on the MgAl₂O₄ using ALD in a homebuilt, static system that has been described in Section 2.1.2. The final step for producing CaTiO₃ films involved calcination in air at 1073 K. Catalysts with Pt and Pd were also prepared using ALD. The precursors for Pd and Pt were Pd(TMHD)₂ (Bis(2,2,6,6-tetramethyl-3,5-heptanedionato) palladium(II), Strem, USA) and Pt(acac)₂ (Platinum acetylacetonate, Strem, USA), respectively. Detailed preparation methods can be found in Section 2.1.2. The bulk Pt-doped perovskite, CaTi₀.⁹₅Pt₀.⁰₅O₃, was synthesized using sol-gel procedures described in Section 2.1.4.

Elemental analyses of selected samples were measured by ICP-OES on a Spectro Genesis spectrometer with a concentric nebulizer. The samples were dissolved by placing them in aqua regia at 333 K overnight and then diluted to a suitable concentration before analysis. The amounts of Ca that were added by ALD were found to be about 5% below that calculated from the mass changes probably due to some carbonate formation, while the Ti compositions from ICP-OES agreed very well with the weight changes.

BET surface areas were determined in a homebuilt apparatus. Metal dispersions were measured volumetrically using CO at room temperature. For both BET and CO chemisorption, average values for three separate measurements were reported; but the measured values were always within 5% of the average.

Ex situ Scanning Transmission Electron Microscopy (STEM) was performed on powder specimens that had been sonicated in methanol and then deposited onto carbon support films on copper grids (Electron Microscopy Sciences). STEM, SAED pattern and elemental mapping via
Energy Dispersive X-ray Spectroscopy (EDS) were performed with a JEOL JEM-F200 STEM operated at 200 kV.

Differential rates for CO oxidation were measured in the flow reactor setup connected to GC with 100-mg samples. The total gas flow rate was maintained at 120 mL·min⁻¹ using a He carrier, with partial pressures of 25 Torr and 12.5 Torr for CO and O₂, respectively. Light-off profiles for CO oxidation and toluene hydrogenation were measured in a separate flow reactor connected to the mass spectrometer for continuous monitoring of the products. The feed conditions for CO oxidation in the light-off setup were the same as that used in the differential reactor. For toluene hydrogenation, the feed was a mixture of toluene and H₂ produced by flowing 20 mL·min⁻¹ of pure H₂ through a toluene bubbler held in an ice bath (toluene partial pressure ~7 Torr) [108].

Fourier transform infrared spectra (FTIR) patterns were collected on a Mattson Galaxy FTIR with a diffuse-reflectance attachment (Collector IITM) purchased from Spectra-Tech Inc. FTIR data was collected for samples under the CO oxidation conditions described above.

The procedures of Temperature-Programmed-Desorption/Thermogravimetric-Analysis (TPD-TGA) measurements is described in Section 2.2.3. For each measurement, 50-mg samples were utilized.

High Sensitivity Low Energy Ion Scattering Spectra (HS-LEIS) were collected using the ION-TOF Qtac spectrometer system at Lehigh University. Samples were analyzed at ambient temperature using a 3-keV, He⁺ ion beam.
5.3 Results

5.3.1 Oxide Film Characterization

The characterization of CaTiO$_3$ films on MgAl$_2$O$_4$ by STEM and X-Ray Diffraction (XRD) has been discussed in some detail in CHAPTER 4. Following deposition of 1-nm films (0.43 g CaTiO$_3$/g MgAl$_2$O$_4$) by ALD, STEM and EDS results demonstrated that both Ca and Ti were uniformly deposited on the surface. After calcination to 1073 K, XRD peaks associated with the perovskite phase were observed.

Since it is difficult to obtain atomic-scale, chemical information on supported catalysts from XRD and STEM, I performed TPD-TGA measurements of adsorbed 2-propanol in order to gain insight into the surface chemistry of the films. The temperature at which adsorbed 2-propanol reacts to produce propene and water on oxides can be used as a measure of the Lewis acidity of the solid [109]. Because 2-propanol probes all surface sites, the measurements also provide information on the uniformity of deposited films in some cases [72]. Here, TPD-TGA were performed on the starting MgAl$_2$O$_4$ material and the MgAl$_2$O$_4$ modified by ALD films of a 0.6-nm of CaO, 0.6-nm of TiO$_2$, or 1-nm of CaTiO$_3$. In all cases the samples with ALD films were calcined to 1073 K after deposition. BET surface areas of the materials are shown in Table 5-1.

<table>
<thead>
<tr>
<th>Sample</th>
<th>MgAl$_2$O$_4$</th>
<th>CaO-MgAl$_2$O$_4$</th>
<th>TiO$_2$-MgAl$_2$O$_4$</th>
<th>CaTiO$_3$-MgAl$_2$O$_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>BET surface area (m$^2$/g)</td>
<td>125</td>
<td>63</td>
<td>95</td>
<td>50</td>
</tr>
</tbody>
</table>

The TPD-TGA results for each of the samples are reported in Figure 5-1. Following exposure to 2-propanol vapor at room temperature and 1-h evacuation, the initial coverage on
MgAl$_2$O$_4$ was 680 $\mu$mol/g. Since this corresponds to $3.3 \times 10^{18}$ molecules/m$^2$, close to the value which would be expected for a monolayer, the entire surface is being probed by the adsorbate. Approximately 200 $\mu$mol/g of alcohol desorbs unreacted (m/e = 45) below 425 K but most of the alcohol reacts to produce propene (m/e = 41) in a very sharp feature at 460 K. Water is difficult to observe because it leaves the surface over a wide temperature range, but the desorption temperature for propene is a good indication of the reaction temperature since propene cannot remain on the surface. Results for 2-propanol TPD-TGA from the TiO$_2$/MgAl$_2$O$_4$ sample were essentially the same as that for the unmodified MgAl$_2$O$_4$. 
Figure 5-1 TPD-TGA of 2-propanol over various samples after calcination in air at 1073 K for three hours: (a) MgAl$_2$O$_4$; (b) CaO/MgAl$_2$O$_4$; (c) TiO$_2$/MgAl$_2$O$_4$; and (d) CaTiO$_3$/MgAl$_2$O$_4$. The desorption features correspond to propene (m/e =41), carbon dioxide (m/e=44) and unreacted 2-propanol (m/e = 45).
TPD-TGA data for 2-propanol from the CaO/MgAl₂O₄ and CaTiO₃/MgAl₂O₄ samples were significantly different. Although the initial adsorbate coverages were lower, ~350 μmol/g, the specific coverages in molecules/m² were nearly the same. A much larger fraction of the 2-propanol desorbed unreacted on these two samples, as demonstrated by the weight changes that occurred prior to propene desorption. The reaction that did occur happened at significantly higher temperatures, ~660 K on CaO/MgAl₂O₄ and 580 K CaTiO₃/MgAl₂O₄. With the CaO/MgAl₂O₄ sample, there was also some CO₂ desorption at the higher temperatures, suggesting that the CaO film had partially converted to a carbonate when exposed to air. Carbonate formation was not observed on the CaTiO₃/MgAl₂O₄ sample. There was no evidence for low-temperature reaction, indicative of exposed MgAl₂O₄, on either CaO/MgAl₂O₄ or CaTiO₃/MgAl₂O₄.

5.3.2 CO Oxidation on Pd/CaTiO₃/MgAl₂O₄ and Pt/CaTiO₃/MgAl₂O₄

It has been reported that Pt can be reversibly incorporated into the CaTiO₃ lattice, while Pd cannot [24]. Therefore, in order to determine whether the thin-film perovskite supports exhibited similar characteristics to bulk CaTiO₃, I set out to compare the properties of Pd/CaTiO₃/MgAl₂O₄ and Pt/CaTiO₃/MgAl₂O₄ catalysts for CO oxidation as a function of oxidation/reduction treatments. The catalysts were prepared from freshly deposited, 30 wt% CaTiO₃ on MgAl₂O₄ for which the ALD film had been calcined to only 773 K. This material had a BET surface area of 87 m²/g. Either Pt or Pd was then added via a single ALD cycle. The metal loadings were determined by ICP-OES to be either 2.9 wt% Pt or 1.2 wt% Pd, respectively. For comparison purposes, a 3.1 wt% Pt/MgAl₂O₄ catalyst was also prepared by a single ALD cycle on the MgAl₂O₄.

Differential CO oxidation rates for the Pt/CaTiO₃/MgAl₂O₄ and Pt/MgAl₂O₄ samples are shown in Figure 5-2 as a function of temperature for various pretreatment conditions, with rates
for Pt/MgAl$_2$O$_4$ shown in Figure 5-2(a) and Pt/CaTiO$_3$/MgAl$_2$O$_4$ shown in Figure 5-2(b). Rates on the most active catalysts were obtained at lower temperatures in order to maintain differential conditions. Pt/MgAl$_2$O$_4$ had the highest activity immediately after calcination to 573 K. When this sample was oxidized at 1073 K, the rates decreased significantly and reduction at 1073 K did not appreciably restore the rates. Five oxidation-reduction cycles at 1073 K caused a further decrease in activity. The loss in activity of the Pt/MgAl$_2$O$_4$ catalyst following these treatments was strictly due to loss of Pt dispersion. CO oxidation on Pt has been shown to be structure insensitive, with area-specific rates that are well known [110]. This implies that Pt dispersions can be calculated not only from CO chemisorption but also from the CO-oxidation rates. The two columns in Table 5-2 report the Pt dispersions determined from both of these measurements and agree remarkably well.

![Figure 5-2](image)

Figure 5-2 Steady-state, differential reaction rates for CO oxidation with 25 Torr of CO and 12.5 Torr O$_2$ for (a) Pt/MgAl$_2$O$_4$ and (b) Pt/CaTiO$_3$/MgAl$_2$O$_4$. The rates were compared for after following pretreatment conditions: (∆) Pristine state (573 K calcination in muffle furnace). (●) 2 h oxidation in 10% O$_2$-He at a flow rate of 100 mL·min$^{-1}$, followed by 1 h reduction at 773 K using 10% H$_2$-He; (♦) 1 h reduction at 1073 K using 10% H$_2$-He. Black symbols denote the first oxidation-reduction cycle, while red symbols show data after the fifth cycle.
Table 5-2 Dispersion values for various samples after different pretreatments

<table>
<thead>
<tr>
<th>Pretreatment</th>
<th>CO adsorption</th>
<th>Est.*</th>
<th>CO adsorption</th>
<th>Est.*</th>
<th>CO adsorption</th>
<th>Est.*</th>
<th>CO adsorption</th>
<th>Est.*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pristine State</td>
<td>27</td>
<td>23.5</td>
<td>21</td>
<td>16.3</td>
<td>16</td>
<td>23</td>
<td>17</td>
<td>11.5</td>
</tr>
<tr>
<td>1st oxidation</td>
<td>5</td>
<td>4.7</td>
<td>0</td>
<td>0.2</td>
<td>4</td>
<td>1.7</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1st reduction</td>
<td>5</td>
<td>3.9</td>
<td>0</td>
<td>4.5</td>
<td>2</td>
<td>1.5</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>5th reduction</td>
<td>0</td>
<td>0.4</td>
<td>0</td>
<td>4.2</td>
<td>0</td>
<td>0.1</td>
<td>2</td>
<td>1.5</td>
</tr>
</tbody>
</table>

*Dispersion values from CO-oxidation rates were calculated from specific rates reported in reference [101].

Results for Pt/CaTiO$_3$/MgAl$_2$O$_4$ were significantly different and showed cyclic behavior similar to what was observed previously with Pd/LaFeO$_3$/MgAl$_2$O$_4$ [58]. Prior to pretreatments, the rates on Pt/CaTiO$_3$/MgAl$_2$O$_4$ were similar but slightly lower than that on Pt/MgAl$_2$O$_4$. However, heating to 1073 K under oxidizing conditions caused the rates to drop precipitously. Activity was partially restored after reduction at 1073 K. Repeated oxidation-reduction cycles at 1073 K caused the catalyst to cycle between inactive and active states; but it is noteworthy that rates after five oxidation-reduction cycles were largely unchanged compared to that after the first cycle. Furthermore, the activity of the high-temperature reduced Pt/CaTiO$_3$/MgAl$_2$O$_4$ was significantly higher than that of Pt/MgAl$_2$O$_4$ after five cycles.

There were several other interesting observations with this sample. First, after the sample had been oxidized at 1073 K, reduction treatments at 773 K or 973 K were insufficient to bring the catalyst back to its active state. Reduction had to be performed at the higher temperature. This is shown in Figure 5-3. Second, after the first, high-temperature oxidation treatment, there was no
measurable CO adsorption on the Pt/CaTiO$_3$/MgAl$_2$O$_4$ sample, even after the sample had been reduced at high temperatures and was in its activated state. As reported in Table 5-2, the expected Pt dispersions based on the specific rates for CO oxidation were sufficiently high that one should have been able to measure them easily. FTIR measurements also indicated that CO coverages were low under CO-oxidation conditions, since no evidence for adsorbed CO could be found in the spectra, even though CO$_2$ was produced.

![Figure 5-3](image)

**Figure 5-3** Steady-state, differential reaction rates for CO oxidation with 25 Torr of CO and 12.5 Torr O$_2$ for Pt/CaTiO$_3$/MgAl$_2$O$_4$. The rates were compared after the following pretreatment conditions: (white) two-hour oxidation in 10% O$_2$ in He at a flow rate of 100 mL·min$^{-1}$ at 1073 K, followed by one-hour reduction at 773 K using 10% H$_2$ in He; (grey) two-hour oxidation in 10% O$_2$ in He at a flow rate of 100 mL·min$^{-1}$ at 1073 K, followed by one-hour reduction at 973 K using 10% H$_2$ in He; (black) two-hour oxidation in 10% O$_2$ in He at a flow rate of 100 mL·min$^{-1}$ at 1073 K, followed by one-hour reduction at 1073 K using 10% H$_2$ in He.

The lack of significant CO coverages on Pt/CaTiO$_3$/MgAl$_2$O$_4$ catalysts which are active for CO oxidation is noteworthy and there are at least three possible explanations for this result. First, the results are reminiscent of the well-known Strong Metal Support Interactions (SMSI) observed on titania-supported materials [111, 112]. Unlike that case, Pt/CaTiO$_3$/MgAl$_2$O$_4$ did not regain its chemisorption properties after oxidation. Also, as shown in **Figure 5-4**, the Pt/TiO$_2$/MgAl$_2$O$_4$ (24
wt% TiO₂) catalyst was somewhat less active than Pt/CaTiO₃/MgAl₂O₄ following high-temperature cycling and did not show the same hysteresis behavior shown in Figure 5-2(b). As shown in Table 5-2, the Pt dispersions determined from CO chemisorption and from CO-oxidation rates coincided reasonably well on Pt/TiO₂/MgAl₂O₄. Although Pt/TiO₂/MgAl₂O₄ and Pt/CaTiO₃/MgAl₂O₄ are clearly not equivalent, the possibility still exists that some oxide species migrates onto the Pt particles with Pt/CaTiO₃/MgAl₂O₄.

A second possibility for explaining CO adsorption suppression is that there is an electronic, bonding interaction between the Pt and the CaTiO₃. The fact that Pt can become part of the perovskite lattice suggests that such bonding is possible; however, these kinds of bonding interactions can only extend a few atomic distances [113]. If this were responsible for adsorption suppression, the support would need to be a few atomic distances from the affected Pt atoms at the surface, implying that the particles would have to be two dimensional. A third possibility is that the
active phase is Pt that is part of the perovskite lattice. A similar proposal was suggested for Pd-substituted BaCeO$_3$ [61]. For this to be true, the Pt would have to remain in the lattice after high-temperature reduction.

CO oxidation rates for Pd/CaTiO$_3$/MgAl$_2$O$_4$ are provided in Figure 5-5 and exhibit similar characteristics to the conventional, Pt/MgAl$_2$O$_4$ catalyst. As expected, rates decreased after high-temperature oxidation treatments and were not restored by high-temperature reduction. Repeated cycling at 1073 K caused further decreases in the rates. As shown in Table 5-2, dispersions calculated from specific rates, using data from Goodman et al. [110], agreed well with dispersions determined from CO chemisorption. With regards to Pd, the CaTiO$_3$/MgAl$_2$O$_4$ support appears to be essentially inert.

![Figure 5-5](image)

Figure 5-5 Steady-state, differential rates for CO oxidation with 25 Torr of CO and 12.5 Torr O$_2$ for Pd/CaTiO$_3$/MgAl$_2$O$_4$. The rates were measured after the following pretreatments: (Δ) Pristine state (773 K calcination) (●) after 2 h oxidation in 10% O$_2$-He at a flow rate of 100 mL·min$^{-1}$, followed by 1 h reduction at 773 K using 10% H$_2$-He; (♦) 1 h reduction at 1073 K using 10% H$_2$-He. Black symbols denote the first oxidation–reduction cycle, while red symbols represent the fifth cycle.
If exsolution were responsible for the properties observed on Pt/CaTiO$_3$/MgAl$_2$O$_4$, the thickness of the CaTiO$_3$ film might be expected to affect the properties. To test for this, a sample was prepared with a 0.5-nm CaTiO$_3$ film (17 wt%) on MgAl$_2$O$_4$, with Pt again added in a single ALD cycle. CO oxidation rates after five high-temperature oxidation or reduction cycles are shown for this sample in Figure 5-6. The results are qualitatively similar to what was observed for the thicker CaTiO$_3$ film. The fact that perovskite film thickness does not affect catalysts properties would suggest that the interaction between the metal and the support is associated with bonding at the surface.

**Figure 5-6** Steady-state, differential reaction rates for CO oxidation with 25 Torr of CO and 12.5 Torr O$_2$ for Pt/0.5 nm CaTiO$_3$/MgAl$_2$O$_4$ after redox cycling. The rates were compared for after following pretreatment conditions: (●) two-hour oxidation in 10% O$_2$ in He at a flow rate of 100 mL·min$^{-1}$, followed by one-hour reduction at 773 K using 10% H$_2$ in He; (♦) one-hour reduction at 1073 K using 10% H$_2$ in He. Black symbols denote the first oxidation-reduction cycle, while red symbols represent the fifth cycle.

5.3.3 **Toluene Hydrogenation on Pt/CaTiO$_3$/MgAl$_2$O$_4$, Pt/CaTiO$_3$, and Pt/MgAl$_2$O$_4**

The fact that both Ni exsolved from LSTN [37] and the Ni/CaTiO$_3$/MgAl$_2$O$_4$ catalyst in **CHAPTER 4** showed a high tolerance against coking implies that these materials likely had very different properties for hydrogenation and dehydrogenation reactions compared to conventional Ni
catalysts. To determine whether Pt/CaTiO$_3$/MgAl$_2$O$_4$ and bulk Pt/CaTiO$_3$ might have similar unique properties, I examined the toluene-hydrogenation reaction on these materials and compared the results to that of the conventional Pt/MgAl$_2$O$_4$. Because each of the catalysts had very different surface areas and likely different metal dispersions, I performed light-off measurements for CO oxidation and toluene hydrogenation on each of the samples. All three samples were oxidized and reduced five times at 1073 K, with the last treatment being the high-temperature reduction. With the bulk Pt/CaTiO$_3$, I adjusted the amount of catalyst in the reactor so that the light-off temperature for CO oxidation was similar to that observed with the high-surface-area catalysts.

Figure 5-7(a) shows CO-oxidation, light-off curves for each of the three catalysts. Rates on Pt/CaTiO$_3$/MgAl$_2$O$_4$ are shifted to lower temperatures by about 20 degrees compared to that of Pt/MgAl$_2$O$_4$. That agrees well with expectations based on the data in Figure 5-2(a), which showed Pt/CaTiO$_3$/MgAl$_2$O$_4$ has a significantly higher activity. Because temperature has such a large impact on rates, the difference between these two materials does not appear to be as dramatic when compared in light-off measurements. By using a large sample size for the Pt/CaTiO$_3$ sample, the CO-oxidation, light-off temperature was between that of the other samples. Figure 5-7(b) provides the toluene-hydrogenation, light-off curves for the same three samples. The Pt/MgAl$_2$O$_4$ sample was by far the most active of the three catalysts, reaching 80% conversion of toluene by 400 K. Rates on both CaTiO$_3$-containing catalysts were shifted to significantly higher temperatures, implying that rates on those materials were dramatically lower. Since CO-oxidation rates on the Pt/CaTiO$_3$/MgAl$_2$O$_4$ sample were a strong function of pretreatment, I also performed a toluene-hydrogenation light-off measurement on this sample after high-temperature oxidation, with results
shown in **Figure 5-8**. Rates for toluene hydrogenation were significantly higher on the oxidized sample, even though CO-oxidation rates were much lower.

![Figure 5-7](image)

**Figure 5-7** Light-off profiles for: (a) CO oxidation and (b) Toluene hydrogenation for (green) CaTi_{0.95}Pt_{0.05}O_3; (black) Pt/CaTiO_3/MgAl_2O_4; and (red) Pt/MgAl_2O_4. All three samples had been treated with five 1073-K redox cycles, with the final step being reduction. The catalyst loadings were 100 mg for Pt/CaTiO_3/MgAl_2O_4 and Pt/MgAl_2O_4 and 500 mg for CaTi_{0.95}Pt_{0.05}O_3.

![Figure 5-8](image)

**Figure 5-8** Light-off profiles for toluene hydrogenation over Pt/CaTiO_3/MgAl_2O_4 after five redox cycles with the final treatment being (gold) oxidation and (black) reduction.
The most interesting point to take away from toluene-hydrogenation rates is that there are interactions between Pt and CaTiO$_3$ that cannot be explained by a simple exsolution process in which the metal is either on the surface or not. These interactions exist for both the Pt/CaTiO$_3$/MgAl$_2$O$_4$ and the bulk Pt/CaTiO$_3$ samples.

### 5.3.4 Characterization by STEM and LEIS

To gain a better understanding of the catalysts used in this study, selected samples were examined by STEM. **Figure 5-9** shows representative low-resolution images of the 2.9 wt% Pt/CaTiO$_3$/MgAl$_2$O$_4$ and 3.1 wt% Pt/MgAl$_2$O$_4$ samples after five oxidation-reduction cycles at 1073 K, with reduction as the final step. The metal particle sizes were clearly smaller on the Pt/CaTiO$_3$/MgAl$_2$O$_4$ sample but more striking is the much higher particle density. This may suggest that the particles on Pt/CaTiO$_3$/MgAl$_2$O$_4$ are more two dimensional. Also, many of the metal particles on Pt/CaTiO$_3$/MgAl$_2$O$_4$ have a square, cubic shape, whereas most of the Pt particles on Pt-MgAl$_2$O$_4$ are irregular in shape.

![Figure 5-9 STEM, bright-field images for (a) Pt/CaTiO$_3$/MgAl$_2$O$_4$ and (b) Pt/MgAl$_2$O$_4$ after five 1073-K redox cycles.](image)

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Figure 5-10 shows a higher resolution, bright-field image of the same reduced Pt/CaTiO$_3$/MgAl$_2$O$_4$ sample, together with EDS maps for the selected atoms. The cubic shape of many, if not most, of the Pt particles is more apparent in this image and the EDS map shows that the particles are indeed Pt. SAED patterns were collected for this sample with the results shown in Figure 5-11. The bright spots in the SAED pattern identified the (111) crystal plane of the FCC Pt lattice. The Ca and Ti remain well dispersed over the surface but there is also clear evidence that both Ca and Ti are concentrated in the regions on or under the Pt particles.

Figure 5-10 Representative STEM results for Pt/CaTiO$_3$/MgAl$_2$O$_4$, after five 1073-K redox cycles, with the final step being reduction, with EDS maps of Mg, Al, Ca, Ti and Pt.
Figure 5-12 provides the corresponding image and elemental maps for this same sample but after oxidation at 1073 K. The Pt particles no longer exhibit their cubic shape. Furthermore, the Ca and Ti maps no longer show higher concentration near the Pt particles. The results appear to indicate that there is movement of both Pt and the CaTiO$_3$ on the molecular scale following the high-temperature oxidation and reduction treatments. The fact that the catalytic activity for CO oxidation is significantly higher on the reduced sample, which also shows higher concentrations of Ca and Ti near the Pt, would seem to argue against encapsulation of the Pt but we cannot rule out the possibility that a thin-film is forming on the metal particles.
The STEM data confirm that the CaTiO₃ thin film is inert to Pd; after five high-temperature redox cycles, the Pd particles agglomerated to much larger sizes. The sample is very similar to what would be observed on a conventional Pd catalyst.
Because LEIS is sensitive to the very top layer of atoms on a sample, measurements were performed on the redox-cycled Pt/CaTiO$_3$/MgAl$_2$O$_4$, after reduction and after oxidation treatments, with representative spectra shown in Figure 5-14. The existence of Mg and Al signals in both the oxidized and reduced samples may indicate some non-uniformity in the CaTiO$_3$ film; however, gaps in the film must be small, or else the 2-propanol TPD in Figure 5-1 would have exhibited peaks associated with MgAl$_2$O$_4$. Unfortunately, the Pt features in the spectra of both oxidized and reduced samples was too small to interpret. What is most interesting is that, relative to the Ca peak, the Ti peak increases significantly upon reduction. This would imply that the oxidized perovskite exists as the Ca-terminated surface, while reduction leads to a reconstruction that presents a mixed, Ca-Ti-O surface composition. Similar reconstructions have been observed in other perovskite systems [114]. However, whether this is important for understanding the role of CaTiO$_3$ in modifying the Pt properties cannot be determined.
To characterize the reducibility of the selected samples, flow-titration measurements were performed in the same reactor used for measuring light-off curves. These measurements provide an average oxidation state of the catalyst as a function of pretreatment conditions. The STEM results do not support the idea that Pt is being incorporated into the perovskite lattice upon oxidation, but there could be a change in oxidation state at the metal-perovskite interface; changes in the oxidation state of Ti could also contribute to the observations. In titration measurements, the samples were reduced in dry, flowing H\textsubscript{2} at 1073 K, after which the samples were reoxidized at 1073 K while measuring the amount of O\textsubscript{2} consumed by the sample.

Results are shown in Table 5-3 for the Pt/CaTiO\textsubscript{3}/MgAl\textsubscript{2}O\textsubscript{4}, Pt/MgAl\textsubscript{2}O\textsubscript{4}, MgAl\textsubscript{2}O\textsubscript{4}, and CaTiO\textsubscript{3}/MgAl\textsubscript{2}O\textsubscript{4} samples after they had been oxidized and reduced at 1073 K five times. First, the addition of 3 \(\mu\text{mol} \ O/g\) onto the reduced Pt/MgAl\textsubscript{2}O\textsubscript{4} sample was observed. Since this sample had 3.1 wt\% Pt (150 \(\mu\text{mol Pt/g}\) and a dispersion of \(\sim 1\%\), this uptake is consistent with surface oxidation of the Pt, with no bulk oxidation. No oxidation or reduction was expected for MgAl\textsubscript{2}O\textsubscript{4}, and the
failure to observe redox in the CaTiO$_3$/MgAl$_2$O$_4$ sample may indicate the inability of the CaTiO$_3$ to dissociate H$_2$. The Pt/CaTiO$_3$/MgAl$_2$O$_4$ sample was the only sample that showed significant oxygen removal upon high-temperature reduction, ~76 μmol O/g; however, even this amount was small relative to the Pt and Ti content. Since 2.8 wt% Pt is 140 μmol Pt/g, the amount of oxygen that is removed from the sample is a small fraction of that which would be expected if Pt$^{4+}$ were being incorporated into the CaTiO$_3$ lattice. Since 30 wt% CaTiO$_3$ corresponds to 2,100 μmol Ti/g, 76 μmol O/g would represent also represent only about 7% reduction of the Ti$^{4+}$ to Ti$^{3+}$. Clearly, the flow-titration results are not consistent with egress or ingress of large amounts of Pt or significant reduction of titania.

**Table 5-3** Results from oxygen titration for various samples

<table>
<thead>
<tr>
<th></th>
<th>Atomic oxygen adsorbed (μmol/g) during air pulse</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgAl$_2$O$_4$</td>
<td>0</td>
</tr>
<tr>
<td>CaTiO$_3$/MgAl$_2$O$_4$</td>
<td>0</td>
</tr>
<tr>
<td>Pt/MgAl$_2$O$_4$</td>
<td>3</td>
</tr>
<tr>
<td>Pt/CaTiO$_3$/MgAl$_2$O$_4$</td>
<td>76</td>
</tr>
</tbody>
</table>
5.4 Discussion

As discussed before, most of the work related to exsolution has focused on the fact that metals can reversibly enter and leave a perovskite lattice under some conditions. While it is clear from past works that exsolution does indeed occur in some cases, this chapter suggests that the effects of the perovskite support can extend beyond simply redispersing the metals. In addition to stabilizing metal-particle sizes, catalytic properties of the metal particles are also affected.

Although there was no evidence for Pt actually entering the CaTiO$_3$ lattice in the thin-film catalysts studied in this chapter, the catalysts did exhibit a number of similarities to the bulk materials where exsolution is known to occur. The fact that Pt, when supported on the CaTiO$_3$ films, was observed to show hysteretic catalytic behavior upon high-temperature oxidation and reduction, while Pd did not, has its counterpart in early reports that Pt can enter the CaTiO$_3$ lattice and Pd cannot [24]. Similarly, the unexpectedly low activity for toluene hydrogenation on Pt/CaTiO$_3$/MgAl$_2$O$_4$ must be related to the similarly low activity observed with Pt exsolved from CaTi$_{0.95}$Pt$_{0.05}$O$_3$.

Because the surface areas of the bulk perovskites tend to be low and because some of the exsolved metal remains in the bulk [48], direct comparisons of catalysts formed by exsolution and conventional supported metals is difficult. However, there are at least two examples from the literature that suggest perovskite-supported metal formed by exsolution can have unique catalytic properties. In earlier work on CO oxidation over Pd-substituted BaCeO$_3$, the authors reported a rate expression and activation energy that was very different from that observed with conventional, Pd-supported catalysts [61]. They suggested that the active species was Pd$^{2+}$ in the perovskite lattice. In a second example, the coke-tolerance observed with Ni ex-sol-ving from LSTN is not typical of
that observed with conventional Ni catalysts [37]. It is noteworthy that Ni supported on CaTiO$_3$/MgAl$_2$O$_4$ also showed extreme coke tolerance, as reported in **CHAPTER 4**.

The factors responsible for the unique properties associated with CaTiO$_3$-supported Pt are not entirely clear. In previous work with Ni on LSTN, the coking resistance was suggested to result from the fact that the particles remained partially embedded in the oxide substrate [41]. Coking in Ni catalysts at high temperatures is associated with the Ni being physically ejected from the support surface on a growing carbon fiber. However, partial embedding of the metal particle cannot explain the suppressed adsorption of CO or the change in the relative rates for CO oxidation and toluene hydrogenation that were observed here. As it was discussed earlier, the adsorption suppression, which was observed on both oxidized and reduced samples, could be caused either by oxide overlayers or by electronic interactions if the metal particles are thin. There was clear evidence from the EDS results that CaTiO$_3$ is mobile, migrating towards the metal during reduction and away from the metal upon oxidation. Previous microscopy results did not report the presence of oxide overlayers, but these could be very difficult to observe if they remain in monolayer form.

It is worth noting that the perovskite films in our study exhibited remarkable stability. Oxidation and reduction at these high temperatures might be expected to cause the CaTiO$_3$ films to form particles. The fact that the films remain uniform after these harsh treatments suggests that the CaTiO$_3$ has attractive interactions with the MgAl$_2$O$_4$. How CaTiO$_3$ would interact with other supports is uncertain.

Whatever the mechanism behind the properties of the Pt/CaTiO$_3$/MgAl$_2$O$_4$ catalysts, their unusual properties could represent an opportunity for some processes. Certainly, the Pt/CaTiO$_3$/MgAl$_2$O$_4$ was much better able to maintain its dispersion compared to Pt/MgAl$_2$O$_4$. 

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Furthermore, by turning off one class of reactions (hydrogenation/dehydrogenation) while maintaining activity for another (oxidation), it may be possible to achieve unique selectivities for some systems. For example, assuming that hydrogenation of toluene is related to the dehydrogenation reactions that lead to coking, it may be possible to use the perovskite-supported material under conditions for which conventional Pt catalysts would be unstable. Additional work is needed to determine the possibilities.

Results in CHAPTER 4 and CHAPTER 5 clearly suggested that the perovskite thin-film support is interacting strongly with the metal deposited on the surface. However, what contributes to the strong interactions remains unclear. Work in the next chapters will focus on other contributing factors to metal-perovskite interactions, specifically the effect of A-site cations in the ATiO₃ structure.
5.5 Conclusions

In this work, I demonstrated that metal catalysts supported on thin CaTiO$_3$ films deposited onto MgAl$_2$O$_4$ by ALD can show similar properties to metals exsolved from bulk CaTiO$_3$. The interactions between the metal catalyst and the perovskite are composition-specific and follow a similar behavior to that observed with the “intelligent” catalysts. In the Pt/CaTiO$_3$/MgAl$_2$O$_4$ system, the Pt particles exhibited improved sintering resistance compared to Pt/MgAl$_2$O$_4$ but showed catalytic performance that depended on pretreatment conditions. Although Pt/CaTiO$_3$/MgAl$_2$O$_4$ was highly active for CO oxidation following high-temperature reduction, the catalyst was inactive for toluene hydrogenation and exhibited suppressed CO adsorption. Possible explanations for the unique catalytic properties of Pt/CaTiO$_3$/MgAl$_2$O$_4$ are the formation of thin oxide overlayers on the Pt and strong electronic interactions between the support and the metal.
CHAPTER 6. INVESTIGATION OF Rh-TITANATE (ATiO₃) INTERACTIONS ON HIGH-SURFACE-AREA PEROVSKITE THIN FILMS PREPARED BY ATOMIC LAYER DEPOSITION

Summary

Thin, ~1-nm films of CaTiO₃, SrTiO₃, and BaTiO₃ deposited onto MgAl₂O₄ by Atomic Layer Deposition (ALD) were studied as catalyst supports for Rh. It was demonstrated that the films had the perovskite structure and formed uniform coatings stable to 1073 K. Evidence from CO-TPR, FTIR, and XPS all indicate that the degree of interaction between Rh and the three perovskite films can be ranked in the following order: Rh/CaTiO₃/MgAl₂O₄ > Rh/SrTiO₃/MgAl₂O₄ > Rh/BaTiO₃/MgAl₂O₄. Bulk exsolution catalysts, synthesized by reduction of ATio.98Rh0.02O₃ (A=Ca, Sr, and Ba), were also examined for comparison.

6.1 Introduction

As mentioned in CHAPTER 4 and CHAPTER 5, uniform films of CaTiO$_3$ have been grown on MgAl$_2$O$_4$ supports with film thicknesses of around 1 nm. The films appear to be very stable to both oxidizing and reducing conditions at temperatures as high as 1073 K. The Ni/CaTiO$_3$/MgAl$_2$O$_4$ and Pt/CaTiO$_3$/MgAl$_2$O$_4$ on thin-film perovskite supports exhibited low activity following high-temperature oxidation and high activity after high-temperature reduction, similar to what would be expected if the metals were going in and out of the perovskite lattice.

Strong support effects with perovskite-supported metals can influence the properties of the metal in other ways. For example, a study of Ni on LaFeO$_3$ films indicated that interfacial contact between the two phases altered the thermodynamics of Ni oxidation by significantly stabilizing NiO [55]. For the Pt/CaTiO$_3$ system mentioned in CHAPTER 5, Pt particles supported on both thin-film and bulk CaTiO$_3$ showed very low activity for toluene hydrogenation, despite being highly active for CO oxidation. The interactions in these two cases also appear to be related to the perovskite structure, since Ni and Pt supported on the individual oxides that make up the perovskites do not exhibit unusual properties. Other evidence for a relationship between exsolution phenomena and strong support interactions came from a comparison of Pt and Pd on CaTiO$_3$ thin films. While catalysts formed by Pt on thin-film CaTiO$_3$ showed evidence of strong support effects, Pd/CaTiO$_3$ was not distinct from Pd catalysts on non-interacting supports. However, because the perovskite film thicknesses were much less than the typical metal particle size observed in exsolution, there must also be differences between the thin-film catalysts and those formed by bulk exsolution.
In this chapter, the successful preparation of 1-nm films of SrTiO$_3$, and BaTiO$_3$ on MgAl$_2$O$_4$ is first demonstrated. CaTiO$_3$/MgAl$_2$O$_4$ was investigated together with these two thin-film samples. Support effects on Rh due to contact with these three perovskite films were investigated. Although these three perovskites are similar, changing the A-site cation leads to very significant changes in the reducibility, activity, and sintering properties of the Rh, with the degree of interaction decreasing dramatically in going from Rh/CaTiO$_3$/MgAl$_2$O$_4$ to Rh/SrTiO$_3$/MgAl$_2$O$_4$ and Rh/BaTiO$_3$/MgAl$_2$O$_4$. Finally, the properties of the thin-film supports were compared with their bulk counterparts and it was shown that there are significant differences.
6.2 Experimental Methods

ALD was used to grow 1-nm films of CaTiO$_3$, SrTiO$_3$, and BaTiO$_3$ on the MgAl$_2$O$_4$. As described in Section 2.1.2, the precursors for the A-site cations, Ca, Sr, and Ba, were bis(2,2,6,6-tetramethyl-3,5-heptanedionato) calcium (Ca(TMHD)$_2$, Strem, USA), bis(2,2,6,6-tetramethyl-3,5-heptanedionato) strontium hydrate (Sr(TMHD)$_2$, Strem, USA) and bis(2,2,6,6-tetramethyl-3,5-heptanedionato) barium hydrate (Ba(TMHD)$_2$, Strem, USA). Titanium chloride (TiCl$_4$, Sigma-Aldrich, USA) was used to deposit Ti.

For comparison purposes, bulk Rh-doped perovskites, ATi$_{0.98}$Rh$_{0.02}$O$_3$ (A=Ca, Sr, and Ba) were synthesized using sol-gel procedures described in Section 2.1.4.

X-ray diffraction (XRD) patterns were recorded on a Rigaku MiniFlex diffractometer equipped with a Cu Kα source ($\lambda = 0.15416$ nm). Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) were performed on a Spectro Genesis spectrometer with a concentric nebulizer. Ex situ, Scanning Transmission Electron Microscopy (STEM) measurements were performed on powder specimens. Imaging and elemental mapping via energy dispersive X-ray Spectroscopy (EDS) were performed with a JEOL NEOARM operated at 200 kV. Surface areas for samples prepared by ALD were measured using BET isotherm, while surface areas for the bulk perovskites were calculated from their crystallite sizes, determined from XRD. Metal dispersions were estimated using CO chemisorption at room temperature, assuming a stoichiometry of one CO per Rh, even though the CO:Rh stoichiometry is known to depend on Rh particle size [115, 116]. Temperature-Programmed Desorption/Thermogravimetric Analysis (TPD-TGA) was also performed on these samples. X-Ray Photoelectron Spectra (XPS) were acquired on a Physical Electronics Versa Probe 5000 (ULVAC-PHI, Inc., Japan) Spectrometer using Al-Kα
monochromatic X-rays. Diffuse Reflectance Fourier Transform Infrared Spectra (DRIFTS) for CO stretching were collected on a Mattson Galaxy FTIR with a diffuse-reflectance attachment (DiffusIR™, Pike Technologies). Description of the sample characterizations can be found in Section 2.2.

CO-oxidation rates were determined under differential conversions. Here the same conditions described in Section 5.2 were utilized. Reducibility of the samples was determined by flow titration using the Mass Spectrometer system described in Section 2.3. 500-mg samples were first reduced in pure H₂ at 1073 K using a flow rate of 20 mL·min⁻¹. After purging the sample with He, the sample was exposed to dry air at 1073 K and a flow rate of 5 mL·min⁻¹. The O₂ uptake was then determined by integrating the difference between the N₂ and O₂ signals in the mass spectrometer.

Temperature-Programmed Reduction (TPR) measurements were performed in the same system. Prior to these experiments, the 500-mg samples were oxidized in dry air for 1 h at 1073 K. The TPR measurements were then performed using 10% CO:He mixtures, with a total flow rate of 20 mL·min⁻¹ and a heating rate of 10 K·min⁻¹ from 298 to 1073 K.
6.3 Results

6.3.1 Preparation of Thin-Film Perovskites

Growth rates for the various precursors were determined gravimetrically and confirmed by Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES). For CaO and TiO$_2$, the sample weights were previously shown in Section 4.3 to increase linearly with the number of ALD cycles, with growth rates of $6.9 \times 10^{13}$ Ca/cm$^2$-cycle (0.015 nm CaO/cycle) and $9.9 \times 10^{13}$ Ti/cm$^2$-cycle (0.025 nm TiO$_2$/cycle). The growth rates did not change when deposition alternated between Ca and Ti, and samples with the correct Ca:Ti ratio could be prepared by depositing six cycles of Ca for every four cycles of Ti. The sample weights also increased linearly with the number of ALD cycles for Sr and Ba, as shown in Figure 6-1; however, in order to reconcile the weight changes with the compositions obtained from ICP-OES, it was necessary to assume that SrCO$_3$ and BaCO$_3$ were formed initially. On that basis, the growth rates for Sr and Ba were $3.6 \times 10^{13}$ Sr/cm$^2$-cycle and $3.7 \times 10^{13}$ Ba/cm$^2$-cycle. The Ti growth rates were not affected by the probable presence of carbonates; and formation of BaTiO$_3$ and SrTiO$_3$ films was achieved by depositing six cycles of either Sr or Ba, followed by two cycles of TiO$_2$. Growth rates for SrTiO$_3$ and BaTiO$_3$ films are shown in Figure 6-2.
Figure 6-1 Growth curves for ALD films on a 120m$^2$/g MgAl$_2$O$_4$ support for (Δ) Sr-ALD process and (□) Ba-ALD process.

Figure 6-2 Growth curves for ALD films on a 120m$^2$/g MgAl$_2$O$_4$ support for (●) SrTiO$_3$/MgAl$_2$O$_4$ and (■) BaTiO$_3$/MgAl$_2$O$_4$ process.
After depositing the prerequisite amounts of perovskite precursors, the samples were heated to 1073 K in a muffle furnace in order to form the perovskite phases. In the cases of SrTiO$_3$ and BaTiO$_3$, a loss of sample weight was observed following calcination, consistent with decomposition of carbonates. The targeted thickness for each mixed-oxide film in this study was 1-nm. Assuming the densities of the films were the same as that of the corresponding bulk perovskites and that the 120-m$^2$/g MgAl$_2$O$_4$ was uniformly covered, this required loadings ranging from 32-wt% for CaTiO$_3$ to 42-wt% for BaTiO$_3$. A list of these samples and their bulk counterparts is given in Table 1 along with some of their key properties. It is noteworthy that the A:Ti ratio for each of the films was within 8% of the correct value for the corresponding perovskites.

**Table 6-1** Key properties for bulk perovskite materials and ALD samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>A:Ti ratio from ICP-OES analysis</th>
<th>Specific surface area (m$^2$/g) after 1073 K calcination</th>
<th>ALD thin film loading</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaTi$<em>{0.98}$Rh$</em>{0.02}$O$_3$</td>
<td>-</td>
<td>11$^a$</td>
<td>-</td>
</tr>
<tr>
<td>SrTi$<em>{0.98}$Rh$</em>{0.02}$O$_3$</td>
<td>-</td>
<td>8$^a$</td>
<td>-</td>
</tr>
<tr>
<td>BaTi$<em>{0.98}$Rh$</em>{0.02}$O$_3$</td>
<td>-</td>
<td>8$^a$</td>
<td>-</td>
</tr>
<tr>
<td>CaTiO$_3$/MgAl$_2$O$_4$</td>
<td>0.93</td>
<td>84</td>
<td>30 wt%$^b$</td>
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<tr>
<td>SrTiO$_3$/MgAl$_2$O$_4$</td>
<td>1.08</td>
<td>71</td>
<td>34 wt%$^b$</td>
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<tr>
<td>BaTiO$_3$/MgAl$_2$O$_4$</td>
<td>1.01</td>
<td>64</td>
<td>41 wt%$^b$</td>
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<tr>
<td>Ca-ALD/MgAl$_2$O$_4$</td>
<td>-</td>
<td>63</td>
<td>23 wt%$^c$</td>
</tr>
<tr>
<td>Sr-ALD/MgAl$_2$O$_4$</td>
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<td>77</td>
<td>16 wt%$^b$</td>
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<td>73</td>
<td>21 wt%$^b$</td>
</tr>
<tr>
<td>Ti-ALD/MgAl$_2$O$_4$</td>
<td>-</td>
<td>95</td>
<td>38 wt%$^c$</td>
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</tbody>
</table>

$^a$: sample surface areas were estimated from crystal size given by Scherrer equation  
$^b$: sample loadings estimated from ICP-OES  
$^c$: sample loadings estimated from weight gains after ALD cycles
6.3.2 Characterization of Perovskite ALD Films

To determine the morphology of the ALD films, the CaTiO$_3$/MgAl$_2$O$_4$, SrTiO$_3$/MgAl$_2$O$_4$, and BaTiO$_3$/MgAl$_2$O$_4$ samples listed in Table 6-1 were analyzed by STEM/EDS, TPD-TGA measurements of 2-propanol, and XRD. To ensure that the films were well crystallized, each of the samples was calcined at 1073 K prior to any measurements. The STEM/EDS results for CaTiO$_3$/MgAl$_2$O$_4$ were reported in Section 4.3, while the analogous results for SrTiO$_3$/MgAl$_2$O$_4$ and BaTiO$_3$/MgAl$_2$O$_4$ can be found in Figure 6-3. The micrographs were similar in all three cases. The MgAl$_2$O$_4$ showed features in the 10-20 nm size range but there were no discernable changes upon addition of the films, even though the weight loadings of the films ranged from 30- to 41-wt%. The EDS mappings were similarly featureless and showed that both Ti and the alkali metals covered the surfaces uniformly. This implies that the component oxides for each perovskite were well mixed on the surface following deposition and that there was no agglomeration of the films into particles, even after heat treatments at 1073 K.

![Figure 6-3](image)

**Figure 6-3** Representative STEM results for (a) SrTiO$_3$/MgAl$_2$O$_4$ (b) BaTiO$_3$/MgAl$_2$O$_4$ after 1073K oxidation with EDS maps of corresponding elements.
Additional evidence for film uniformity was obtained from the TPD-TGA profiles of 2-propanol shown in Figure 6-4. Measurements on each of the samples were performed after exposure to 2-propanol vapor at room temperature, followed by 1-h evacuation. On MgAl₂O₄, 680 μmol/g of 2-propanol remained on the surface following evacuation, corresponding to 3.3×10¹⁸ molecules/m² for the 120-m²/g sample. This is close to what would be expected for a monolayer, implying that the entire surface was probed by the adsorbate. It is important to notice that all of the adsorbed alcohol desorbs below 500 K, with a significant fraction desorbing as propene (m/e = 41) in a very sharp feature at 460 K. The additional weight change at higher temperatures was due to water desorption, which occurred over a broad temperature range. The reaction of 2-propanol on MgAl₂O₄ is due to the Lewis acidity of the surface [109, 117].

The analogous TPD-TGA results for CaTiO₃/MgAl₂O₄, SrTiO₃/MgAl₂O₄, and BaTiO₃/MgAl₂O₄ were significantly different. The initial coverages after exposure and 1-h evacuation were slightly lower on these three samples, ranging from 2.0 to 2.8×10¹⁸ molecules/m², but still close to that expected for a monolayer. However, the fractions of 2-propanol which desorbed unreacted were significantly higher and the reaction temperatures increased with the mass of the alkali cation. The peak reaction temperature on CaTiO₃/MgAl₂O₄ was 600 K; on BaTiO₃/MgAl₂O₄, there was essentially no reaction. If any of the MgAl₂O₄ had remained uncovered, a reaction peak below 500 K should have been observed, implying that the mixed oxide films must completely cover the support surface. The higher peak temperatures and lower reactivity of the CaTiO₃/MgAl₂O₄, SrTiO₃/MgAl₂O₄, and BaTiO₃/MgAl₂O₄ samples is consistent with a decrease in Lewis-acid strength of these surfaces. It is also potentially significant that TiO₂ was also added last in our ALD synthesis of CaTiO₃/MgAl₂O₄, SrTiO₃/MgAl₂O₄, and BaTiO₃/MgAl₂O₄. TiO₂ has Lewis acidity and it was shown that TPD-TGA results for 2-propanol
from ALD-prepared TiO$_2$/MgAl$_2$O$_4$ were very similar to that of MgAl$_2$O$_4$. If the mixed-oxide films were simply a simple sum of TiO$_2$ and the alkali oxide, with TiO$_2$ at the outer surface, reaction of the 2-propanol at lower temperatures should have been observed.

As discussed earlier, the targeted film thickness was 1-nm for each of these samples and the weight loadings correspond to that value. Since this is only a two-unit-cell thickness of the corresponding perovskites, film uniformity implies that most of the deposited material must be present in the films. If a significant number of larger particles were present, there would not be sufficient material to still cover the surface of the MgAl$_2$O$_4$ support.
Figure 6-4 TPD-TGA profiles for 2-propanol. Samples had been calcined at 1073 K for 3 h: (a) MgAl$_2$O$_4$, (b) CaTiO$_3$/MgAl$_2$O$_4$, (c) SrTiO$_3$/MgAl$_2$O$_4$ and (d) BaTiO$_3$/MgAl$_2$O$_4$. Desorption features correspond to propene (m/e=41) and unreacted 2-propanol (m/e=45 and 41).
XRD patterns for the CaTiO$_3$/MgAl$_2$O$_4$, SrTiO$_3$/MgAl$_2$O$_4$, and BaTiO$_3$/MgAl$_2$O$_4$ samples are shown in Figure 6-5, with the pattern for MgAl$_2$O$_4$ shown at the bottom for comparison. In each case, all peaks can be assigned to either the MgAl$_2$O$_4$ support or the corresponding perovskite phase. For BaTiO$_3$/MgAl$_2$O$_4$, there is significant overlap in the peak positions for BaTiO$_3$ and MgAl$_2$O$_4$; however, the relative ratio of peaks, particularly those centered at 32 and 37 degrees 2θ, make it clear that the XRD pattern for BaTiO$_3$/MgAl$_2$O$_4$ is due to a mixture of MgAl$_2$O$_4$ and the perovskite structure. In order to determine whether the relative intensities of XRD peaks are consistent with the loading of the perovskite films, Rietveld Analysis was performed on the CaTiO$_3$/MgAl$_2$O$_4$ sample after it had been redox cycled five times at 1073 K in order to ensure complete crystallization of the perovskite phase. The results of this analysis are shown in Figure 6-6 and Table 6-2. No additional peaks were observed following the redox treatments but the peaks associated with the perovskite phase were somewhat narrower. Rietveld analysis indicated the loading of the CaTiO$_3$ phase to be 24-wt%, only slightly lower than the ICP value of 30-wt%. 
Estimations of the average crystallite size of the thin CaTiO$_3$ and SrTiO$_3$ films using the Scherrer Equation gave values of ~ 20 nm. However, the presence of a significant concentration of three-dimensional crystallites this large is inconsistent with the uniform coverage of the MgAl$_2$O$_4$ support seen by STEM and 2-propanol TPD. As discussed in more detail elsewhere [118], the perovskite phase is likely present as randomly oriented platelets. The crystallite size associated with the diffraction linewidths is then the in-plane dimension of the two-dimensional crystallites.

Figure 6-5 XRD patterns for (a) MgAl$_2$O$_4$, (b) CaTiO$_3$/MgAl$_2$O$_4$, (c) SrTiO$_3$/MgAl$_2$O$_4$ and (d) BaTiO$_3$/MgAl$_2$O$_4$ after 1073 K oxidation.
Table 6-2 Results from Rietveld analysis of the XRD patterns of the CaTiO$_3$/MgAl$_2$O$_4$ after high temperature redox cycles, in comparison with the cell parameters reported for the parent pure phases

<table>
<thead>
<tr>
<th>Phase (Space Group)</th>
<th>Amount (wt%)</th>
<th>CaTiO$_3$/MgAl$_2$O$_4$</th>
<th>Parent pure phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgAl$_2$O$_4$ (Fd$ar{3}$m)</td>
<td>76.5%</td>
<td>$a = 0.8008$</td>
<td>$a = 0.8081$</td>
</tr>
<tr>
<td>CaTiO$_3$ (Pnma)</td>
<td>23.5%</td>
<td>$a = 0.5435$</td>
<td>$a = 0.5442$</td>
</tr>
</tbody>
</table>

Figure 6-6 Rietveld refinement for the CaTiO$_3$/MgAl$_2$O$_4$ samples.
6.3.3 Characterization of Rh Particles on Perovskite ALD Films

Rh was added to each of the supports by ALD using Rhodium(III) acetylacetonate (Rh(acac)_3, Strem, USA). The procedure was similar to that used to deposit the alkali cations, except that the deposition temperature was 523 K. Removal of the ligands was again achieved by calcining the samples in a muffle furnace at 773 K. Because the growth rate for Rh was $\sim 1.3 \times 10^{14}$ Rh/cm$^2$-cycle on each of the samples, a single ALD cycle was sufficient to achieve a metal loading of close to 2-wt%. The properties of these samples are listed in Table 6-3.

**Table 6-3** Key features of the added Rh for various samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Rh loading confirmed by ICP-OES (wt%)</th>
<th>Dispersion values by CO chemisorption after redox cycles with the final treatment being:</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rh/MgAl$_2$O$_4$</td>
<td>2.0</td>
<td>573 K reduction: 10% 1073 K reduction: 25%</td>
</tr>
<tr>
<td>Rh/CaTiO$_3$/MgAl$_2$O$_4$</td>
<td>2.1</td>
<td>573 K reduction: 0% 1073 K reduction: 0%</td>
</tr>
<tr>
<td>Rh/SrTiO$_3$/MgAl$_2$O$_4$</td>
<td>2.1</td>
<td>573 K reduction: 17% 1073 K reduction: 20%</td>
</tr>
<tr>
<td>Rh/BaTiO$_3$/MgAl$_2$O$_4$</td>
<td>1.8</td>
<td>573 K reduction: 14% 1073 K reduction: 23%</td>
</tr>
<tr>
<td>Rh/CaO/MgAl$_2$O$_4$</td>
<td>-</td>
<td>573 K reduction: 27% 1073 K reduction: 32%</td>
</tr>
<tr>
<td>Rh/TiO$_2$/MgAl$_2$O$_4$</td>
<td>-</td>
<td>573 K reduction: 3% 1073 K reduction: 21%*</td>
</tr>
</tbody>
</table>

*To avoid effects of SMSI, the dispersion here was measured after the same was reduced at high temperatures, oxidized at 673 K, then reduced at 673 K.

As an initial indication of how Rh interacts with the three perovskite films, STEM measurements were performed on the first four Rh-containing samples reported in Table 6-3. In each case, the Rh was added by 1 ALD cycle and the samples were then oxidized and reduced five times at 1073 K, with the 1073-K reduction being the last step. A STEM image of the Rh/MgAl$_2$O$_4$ sample, shown in Figure 6-7, indicates Rh particles ranging in size from 1 to 10 nm. This range of
particle sizes agrees reasonably well with the Rh dispersion determined from CO chemisorption, reported in Table 6-3.

![STEM result](image)

**Figure 6-7** STEM result for Rh/MgAl$_2$O$_4$, after five 1073-K redox cycles, with the final step being reduction.

The STEM images and EDS maps for Rh on the CaTiO$_3$/MgAl$_2$O$_4$, SrTiO$_3$/MgAl$_2$O$_4$, and BaTiO$_3$/MgAl$_2$O$_4$ supports, reported in Figure 6-8, Figure 6-9 and Figure 6-10, were significantly different. Even after this relatively harsh redox cycling, I was unable to detect Rh particles in the STEM images of the Rh/CaTiO$_3$/MgAl$_2$O$_4$ sample, **Figure 6-8**. EDS mapping showed that the Rh was uniformly distributed over the sample and gave a bulk concentration that was in good agreement with elemental analysis, suggesting that the Rh must exist as particles less than about 1 nm in size. It is noteworthy that this does not agree with the very low dispersion measurements reported in Table 6-3 for this catalyst. CO did not appreciably adsorb on this sample.
Small Rh particles were found on the Rh/SrTiO$_3$/MgAl$_2$O$_4$ sample, Figure 6-9. The particles were very uniform in size and about 1-2 nm in diameter. This is slightly smaller than the particle size calculated from CO chemisorption measurements, which gave values on the order of 5 nm, suggesting that adsorption may be somewhat suppressed in the same way as it was observed on the Rh/CaTiO$_3$/MgAl$_2$O$_4$ sample. Finally, the STEM image of the Rh/BaTiO$_3$/MgAl$_2$O$_4$, Figure 6-10, was similar to that measured on the Rh/MgAl$_2$O$_4$. The sample contained a large distribution of particle sizes, ranging from 2- to 10-nm in diameter, in good agreement with the particle-size estimated from CO chemisorption.
Figure 6-9 Representative STEM/EDS results for Rh/SrTiO$_3$/MgAl$_2$O$_4$ after five 1073-K redox cycles with the final treatment being reduction.

Figure 6-10 Representative STEM/EDS results for Rh/BaTiO$_3$/MgAl$_2$O$_4$ after five 1073-K redox cycles with the final treatment being reduction.
An indication of the differences in the Rh particles on the various supports can also be seen from the DRIFTS measurements in Figure 6-11. Rh single-atom catalysts exhibit the symmetric and asymmetric stretches of a dicarbonyl species, while larger Rh particles show peaks associated with terminal- and bridge-bonded CO [116]. Consistent with the STEM results, DRIFTS data for the Rh/MgAl₂O₄ and Rh/BaTiO₃/MgAl₂O₄, Figure 6-11(a) and Figure 6-11(d), show the expected terminal-bonded (~2083 cm⁻¹) and bridge-bonded (~1855 cm⁻¹) species. Consistent with the small amount of CO adsorption on Rh/CaTiO₃/MgAl₂O₄, Figure 6-11(b), only very weak vibrational bands were observed on this sample. In agreement with the small particle size observed with Rh/SrTiO₃/MgAl₂O₄, the DRIFTS results, Figure 6-11(c), exhibit intense peaks at 2017 cm⁻¹ and 2090 cm⁻¹, indicative of adsorption as a dicarbonyl. The one surprising aspect of this result is the Rh dispersion on this sample, obtained from CO adsorption and reported in Table 6-3, was only 20%, assuming a stoichiometry of one CO per Rh. With formation of a dicarbonyl, the CO:Rh ratio should be two. If all of the Rh were indeed exposed, one should have expected CO uptakes ten times that which was observed.
Finally, to eliminate the possibility that the low CO adsorption coverages on Rh/CaTiO$_3$/MgAl$_2$O$_4$ are due to Rh interactions with either CaO or TiO$_2$, DRIFTS measurements were performed on the Rh that had been deposited on films of either CaO or TiO$_2$ on MgAl$_2$O$_4$. The pretreatment conditions on these samples were the same as that used on the perovskite films and the final treatment was again a reduction step at 1073 K. The results are shown in Figure 6-12.

For Rh/CaO/MgAl$_2$O$_4$ in Figure 6-12(a), the spectra show dicarbonyl stretches indicative of small Rh particles, together with a large carbonate band centered at 1875 cm$^{-1}$. The DRIFT spectrum for
Rh/TiO$_2$/MgAl$_2$O$_4$ is representative of CO stretching on larger Rh particles, with a peak at 2075 cm$^{-1}$ being the strongest signal. The fact that one can detect CO stretching for Rh deposited on the individual CaO and TiO$_2$ samples provides additional evidence that suppression of CO adsorption on CaTiO$_3$/MgAl$_2$O$_4$ is related in some way to the perovskite structure.

![FTIR patterns](image)

**Figure 6-12** FTIR patterns obtained for (a) Rh/CaO/MgAl$_2$O$_4$ and (b) Rh/TiO$_2$/MgAl$_2$O$_4$ after exposure to CO at room temperature after five 1073 K redox cycles with the final treatment being reduction.

### 6.3.4 CO Oxidation Rates

To determine how the different perovskite films affect catalytic properties, CO-oxidation activities were obtained on each of the thin-film catalysts, as well as the bulk exsolution catalysts. Again, each of the thin-film catalysts was aged by five redox cycles at 1073 K, but the final step before rate measurements was the 1073-K oxidation step. Because high-temperature reduction is required to activate exsolution catalysts, differential rates were measured after no reduction, reduction in 10% H$_2$ for 1 h at 573 K, and reduction for 1 h at 1073 K. Rates were measured in 25 Torr CO and 12.5 Torr O$_2$ and are shown in **Figure 6-13**. On the oxidized Rh/MgAl$_2$O$_4$ **Figure 6-13(a)**, rates were initially low but increased upon reduction at 573 K and even more after reduction at 1073 K. Clearly, the oxidized Rh is not as active as metallic Rh and 573 K was not
sufficient to completely reduce the larger Rh particles supported on MgAl₂O₄. The normalized rates on the reduced Rh/MgAl₂O₄ were essentially identical to what has been reported in previous work [119, 120].

Figure 6-13 Steady-state, differential reaction rates for CO oxidation with 25 Torr of CO and 12.5 Torr O₂ for (a) Rh/MgAl₂O₄, (b) Rh/CaTiO₃/MgAl₂O₄, (c) Rh/SrTiO₃/MgAl₂O₄, and (d) Rh/BaTiO₃/MgAl₂O₄ as a function of reduction temperature. Reduction pretreatment temperature: (white) no reduction, (grey) 573 K reduction, and (black) 1073 K reduction.

The analogous results on Rh/CaTiO₃/MgAl₂O₄ are shown in Figure 6-13(b). The rates on this catalyst were initially lower than that on Rh/MgAl₂O₄ and did not increase significantly upon...
reduction at either 573 or 1073 K. The rates on the reduced Rh/CaTiO\textsubscript{3}/MgAl\textsubscript{2}O\textsubscript{4} catalysts were more than a factor of 20 lower than those on reduced Rh/MgAl\textsubscript{2}O\textsubscript{4}. Rate data for Rh/SrTiO\textsubscript{3}/MgAl\textsubscript{2}O\textsubscript{4} in Figure 6-13(c) were similar to what was observed on Rh/MgAl\textsubscript{2}O\textsubscript{4}, with rates increasing with reduction temperature, as well as being very similar in magnitude after reduction at 1073 K. As shown in Figure 6-13(d), the Rh/BaTiO\textsubscript{3}/MgAl\textsubscript{2}O\textsubscript{4} appears to already be completely reduced at 573 K and reduction at higher temperatures did not significantly change the rates.

To determine whether the catalytic properties are affected if the perovskite is B-site deficient, three additional ALD cycles of CaO was deposited onto the CaTiO\textsubscript{3}/MgAl\textsubscript{2}O\textsubscript{4} sample to determine whether this would affect the properties of the supported Rh. Figure 6-14 shows that a Rh/CaTiO\textsubscript{3}/MgAl\textsubscript{2}O\textsubscript{4} sample with a nominal Ca:Ti stoichiometry of 1.1 exhibited catalytic rates that were essentially the same as what is shown in Figure 6-13(b).

**Figure 6-14** Steady-state, differential reaction rates for CO oxidation with 25 Torr of CO and 12.5 Torr O\textsubscript{2} for Rh/CaTiO\textsubscript{3}/MgAl\textsubscript{2}O\textsubscript{4} with extra Ca (Ca:Ti=1.1) as a function of reduction temperature. Reduction pretreatment temperature: (white) no reduction, (grey) 573 K reduction, and (black) 1073 K reduction.
To eliminate the possibility that the low catalytic activity of Rh/CaTiO$_3$/MgAl$_2$O$_4$ came from one of the individual components that make up CaTiO$_3$, rates were measured on the Rh/CaO/MgAl$_2$O$_4$ and Rh/TiO$_2$/MgAl$_2$O$_4$ samples, with results reported in Figure 6-15. For Rh/CaO/MgAl$_2$O$_4$, the activity was essentially the same as with Rh/MgAl$_2$O$_4$. The catalyst was easily reduced at 573 K and exhibited similar rates. Rates on Rh/TiO$_2$/MgAl$_2$O$_4$ were somewhat lower than that observed on either Rh/MgAl$_2$O$_4$ or Rh/CaO/MgAl$_2$O$_4$ after high temperature reduction, probably due to an “SMSI” effect in which the Rh particles are partially covered by TiO$_2$. However, both single-component catalysts were significantly more active than Rh/CaTiO$_3$/MgAl$_2$O$_4$.

![Figure 6-15](image)

**Figure 6-15** Steady-state, differential reaction rates for CO oxidation with 25 Torr of CO and 12.5 Torr O$_2$ for (a) Rh/CaO/MgAl$_2$O$_4$ (b) Rh/TiO$_2$/MgAl$_2$O$_4$ as a function of reduction temperature. Reduction pretreatment temperature: (white) no reduction, (grey) 573K reduction and (black) 1073K reduction.

It is interesting to compare Rh on the thin-film perovskites to Rh ex-soliving from the bulk counterparts. Results for CO oxidation on CaTi$_{0.98}$Rh$_{0.02}$O$_3$, SrTi$_{0.98}$Rh$_{0.02}$O$_3$, and BaTi$_{0.98}$Rh$_{0.02}$O$_3$ are shown as a function of the reduction temperature in Figure 6-16. Because the surface areas of these materials were much lower, the catalyst loadings were ten times higher and the rates are
shown on a different scale, even though the Rh loadings are much higher. Unlike the case with the thin-film perovskites, rates on the three bulk samples were very similar. Without reduction, each showed very low activity. Reduction at 573 K increased rates by a factor roughly ten and reduction at 1173 K increased rates by another factor of ten, almost certainly due to Rh being brought to the surface.

**Figure 6-16** Steady-state, differential reaction rates for CO oxidation with 25 Torr of CO and 12.5 Torr O$_2$ for (a) CaTi$_{0.98}$Rh$_{0.02}$O$_3$, (b) SrTi$_{0.98}$Rh$_{0.02}$O$_3$, and (c) BaTi$_{0.98}$Rh$_{0.02}$O$_3$ as a function of reduction temperature. Reduction pretreatment temperature: (white) no reduction, (grey) 573 K reduction, and (black) 1173 K reduction.

### 6.3.5 Rh Oxidation State

To determine whether Rh is being completely reduced in the thin-film perovskite catalysts, flow-titration measurements were performed to determine the amount of oxygen that could be taken up by catalysts at 1073 K after they had been reduced in flowing, 10% H$_2$ for 1 h at either 573 or 1073 K. These results are reported in Table 6-4. Oxygen uptakes on each of the support materials were negligible, even after reduction at 1073 K. Only the BaTiO$_3$/MgAl$_2$O$_4$ and TiO$_2$/MgAl$_2$O$_4$ samples showed any measurable uptake; and, even for this sample, the uptake was a small fraction of the uptakes on the Rh-containing samples. Since each of the Rh-containing catalysts were approximately 2-wt% Rh (2.0-wt% = 194 μmol Rh/g), complete oxidation of metallic Rh to Rh$_2$O$_3$
corresponds to ~300 μmol O/g. For Rh/MgAl₂O₄, Rh reduction at 573 K was incomplete but the O:Rh stoichiometry after reduction at 1073 K matched well that expected for the Rh-Rh₂O₃ transition. Results for Rh/BaTiO₃/MgAl₂O₄ differed from that of Rh/MgAl₂O₄ only in that reduction was nearly complete after 573 K. Rh/SrTiO₃/MgAl₂O₄ appears to have been more difficult to reduce and the total oxygen uptake was slightly less than that expected for a completely reduced catalyst, even after reduction at 1073 K.

However, while results for Rh/SrTiO₃/MgAl₂O₄ after reduction at 1073 K were close to that expected theoretically, results for Rh/ČaTiO₃/MgAl₂O₄ clearly did not match the theoretical oxygen uptakes. Even after reduction at 1073 K, the oxygen uptake was only 100 μmol/g, a third of the theoretical value. Reducibilities of Rh/ČaO/MgAl₂O₄ and Rh/TiO₂/MgAl₂O₄ were similar to those that were expected, demonstrating again that support effects with the ČaTiO₃ perovskite film were different from that of the individual oxides making up ČaTiO₃.
The reduction kinetics for the Rh/MgAl₂O₄, Rh/CaTiO₃/MgAl₂O₄, Rh/SrTiO₃/MgAl₂O₄, and Rh/BaTiO₃/MgAl₂O₄ were also quantified by CO TPR measurements, with results given in Figure 6-17. The Rh on MgAl₂O₄ reduced in two temperature regions, reacting in peaks centered at 580 K and 810 K. The 580-K peak is almost certainly associated with reduction of Rh near the surface of the Rh particles. Because this sample also has larger Rh particles, the second peak may be due to reduction of the bulk oxide. The TPR data for Rh/BaTiO₃/MgAl₂O₄ were very similar to that of Rh/MgAl₂O₄; but Rh/SrTiO₃/MgAl₂O₄ reduction was clearly more sluggish, with peaks shifted to higher temperatures. Since the Rh particle size on the Rh/SrTiO₃/MgAl₂O₄ samples were small, it seems unlikely that the increased peak temperatures are due to bulk reduction, again
suggesting some kind of interaction between Rh and the SrTiO$_3$. In agreement with the flow-titration data, much less oxygen could be removed from the Rh/CaTiO$_3$/MgAl$_2$O$_4$ sample and all reduction that did occur happened at high temperatures. Again, TPR profiles for Rh/CaO/MgAl$_2$O$_4$ and Rh/TiO$_2$/MgAl$_2$O$_4$, shown Figure 6-18, were dissimilar from Rh/CaTiO$_3$/MgAl$_2$O$_4$.

![Figure 6-17 CO-TPR profile for (a) Rh/MgAl$_2$O$_4$, (b) Rh/CaTiO$_3$/MgAl$_2$O$_4$, (c) Rh/SrTiO$_3$/MgAl$_2$O$_4$, and (d) Rh/BaTiO$_3$/MgAl$_2$O$_4.

\[ \text{Figure 6-17 CO-TPR profile} \]
Because the flow-titration measurements only determine the change in oxygen content in going from reducing to oxidizing conditions, it is possible that the Rh/CaTiO$_3$/MgAl$_2$O$_4$ is never completely oxidized. To gain additional insights into the Rh oxidation states, XPS spectra were measured on the Rh/CaTiO$_3$/MgAl$_2$O$_4$, Rh/SrTiO$_3$/MgAl$_2$O$_4$, and Rh/BaTiO$_3$/MgAl$_2$O$_4$ samples, with results shown in Figure 6-19 for both oxidized and reduced samples. For all three samples, there is a shift of around 1.6 eV between oxidized and reduced samples, suggesting a change in oxidation states between Rh$^{3+}$ and Rh$^{0}$. For the reduced samples, the Rh peaks for the Rh/BaTiO$_3$/MgAl$_2$O$_4$ sample were centered at 306.7 eV and 311.4 eV and can be assigned to the metallic Rh doublet (3d$_{5/2}$ and 3d$_{3/2}$). The Rh spectrum for Rh/SrTiO$_3$/MgAl$_2$O$_4$ is almost identical to that of Rh/BaTiO$_3$/MgAl$_2$O$_4$, again implying an oxidation state of Rh$^{0}$. The XPS spectrum for Rh on the reduced Rh/CaTiO$_3$/MgAl$_2$O$_4$ was shifted 0.6 eV shift towards higher energy level, probably due to final-state effects [121], since the shift was also observed in the oxidized samples.
Obviously, there is an apparent discrepancy between the oxygen uptakes observed in the redox measurements and the XPS results for the Rh/CaTiO$_3$/MgAl$_2$O$_4$ sample. A possible explanation for the discrepancy, as well as for the low catalytic activity of this sample, is that the reduced Rh is moving subsurface to the CaTiO$_3$-MgAl$_2$O$_4$ interface. There is some evidence for this from the Rh:A-site cation peak ratios shown in Table 6-5. The Rh:Ca ratio decreased by a factor of roughly 10 upon sample reduction. Since the STEM images indicated the dispersion is high in both cases, the reduction in Rh peak intensity cannot be due to an increase in particle size. Since the mean-free-path for electrons in XPS is typically less than 1 nm, migration of Rh below the perovskite film should result in a significant reduction in the Rh XPS peak intensity. The presence of metallic Rh in the bulk of the support could also change the O:Rh stoichiometry. Finally, the Rh:A-site cation intensities for the Rh/SrTiO$_3$/MgAl$_2$O$_4$ and Rh/BaTiO$_3$/MgAl$_2$O$_4$ samples are easily explained by formation of reduced Rh particles at the perovskite surfaces upon reduction. For Rh/SrTiO$_3$/MgAl$_2$O$_4$, the Rh particles are very small so that all of the reduced Rh is essentially at the surface. For Rh/BaTiO$_3$/MgAl$_2$O$_4$, the Rh signal is reduced due to the formation of very large Rh particles.
Table 6-5: Rh: A-site Cation XPS area ratio comparison

<table>
<thead>
<tr>
<th>Sample</th>
<th>Oxidized</th>
<th>Reduced</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rh/ CaTiO₃/ MgAl₂O₄</td>
<td>0.70</td>
<td>0.06</td>
</tr>
<tr>
<td>Rh/SrTiO₃/ MgAl₂O₄</td>
<td>0.40</td>
<td>0.96</td>
</tr>
<tr>
<td>Rh/BaTiO₃/ MgAl₂O₄</td>
<td>0.48</td>
<td>0.16</td>
</tr>
</tbody>
</table>

*: Rh 3d (~307 eV), Ca 2p (~347 eV), Sr 3d (~133 eV), and Ba 3d (~780 eV) signals were used for integration.
6.4 Discussion

The results of this chapter raise interesting questions about the nature of metal-support interactions with perovskites and about differences between bulk and surface perovskites. Each of these points will be addressed below.

It is important first to address the question of differences and similarities between bulk and surface perovskites as supports for metal catalysts. It has been shown that there are at least some similarities. For example, with bulk catalysts, it is expected that high-temperature oxidation will drive the metal into the lattice and that high-temperature reduction would then be required to bring metal back to the surface and restore activity. Similar to this, activity is low after high-temperature oxidation and restored only upon high-temperature reduction in many of the thin-film catalysts, the Ni/CaTiO$_3$/MgAl$_2$O$_4$ system and the Pt/CaTiO$_3$/MgAl$_2$O$_4$ system discussed in CHAPTER 4 and CHAPTER 5 are good examples. Second, with Ni-based reforming catalysts, both bulk and thin-film catalysts show greatly increased tolerance against coking. Third, both bulk and thin-film catalyst exhibit specificity (e.g. Pd shows negligible interactions with CaTiO$_3$ films and does not enter the bulk CaTiO$_3$ lattice.). Finally, Pt-CaTiO$_3$ thin-film and bulk catalysts that were highly active for CO oxidation showed low activity for toluene hydrogenation.

However, it is not surprising that metals exsolved from bulk perovskites would also show important differences from metals on thin-films when the film thickness is less than the particle diameter. Rh/CaTiO$_3$ catalysts prepared by exsolution from bulk perovskites were catalytically very active, both in this work and in past studies [50], while the thin-film version was inactive. The reasons for the low activity of Rh/CaTiO$_3$/MgAl$_2$O$_4$ are not completely clear since the Rh remained very well dispersed. The flow-titration data suggest that the Rh may not be completely reduced, but
that in itself is unusual behavior given the ease with which Rh is normally reduced and the severe reducing conditions that were used in the present study. Based on this explanation, one would also expect the bulk catalyst to be similarly difficult to reduce. An alternative explanation is that Rh migrates to the CaTiO$_3$-MgAl$_2$O$_4$ interface at some point during the catalyst treatment and remains subsurface upon reduction. While this would not prevent observation of Rh by XPS given the perovskite film thickness is similar to the expected mean-free-path of electrons [122], the Rh:Ca intensity ratio is expected to be lower since Rh is subsurface. In fact, this is exactly what was observed.

Specific support interactions in perovskite-supported catalysts are often neglected, perhaps in part because the exsolved metal particles are so large that the surface metal atoms are not affected by the support [113]. It is not surprising that metal-perovskite interactions will be important for smaller particles, given the specificity that has previously been demonstrated [24]. Indeed, the exsolution process itself may be different in some systems. For example, with Ni exsolution from La$_x$SrNiTiO$_x$ [37, 41, 42], Ni particles nucleate in the bulk and migrate to the surface, while extrusion of Pd nanowires was reported for Pd-BaCeO$_3$ system [123].

It is interesting that perovskites as similar as CaTiO$_3$, SrTiO$_3$, and BaTiO$_3$ would exhibit such strong differences in their thin-film versions. One possibility is that differences in the surface energies of the different perovskites changes the interaction energies with Rh. Evidence for differences between the perovskites was show clearly by the isopropanol TPD-TGA results. From previous Low Energy Ion Scattering (LEIS) measurements in Section 5.3.4, the CaTiO$_3$ films were shown to be A-site terminated. With the larger cations, the surface may be B-site terminated. Finally, the free volumes for these three perovskite materials change with the size of the cations. Taking the free volume to be the difference in volumes of the perovskite cell and the volume of all
anions and cations in that cell, CaTiO₃ has the largest free volume of around 80%. All these
differences could be related to differences of surface energies in thin film perovskites.

There is obviously much that one still need to learn about both exsolution catalysts and
about the differences between bulk and thin-film perovskites. It is almost certain that the behaviors
observed were thermodynamically-driven, and factors such as metal-perovskite combination
selections, relative sizes between doped metals and perovskites, and addition of a third component
(high-surface-area supports) can all contribute to the changes of thermally-stable state at given
conditions. Thermodynamic understanding for all these systems can certainly lead to better catalyst
design. But whatever the mechanism is, demonstration of high-surface area perovskites leads to the
creation of systems that permitted us to better explore the relationships between structure and
catalytic properties.
6.5 Conclusions

Important differences were observed for Rh catalysts supported on 1-nm films of CaTiO₃, SrTiO₃, and BaTiO₃ on MgAl₂O₄. Large Rh particles were formed after redox cycling at 1073 K when Rh was supported on MgAl₂O₄ or BaTiO₃ films; however, Rh formed only small particles on SrTiO₃ films and appeared to remain almost atomically dispersed on CaTiO₃ films. Rh catalysts prepared from the CaTiO₃ films exhibited very low activity for CO oxidation, possibly because the Rh resides under the CaTiO₃ surface. Interestingly, the large differences observed for the thin-film catalysts were not observed when Rh was exsolved from the bulk perovskites, suggesting that there may be important differences between thin-film and bulk perovskites.
CHAPTER 7. A THERMODYNAMIC INVESTIGATION OF Ni ON THIN-FILM TITANATES (ATiO$_3$)

Summary

The ATiO$_3$/MgAl$_2$O$_4$ (A=Ca, Sr and Ba) samples mentioned in CHAPTER 6 were studied as catalyst supports for ~5 wt% of Ni that was added to the surface by Atomic Layer Deposition. Scanning Transmission Electron Microscopy demonstrated that both the Ni and the perovskites uniformly covered the surface of the support following oxidation at 1073 K, even after redox cycling; but large Ni particles following reduction at 1073 K. Compared to Ni/MgAl$_2$O$_4$, the perovskite-containing catalysts required significantly higher temperatures for Ni reduction. Equilibrium constants for Ni oxidation, determined from Coulometric Titration, indicated that oxidation of Ni shifted to lower P$_{O_2}$ on the perovskite-containing materials. Based on Ni equilibrium constants, Ni interactions are strongest with CaTiO$_3$, followed by SrTiO$_3$ and BaTiO$_3$. The shift in the equilibrium constant was shown to cause reversible deactivation of the Ni/CaTiO$_3$/MgAl$_2$O$_4$ catalyst for CO$_2$ reforming of CH$_4$ at high CO$_2$ pressures due to oxidation of the Ni.

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6 This chapter was published as C. Lin, A.C. Foucher, E.A. Stach, R.J. Gorte, A Thermodynamic Investigation of Ni on Thin-Film Titanates (ATiO$_3$), Inorganics, 8 (2020) 69. Copyright 2020, MDPI.
7.1 Introduction

As discussed in the previous chapters, although metals supported on these thin-film, perovskite supports are not catalytically identical to bulk, exsolution metals [124], many of their properties are similar. Most of these catalysts are only active after high-temperature reduction. In CHAPTER 4, I showed that perovskite-supported, Ni catalysts also exhibit a high tolerance against coking. In CHAPTER 5, it was demonstrated that supported Pt catalysts based on both thin-film and bulk perovskites showed similar differences from conventional Pt catalysts in their relative inactivity for hydrogenation reactions compared to oxidation reactions.

There are indications that some of the support effects associated with perovskites are due to the formation of chemical bonds with the metal. First, the nature of interactions is metal and perovskite specific, as expected when chemical bonding is important. While Pt and Rh can enter the bulk CaTiO$_3$ lattice and both metals exhibit strong support interactions in their thin-film variants, Pd cannot be doped into CaTiO$_3$ and Pd supported on CaTiO$_3$ films shows normal behavior. As discussed in CHAPTER 6, metal-perovskite interactions were also shown to depend on the perovskite composition in a comparison of Rh catalysts supported on thin films of CaTiO$_3$, SrTiO$_3$, and BaTiO$_3$. Rh interacted very strongly with CaTiO$_3$ but only weakly with BaTiO$_3$. A second piece of evidence for bonding interactions is that the perovskite support can change the thermodynamic properties for oxidation of the supported metal. This was demonstrated for Ni on LaFeO$_3$ films, where the equilibrium constant for the reaction Ni to NiO was observed to shift by four orders of magnitude to lower PO$_2$ in the presence of the perovskite [55].

A better understanding of the nature of metal-perovskite interactions is clearly required before these materials can find wider application. In this Chapter, the equilibrium properties for Ni
oxidation were examined on thin films of CaTiO$_3$, SrTiO$_3$, and BaTiO$_3$ supported on MgAl$_2$O$_4$. Ni-based catalysts are convenient for this comparison because previous work has shown that the support can change the equilibrium constant for Ni oxidation to NiO by a significant amount [55]. For the reaction, Ni + $\frac{1}{2}$O$_2$ = NiO, the equilibrium constant, $K_{\text{NiO}}$, is equal to $P_{O_2}^{-\frac{1}{2}}$ and given by $\exp(-\Delta G/RT)$, where $\Delta G$ is the free energy of reaction. $K_{\text{NiO}}$, and therefore $\Delta G$, can be obtained by measuring the $P_{O_2}$ at which both Ni and NiO exist in equilibrium. I found that similar to what was observed for Rh on these perovskite supports, Ni interacts most strongly with CaTiO$_3$, followed by SrTiO$_3$ and BaTiO$_3$. 
7.2 Experimental Methods

A list of the samples discussed in this chapter together with some of their key properties is given in Table 7-1. The CaTiO$_3$/MgAl$_2$O$_4$, SrTiO$_3$/MgAl$_2$O$_4$, and BaTiO$_3$/MgAl$_2$O$_4$ supports were prepared using procedures that are identical to those used in CHAPTER 6. The targeted perovskite film thicknesses were 1 nm, assuming that the perovskite film densities were the same as that of the corresponding bulk perovskites and that the 120 m$^2$/g MgAl$_2$O$_4$ was uniformly covered. The Ni loadings were achieved using 5 ALD cycles of the Ni precursor, Ni(TMHD)$_2$. Detailed parameters for ALD processes can be found in Section 2.1.2. The properties shown in Table 7-1 were measured after the sample had been oxidized and reduced five times at 1073 K in order to ensure that the samples had reached an equilibrium state.

**Table 7-1 Key properties of the samples used in this chapter**

<table>
<thead>
<tr>
<th></th>
<th>Specific surface area (m$^2$/g) after 1073 K redox cycles</th>
<th>ALD thin film loading (wt%)</th>
<th>Ni Loading (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni/MgAl$_2$O$_4$</td>
<td>115</td>
<td>N/A</td>
<td>4.8</td>
</tr>
<tr>
<td>Ni/CaTiO$_3$/MgAl$_2$O$_4$</td>
<td>73</td>
<td>29</td>
<td>4.6</td>
</tr>
<tr>
<td>Ni/SrTiO$_3$/MgAl$_2$O$_4$</td>
<td>67</td>
<td>33</td>
<td>3.7</td>
</tr>
<tr>
<td>Ni/BaTiO$_3$/MgAl$_2$O$_4$</td>
<td>59</td>
<td>39</td>
<td>4.1</td>
</tr>
</tbody>
</table>

X-ray diffraction (XRD) patterns were recorded on a Rigaku MiniFlex diffractometer equipped with a Cu Kα source (λ = 0.15416 nm). BET surface areas were measured using N$_2$ adsorption at 78 K. Ex situ, Scanning Transmission Electron Microscopy (STEM) measurements were performed on powder specimens. Imaging and elemental mapping via Energy Dispersive X-ray Spectroscopy (EDS) were performed with a JEOL NEOARM operated at 200 kV.
Rates for methane dry reforming were determined from differential conversions in a reactor connected to Gas Chromatograph (GC) equipped with a TCD detector as described in Section 2.3. The total gas flow rate was maintained at 120 mL·min\(^{-1}\). Methane flow was kept at 5 mL·min\(^{-1}\) throughout the measurements. CO\(_2\) and He flows were adjusted to achieve different CO\(_2\):CH\(_4\) ratios while maintaining a constant flow rate.

The reducibilities of the samples were quantified by flow titration and Coulometric Titration (CT). The flow-titration experiments were performed in a tubular reactor at 1 atm with 200-mg samples. After reducing the samples in flowing H\(_2\) at desired temperatures, followed by purging with He, the samples were exposed to dry air at 1073 K at a flow rate of 5 mL·min\(^{-1}\) while monitoring the reactor effluent with a mass spectrometer. The O\(_2\) uptake was then determined by integrating the difference between the N\(_2\) and O\(_2\) signals in the effluent. Equilibrium constants for oxidation of Ni were probed by CT at 1073 K. Detailed CT setup is described in Section 2.4.2. After flowing a mixture of 10% H\(_2\), 10% H\(_2\)O, and 80% He over the sample at 1073 K, the tube was sealed with cajon fittings. Known quantities of oxygen were then electrochemically pumped into or out of the YSZ tube by applying a known charge across the metal electrodes using a Gamry instruments potentiostat. After allowing the system to come to equilibrium with the electrodes at open circuit, the equilibrium P\(_{O_2}\) was calculated from the electrode open-circuit potential using the Nernst Equation.
7.3 Results

The perovskite-containing samples listed in Table 7-1 were analyzed by STEM/EDS and XRD. In all cases, the samples were pretreated using five redox cycles at 1073 K before the measurements were performed. Results are shown after oxidation at 1073 K and after reduction at 1073 K. STEM/EDS results for the oxidized and reduced samples are shown in Figure 7-1 through Figure 7-6. For the oxidized samples, the images for each of the three samples were indistinguishable from the that of the MgAl\(_2\)O\(_4\) support; and the EDS maps showed a spatial distribution of A-site cations, Ti, and Ni that matched well with the Mg and Al variations. All of this implies that each of the species deposited by ALD are uniformly distributed over the surface of the MgAl\(_2\)O\(_4\) support and remain uniformly distributed, even after redox cycling. The CaTiO\(_3\), SrTiO\(_3\), and BaTiO\(_3\) films remained largely unchanged after reduction at 1073 K but Ni particles were formed on each of the three samples after this treatment. The Ni particles appeared to be slightly smaller for Ni/CaTiO\(_3\)/MgAl\(_2\)O\(_4\), ~10 to 20 nm, and largest on Ni/BaTiO\(_3\)/MgAl\(_2\)O\(_4\), ~30 to 50 nm, with Ni/SrTiO\(_3\)/MgAl\(_2\)O\(_4\) in between. It is noteworthy that formation of Ni particles was reversible on each of the samples, since the uniform Ni films were restored by oxidation.
Figure 7-1 Representative STEM results for Ni/CaTiO$_3$/MgAl$_2$O$_4$ after 1073 K oxidation followed by 773 K reduction with EDS maps of corresponding elements.

Figure 7-2 Representative STEM results for Ni/CaTiO$_3$/MgAl$_2$O$_4$ after 1073 K oxidation followed by 1073 K reduction with EDS maps of corresponding elements.
Figure 7-3 Representative STEM results for Ni/SrTiO$_3$/MgAl$_2$O$_4$ after 1073 K oxidation followed by 773 K reduction with EDS maps of corresponding elements.

Figure 7-4 Representative STEM results for Ni/SrTiO$_3$/MgAl$_2$O$_4$ after 1073 K oxidation followed by 1073 K reduction with EDS maps of corresponding elements.
Figure 7-5 Representative STEM results for Ni/BaTiO$_3$/MgAl$_2$O$_4$ after 1073 K oxidation followed by 773 K reduction with EDS maps of corresponding elements.

Figure 7-6 Representative STEM results for Ni/BaTiO$_3$/MgAl$_2$O$_4$ after 1073 K oxidation followed by 1073 K reduction with EDS maps of corresponding elements.
XRD patterns for the oxidized and reduced samples are reported in Figure 7-7. For oxidized Ni/CaTiO$_3$/MgAl$_2$O$_4$ and Ni/SrTiO$_3$/MgAl$_2$O$_4$, all peaks can be assigned to either the MgAl$_2$O$_4$ support or the corresponding perovskite phase. Upon reduction, peaks associated with metallic Ni were also observed. For BaTiO$_3$/MgAl$_2$O$_4$, there is significant overlap in the peak positions for BaTiO$_3$ and MgAl$_2$O$_4$; however, the relative ratio of peaks, particularly those centered at 32 and 37 degrees 2θ, make it clear that the major peaks are due to a mixture of MgAl$_2$O$_4$ and BaTiO$_3$. Small peaks that could be indexed to BaCO$_3$ were also observed on the Ni/BaTiO$_3$/MgAl$_2$O$_4$ sample. Again, the XRD pattern of the reduced sample was unchanged except for the additional features associated with metallic Ni.

![XRD patterns for Ni/CaTiO$_3$/MgAl$_2$O$_4$, Ni/SrTiO$_3$/MgAl$_2$O$_4$, and Ni/BaTiO$_3$/MgAl$_2$O$_4$](image)

**Figure 7-7** XRD patterns for (a) Ni/CaTiO$_3$/MgAl$_2$O$_4$, (b) Ni/SrTiO$_3$/MgAl$_2$O$_4$, (c) Ni/BaTiO$_3$/MgAl$_2$O$_4$ after (black) 1073 K oxidation followed by 773 K reduction and (red) 1073 K oxidation followed by 1073 K reduction.

As discussed elsewhere [125], the presence of intense perovskite diffraction peaks for uniformly-deposited films that are nominally 1-nm thick suggests formation of relatively large, two-dimensional crystals, randomly oriented with respect to the support. Based on the width of the peaks, the nominal sizes of the perovskite crystallites are 22 nm for CaTiO$_3$, 18 nm for SrTiO$_3$, and 18 nm for BaTiO$_3$. Particle sizes were also estimated from XRD peak widths for the Ni particles in
the reduced samples. These gave reasonable agreement with the values obtained from STEM, with values of 21 nm for Ni/CaTiO$_3$/MgAl$_2$O$_4$, 25 nm for Ni/SrTiO$_3$/MgAl$_2$O$_4$, and 31 nm for Ni/BaTiO$_3$/MgAl$_2$O$_4$.

The extent of reduction was measured as a function of temperature for each of the samples in Table 7-1, with results shown in Table 7-2. Samples were first oxidized at 1073 K in flowing air and then reduced in 10% H$_2$-He mixture at the indicated temperature for 30 minutes. The amount of oxygen required to completely oxidize the sample at 1073 K was then measured using flow titration. First, there was no measurable reduction of the CaTiO$_3$/MgAl$_2$O$_4$ and SrTiO$_3$/MgAl$_2$O$_4$ supports, even at 1073 K; but there was some reduction of the BaTiO$_3$/MgAl$_2$O$_4$ sample at the highest temperature. Therefore, with the exception of Ni/BaTiO$_3$/MgAl$_2$O$_4$ at 1073 K, the results in Table 7-2 indicate the extent of reduction of the Ni in each of the samples. For Ni/MgAl$_2$O$_4$, only 38% of the Ni was reduced at 773 K and 87% at 1073 K. That such harsh conditions are required to reduce some of the Ni may indicate that a fraction of Ni has reacted with the MgAl$_2$O$_4$ support after the five redox cycles at 1073 K, with Ni replacing Mg and forming NiAl$_2$O$_4$. For Ni/CaTiO$_3$/MgAl$_2$O$_4$ and Ni/SrTiO$_3$/MgAl$_2$O$_4$, reduction of Ni was insignificant at temperatures below 1073 K. At that temperature, most of the Ni in these samples was reduced. There was some reduction of Ni at lower temperatures on Ni/BaTiO$_3$/MgAl$_2$O$_4$ but 1073 K was again required for a majority of the Ni to be reduced.
Table 7-2 Oxygen uptakes from flow titration for samples after different reduction pretreatments

<table>
<thead>
<tr>
<th>Samples</th>
<th>Oxygen uptakes (μmol O/g) and corresponding Ni reduction extents* (%) after dry H₂ reduction at various temperatures</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>773-K reduction</td>
</tr>
<tr>
<td>Ni/MgAl₂O₄</td>
<td>310 (38%)</td>
</tr>
<tr>
<td>Ni/CaTiO₃/MgAl₂O₄</td>
<td>0 (0%)</td>
</tr>
<tr>
<td>Ni/SrTiO₃/MgAl₂O₄</td>
<td>0 (0%)</td>
</tr>
<tr>
<td>Ni/BaTiO₃/MgAl₂O₄</td>
<td>60 (9%)</td>
</tr>
<tr>
<td>CaTiO₃/MgAl₂O₄</td>
<td>-</td>
</tr>
<tr>
<td>SrTiO₃/MgAl₂O₄</td>
<td>-</td>
</tr>
<tr>
<td>BaTiO₃/MgAl₂O₄</td>
<td>-</td>
</tr>
</tbody>
</table>

To better understand the effect of the perovskite supports on Ni reducibility, CT measurements were performed at 1073 K on each of the samples, with the results shown in Figure 7-8. At this temperature, tabulated values of ΔG for bulk Ni would indicate the equilibrium P₀₂ should be 10⁻¹⁴ atm [126]. Data for Ni/MgAl₂O₄, reproduced here from a previous publication [55], found that the amount of oxygen taken up by the sample was very close to the value obtained from flow titration reported in Table 7-2 and that oxidation of the Ni component occurred between 10⁻¹⁵ and 10⁻¹⁶ atm. The relatively small change in the equilibrium P₀₂ from that reported for bulk Ni may be due to the Ni particle size or to interactions with the MgAl₂O₄ support. The equilibrium P₀₂ for each of the perovskite-containing samples were shifted to lower values. The shift was largest for Ni/CaTiO₃/MgAl₂O₄, with oxidation occurring in the range of 10⁻¹⁸ to 10⁻¹⁹ atm, and smallest for Ni/BaTiO₃/MgAl₂O₄, between 10⁻¹⁶ and 10⁻¹⁷ atm. The Ni/BaTiO₃/MgAl₂O₄ sample also took
up slightly more oxygen in the CT experiments, in agreement with the flow-titration results. Even though the equilibrium $P_{O_2}$ for Ni were shifted to lower values by interactions with the titanates, the changes were less than that observed previously with Ni/LaFeO$_3$/MgAl$_2$O$_4$, for which the equilibrium $P_{O_2}$ was $10^{-20}$ atm at 1073 K.

![Figure 7-8](image)

**Figure 7-8** Oxidation isotherm obtained using coulometric titration at 1073 K for (X) Ni/MgAl$_2$O$_4$; (▲) Ni/CaTiO$_3$/MgAl$_2$O$_4$; (◊) Ni/SrTiO$_3$/MgAl$_2$O$_4$ and (●) Ni/BaTiO$_3$/MgAl$_2$O$_4$.

To determine whether these equilibrium properties affect catalytic activities, methane dry reforming (MDR) was investigated on all four Ni catalysts in Table 7-1. To determine the effect of reduction temperature on each of the catalysts, methane conversions were measured at 873 K, using 4.2% CH$_4$, 8.3% CO$_2$, and a 72000 mL·g$^{-1}$·h$^{-1}$ Gas Hourly Space Velocity (GHSV), with results shown in Figure 7-9(a). In each case, the catalysts were oxidized at 1073 K and then reduced in dry 10% H$_2$ for 30 min at the indicated temperatures before measuring the conversion. Ni/MgAl$_2$O$_4$ showed significant conversion after reduction at 773 K, and the conversions increased with reduction temperature. This corresponds well to the flow-titration results, which indicated that
Ni was somewhat reduced on this sample at 773 K but that higher reduction temperatures increased the fraction of Ni reduction. Each of the perovskite-containing samples was completely inactive for reduction at temperatures below 1073 K but showed reasonable activity after reduction at that temperature. Differential reaction rates are shown for each of the samples in the Arrhenius plots of Figure 7-9(b). Rates were about a factor of two lower on the perovskite-containing samples but all of the catalysts showed a similar temperature dependence.

With Ni on LaFeO$_3$ films, the shift to lower P$_{O_2}$ in the equilibrium constants for Ni oxidation is sufficient for Ni to be oxidized under some MDR reaction conditions [55]. Although equilibrium constants for the titanates are closer to that of bulk Ni, I investigated the MDR reaction on Ni/MgAl$_2$O$_4$ and Ni/CaTiO$_3$/MgAl$_2$O$_4$ as a function of the CH$_4$:CO$_2$ ratio to see if oxidation of Ni could occur in these catalysts as well. The reaction was studied at integral conversions to produce CO and H$_2$; an equilibrium P$_{O_2}$ is then established by the CO$_2$:CO ratio. For these
measurements, the CH$_4$ flow rate was kept at 5 mL·min$^{-1}$ and the CO$_2$ and He flows were tuned to achieve a desired CO$_2$:CH$_4$ ratio while keeping the space velocity the same. All the conversions were measured at 873 K, with the results shown in Figure 7-10.

![Graph](image)

**Figure 7-10** Methane conversion for MDR reaction at 873K for (X) Ni/MgAl$_2$O$_4$ and (▲) Ni/CaTiO$_3$/MgAl$_2$O$_4$ as a function of CO$_2$:CH$_4$ ratio. The total flow rate and the methane flow rate were controlled at 120 mL·min$^{-1}$ and 5 mL·min$^{-1}$ respectively while He and CO$_2$ flows were adjusted accordingly to achieve the desired ratios. The loading is 100 mg for Ni/MgAl$_2$O$_4$ and 200 mg for Ni/CaTiO$_3$/MgAl$_2$O$_4$ to ensure similar starting point for the methane conversion. Both samples were reduced at 1073K prior to catalytic measurements.

For the Ni/MgAl$_2$O$_4$ sample, I observed an increase in CH$_4$ conversion with increasing CO$_2$ concentration. This is the expected result for reactions with a positive reaction order. For Ni/CaTiO$_3$/MgAl$_2$O$_4$, the CH$_4$ conversion decreased with increasing CO$_2$ concentration, similar to what was observed previously for Ni/LaFeO$_3$/MgAl$_2$O$_4$ [55]. This deactivation was not due to coking, since the conversions in Figure 7-10 were stable and did not depend on whether the CO$_2$ concentration was increasing or decreasing. With the LaFeO$_3$-supported Ni, the deactivation was easier to observe because of the larger change in the equilibrium constant.
7.4 Discussion

In agreement with a previous study of Ni on LaFeO$_3$ films [55], this chapter demonstrates that the support can affect the oxidation thermodynamics of the Ni. Because the effects of the support on a metal cannot extend more than a few atomic distances from the interface [113], most of the Ni must be in direct contact with the support. Indeed, the STEM/EDS data indicate that is the case, at least for the oxidized samples. While thermodynamic properties do not indicate how large the kinetic barriers will be for reduction, the fact that the perovskite-supported catalysts require high temperatures for Ni reduction is additional evidence that there must be strong bonding interactions between the support and the Ni.

Changes in Ni geometry upon different pretreatments are also worth noting. While previous studies had suggested that interactions between Ni and some supports can lead to redispersion of Ni, the conditions used were found to be harsher and the redispersion less complete than the results reported here [127]. Our results would indicate that Ni atoms can migrate relatively long distances, along the surface of the perovskite thin films. It seems likely that Ni is incorporated as a strongly interacting phase, different from normal NiO, when supported on perovskite thin films, thus leading to the changes in equilibrium $P_{O_2}$.

Similar to what was observed for Rh on CaTiO$_3$, SrTiO$_3$, and BaTiO$_3$ films, support interactions depend on the A-site cations in this series. With Rh, the differences were stronger than what I observed here with Ni. Rh supported on CaTiO$_3$-MgAl$_2$O$_4$ was almost unreducible and catalytically inactive, while support effects for Rh on BaTiO$_3$-MgAl$_2$O$_4$ were negligible. The ordering of support interactions for Ni were the same as with Rh in that CaTiO$_3$ interacts most strongly and BaTiO$_3$ least. How the A-site cations affect these interactions is uncertain. One
possibility is that differences in the surface energies of these titanates changes the surface terminations. For example, in **CHAPTER 5**, it has been established by Low Energy Ion Scattering that CaTiO$_3$ films are terminated by Ca and it is possible that BaTiO$_3$ prefers to be B-site terminated due to the relative sizes of the ions. The free volumes for these three perovskite materials also change with the size of the A-site cations and this may affect how easily catalytic metal cations can enter the lattice.

It is also interesting to ask why the differences for Ni on the various titanates were less than what was observed for Rh. One possible reason for this could be the nominal charge on the cations. It was previously shown that Pd, which like Ni is expected to exist in the +2 state when oxidized, does not interact with CaTiO$_3$ and cannot enter the CaTiO$_3$ lattice [57]. The ability of Rh to have multiple, stable oxidation states may also play a role in allowing Rh to interact more strongly with the perovskite lattices.

There is obviously much that we need to learn about both exsolution catalysts and about the differences between bulk and thin-film perovskites. The fact that support interactions with these perovskite-supported metals are so specific to the compositions of the metal and the support represents both a challenge and an opportunity to tailor the catalytic properties for specific applications.
7.5 Conclusions

Ni catalysts supported on 1-nm films of CaTiO$_3$, SrTiO$_3$, and BaTiO$_3$ on MgAl$_2$O$_4$ were found to have different properties compared to the Ni/MgAl$_2$O$_4$ catalyst. 1073-K reduction is required to activate the Ni/ATiO$_3$/MgAl$_2$O$_4$ catalysts. By contrast, the Ni/MgAl$_2$O$_4$ catalyst was found to be active for methane dry reforming (MDR) upon 773-K reduction, and the catalytic performance increased with reduction temperature due to more complete reduction of Ni. Equilibrium oxidation constants for Ni, obtained from Coulometric Titration (CT), suggested that the equilibrium $P_{O_2}$ for Ni oxidation is shifted to lower values for Ni/ATiO$_3$/MgAl$_2$O$_4$ samples. The equilibrium $P_{O_2}$ for Ni oxidation was found to decrease in the order of Ni/CaTiO$_3$/MgAl$_2$O$_4$< Ni/SrTiO$_3$/MgAl$_2$O$_4$<Ni/BaTiO$_3$/MgAl$_2$O$_4$<Ni/MgAl$_2$O$_4$. As a result, catalyst deactivation due to Ni oxidation was observed on the Ni/CaTiO$_3$/MgAl$_2$O$_4$ sample when increasing the feed CO$_2$: CH$_4$ ratio.
CHAPTER 8. INVESTIGATION OF Pt-TITANATE (ATiO$_3$) INTERACTIONS ON HIGH-SURFACE-AREA PEROVSKITE THIN FILMS PREPARED BY ATOMIC LAYER DEPOSITION

Summary

The interactions between Pt and the three different titanate (CaTiO$_3$, SrTiO$_3$ and BaTiO$_3$) thin films were investigated. Unlike the results reported in CHAPTER 6 and CHAPTER 7, the experimental findings suggest that the interactions between Pt and the three perovskite thin films were similar and most of the results reported in CHAPTER 5 for Pt/CaTiO$_3$/MgAl$_2$O$_4$ can be reproduced on the Pt/SrTiO$_3$/MgAl$_2$O$_4$ and Pt/BaTiO$_3$/MgAl$_2$O$_4$ systems. For all three systems, high-temperature reduction is required to activate the samples for CO oxidation and high-temperature oxidation can drive the samples to an inactive state. Scanning Transmission Electron Microscope/Energy-Dispersive X-ray Spectroscopy (STEM/EDS) suggested that changes of Pt particle geometries to rhombohedral shapes can be found on all three systems upon high temperature reduction. However, the interactions between Pt and the three perovskite thin films are not exactly the same. A more detailed investigation of activities as a function of pretreatment conditions suggests that the temperature required to achieve ultimate performance of these samples were different. The interaction between Pt and the perovskite thin films can be ranked in the order of Pt/CaTiO$_3$/MgAl$_2$O$_4$ > Pt/SrTiO$_3$/MgAl$_2$O$_4$ > Pt/BaTiO$_3$/MgAl$_2$O$_4$.

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7 This chapter was adapted from Insights into the Platinum Exsolution Phenomena From Perovskite Hosts ATiO$_3$ (A = Ca/Sr/Ba) Using First Principles and Atomic Layer deposition, in preparation.
8.1 Introduction

In CHAPTER 5, interactions between Pt and CaTiO\textsubscript{3} thin films are reported. While interactions similar to bulk “intelligent catalysts” were observed and the catalysts showed good sintering resistance, there are still many remaining questions to be answered. First of all, changes in particle geometries and the surface reconstruction were observed, but the source of the interactions responsible for these changes has yet to be determined. Pt supported on the perovskite thin films also have unique properties. For example, the reduced Pt/CaTiO\textsubscript{3}/MgAl\textsubscript{2}O\textsubscript{4} was found to be only active for CO oxidation while remaining inactive for reactions such as toluene hydrogenation. Even though Pt/CaTiO\textsubscript{3}/MgAl\textsubscript{2}O\textsubscript{4} is active for CO oxidation, no CO chemisorption could be measured. The mechanisms behind all these unusual behaviors remain unclear. Given the potential benefit that could be brought by using perovskite thin films as a support, a systematic investigation of interactions between Pt and perovskite thin films was deemed to be worthwhile.

It has been demonstrated that the A-site cations can have a significant impact on determining the metal-perovskite interactions when the perovskite materials are presented as thin films with thicknesses of around 1 nm. For the Rh-ATiO\textsubscript{3} systems reported in CHAPTER 6, changing A-site cations was found to change the Rh particle geometries, reducibilities and the catalytic properties significantly. As discussed in CHAPTER 7, the thermodynamic investigation suggested that Ni is harder to be reduced when supported on perovskite thin films, and shift in equilibrium PO\textsubscript{2} were different for titanates with different A-site cations.

Here, a systematic investigation of the interactions between Pt and three titanate thin films were performed. Unlike what was reported in CHAPTER 6 and CHAPTER 7, interactions between Pt and the three perovskite thin films were found to be similar. High-temperature reduction
was required to activate all three samples for CO oxidation and the Pt particles were found to be rhombohedral when in their active phase. However, there were minor differences between these samples. The pretreatment temperatures required to activate the catalysts varied with composition of the A-site cations. Interactions between Pt and three perovskite thin films suggest that Pt interacts most strongly with CaTiO$_3$/MgAl$_2$O$_4$, followed by SrTiO$_3$/MgAl$_2$O$_4$ and BaTiO$_3$/MgAl$_2$O$_4$. 
8.2 Experimental Methods

The ATiO$_3$/MgAl$_2$O$_4$ supports were the same as what have been utilized in CHAPTER 6 and CHAPTER 7. Detailed preparation and characterizations of the three perovskite thin films can be found in CHAPTER 6. The perovskite thin films were shown to be stable to 1073 K. Pt was then deposited to the sample surface by ALD. To examine the effect of deposition orders, a sample was prepared in which Pt was first deposit onto MgAl$_2$O$_4$ first, after which a 1-nm film of the perovskite was deposited by ALD. This sample is referred to as the “overcoat” sample.

Surface areas for samples prepared by ALD were measured using BET isotherm in a homemade apparatus. X-ray diffraction (XRD) patterns were recorded on a Rigaku MiniFlex diffractometer equipped with a Cu Kα source (λ = 0.15416 nm). ICP-OES were performed on a Spectro Genesis spectrometer with a concentric nebulizer. Ex situ, Scanning Transmission Electron Microscopy Energy Dispersive X-ray Spectroscopy (STEM/EDS) measurements were performed with a JEOL NEOARM.

CO-oxidation rates were determined under differential conversions in a 0.25-inch, quartz, tubular-flow reactor at atmospheric pressure using the GC system described in Section 2.3. The catalyst loadings were 100 mg for all samples. The total gas flow rate was maintained at 120 mL·min$^{-1}$, with partial pressures of 25 torr CO and 12.5 Torr O$_2$, with the balance being He. To investigate the catalytic performance upon different pretreatment conditions, the samples were oxidized in flowing 10% O$_2$:He mixtures at 1073 K for 1 h and reduced in 10% H$_2$:He mixtures at the desired temperatures.
8.3 Results

8.3.1 Preparation of Pt-doped Thin-Film Perovskites

Successful perovskite preparation has been described in CHAPTER 6. When depositing the perovskite first, formation of CaTiO$_3$ was achieved by depositing six cycles of Ca, followed by two cycles of TiO$_2$. For BaTiO$_3$ and SrTiO$_3$ films, to obtain the correct stoichiometry ratio, the deposition was adjusted to six cycles of either Sr or Ba, followed by two cycles of TiO$_2$. After depositing the prerequisite amounts of perovskite precursors, the samples were heated to 1073 K in a muffle furnace in order to form the perovskite phases. It is worth mentioning that deposition of one cycle of Pt prior to depositing the perovskite had minimal impact on the overall growth rates, and the overcoat samples were prepared using the identical order and number of A-site cation and Ti ALD steps. Key properties of the materials used in this manuscript can be found in Table 8-1.

Table 8-1 Key properties for ALD samples in this chapter

<table>
<thead>
<tr>
<th></th>
<th>Specific surface area (m$^2$/g) after 1073 K calcination</th>
<th>ALD thin film loading</th>
<th>Pt loading</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt/CaTiO$_3$/MgAl$_2$O$_4$</td>
<td>84</td>
<td>30 wt%</td>
<td>2.6 wt%</td>
</tr>
<tr>
<td>Pt/SrTiO$_3$/MgAl$_2$O$_4$</td>
<td>71</td>
<td>34 wt%</td>
<td>2.5 wt%</td>
</tr>
<tr>
<td>Pt/BaTiO$_3$/MgAl$_2$O$_4$</td>
<td>64</td>
<td>41 wt%</td>
<td>2.5 wt%</td>
</tr>
<tr>
<td>CaTiO$_3$/Pt/MgAl$_2$O$_4$</td>
<td>77</td>
<td>29 wt%</td>
<td>3.3 wt%</td>
</tr>
<tr>
<td>(overcoat)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SrTiO$_3$/Pt/MgAl$_2$O$_4$</td>
<td>73</td>
<td>34 wt%</td>
<td>3.3 wt%</td>
</tr>
<tr>
<td>(overcoat)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
8.3.2 Characterization of Pt/ATiO₃/MgAl₂O₄ Samples

To determine the morphology of the ALD films, samples listed in Table 8-1 were analyzed by STEM/EDS. To ensure that the films were well crystallized, each of the samples was calcined at 1073 K and then reduced at the same temperature prior to any measurements. The STEM/EDS results for Pt/CaTiO₃/MgAl₂O₄ were reported in Section 5.3.4, but are reproduced here. STEM/EDS results can be found in Figure 8-1, Figure 8-2 and Figure 8-3 for the samples after 1073-K reduction. The micrographs were similar in all three cases. The MgAl₂O₄ showed features in the 10- to 20-nm size range but there were no discernable changes upon addition of the perovskite films. The EDS mappings were similarly featureless and showed that both Ti and the alkali metals covered the surfaces uniformly. This implies that the component oxides for each perovskite were well mixed on the surface following deposition and that there was no agglomeration of the films into particles, even after heat treatments at 1073 K. In Section 5.3.4, it was reported that rhombohedral Pt particles were found when Pt was supported on CaTiO₃ thin films, after high-temperature reduction. Results for the “overcoat” sample in which CaTiO₃ was deposited onto the Pt were indistinguishable from those in which the perovskite was deposited first. Similar to the previous findings, the particles on SrTiO₃ and BaTiO₃ films were found to exhibit rhombohedral shapes. There was also evidence for a surface reconstruction on the Pt/SrTiO₃/MgAl₂O₄ and Pt/BaTiO₃/MgAl₂O₄ samples, since the signals for the perovskite materials, especially the titanium signal, were found concentrated near the Pt particles.
Figure 8-1 Representative STEM results for Pt/CaTiO$_3$/MgAl$_2$O$_4$, after five 1073-K redox cycles, with the final step being reduction, with EDS maps of Mg, Al, Ca, Ti and Pt.

Figure 8-2 Representative STEM results for Pt/SrTiO$_3$/MgAl$_2$O$_4$, after five 1073-K redox cycles, with the final step being reduction, with EDS maps of Mg, Al, Sr, Ti and Pt.
For all three Pt/ATiO\textsubscript{3}/MgAl\textsubscript{2}O\textsubscript{4} samples, I observed similar XRD patterns. In each case, all of the peaks can be assigned to either the MgAl\textsubscript{2}O\textsubscript{4} support, the corresponding perovskite phase, or the Pt metal peaks. It is worth mentioning that large Pt XRD peaks were observed on all three samples, potentially due to the rhombohedral shape of the particles, as well as the alignment with the supporting perovskite thin films.

**Figure 8-3** Representative STEM results for Pt/BaTiO\textsubscript{3}/MgAl\textsubscript{2}O\textsubscript{4}, after five 1073-K redox cycles, with the final step being reduction, with EDS maps of Mg, Al, Ba, Ti and Pt.
8.3.3 CO Oxidation Rates

Rate measurements were performed to understand the similarities and differences between these three perovskite thin films. CO-oxidation activities were obtained on each of the thin-film catalysts loaded with Pt. Each of the thin-film catalysts was first aged by five redox cycles at 1073 K, but the final step before rate measurements was the 1073-K oxidation step. Because the catalyst properties of exsolution catalysts are sensitive to the reduction temperature, differential rates were measured after reduction in 10% dry H₂ in He for 1 h at 573 K, 773 K, 973 K and 1073 K to probe the degree of interactions between Pt and the three different perovskites. The hypothesis was that...
interaction strength can be correlated to the reduction temperature required to achieve high catalytic performance.

Figure 8-5 Steady-state, differential reaction rates for CO oxidation with 25 Torr of CO and 12.5 Torr O₂ for (a) Pt/CaTiO₃/MgAl₂O₄, (b) Pt/SrTiO₃/MgAl₂O₄, and (c) Pt/BaTiO₃/MgAl₂O₄ as a function of reduction temperature. Reduction pretreatment temperature: (white) 573 K reduction, (light grey) 573 K reduction, (dark grey) 973 K reduction, and (black) 1073 K reduction.

To determine whether catalyst properties depend on whether the perovskite is deposit before or after the Pt, rates for Pt/CaTiO₃/MgAl₂O₄ and Pt/SrTiO₃/MgAl₂O₄ were compared with CaTiO₃/Pt/MgAl₂O₄ (overcoat) and SrTiO₃/Pt/MgAl₂O₄ (overcoat). As shown in Figure 8-6, both the overcoat samples show a relatively better catalytic performance initially. It is possible that the overcoat layer acted to prevent Pt sintering. However, when probing the effect of reduction temperature, the trend was found to be identical to the samples in which the metal was deposited onto the perovskite.
Rates for the Pt/ATiO\textsubscript{3}/MgAl\textsubscript{2}O\textsubscript{4} samples as a function of reduction temperature were measured and compared in Figure 8-5. Although Pt can be oxidized and form volatile PtO\textsubscript{2} vapor at elevated temperatures [128, 129], no evidence for loss of Pt was observed here. Strong interactions between Pt and the perovskite films can lead to different catalytic behavior, however. CO oxidation performance Pt/CaTiO\textsubscript{3}/MgAl\textsubscript{2}O\textsubscript{4} as a function of pretreatment conditions were reproduced in Figure 8-5(a). As discussed in Section 5.3.2, the oxidized Pt/CaTiO\textsubscript{3}/MgAl\textsubscript{2}O\textsubscript{4} showed low CO-oxidation rates, indicating that the strong interaction led to the poor performance when the sample is oxidized. A significant increase of CO oxidation rates can only be observed when the sample is reduced at 1073 K. Clearly, reduction temperatures below 1073 K were not sufficient to place the sample into its active phase.

Results on Pt/SrTiO\textsubscript{3}/MgAl\textsubscript{2}O\textsubscript{4} are shown in Figure 8-5(b). The absolute rates for the sample after different pretreatments were slightly different from what was found for
Pt/CaTiO$_3$/MgAl$_2$O$_4$, potentially due to some degree of promotion provided by the SrTiO$_3$ thin films, or due to the relatively smaller Pt particle sizes in this sample. Different from what was found for the Pt/CaTiO$_3$/MgAl$_2$O$_4$ sample, a lower reduction temperature is able to partially activate the catalyst. At higher the reduction temperatures, higher rates were observed. Upon reduction at 1073 K, the sample reached its highest catalytic performance.

Rate data for Pt/BaTiO$_3$/MgAl$_2$O$_4$ in Figure 8-5(c) suggest a different trend for the catalytic performance as a function of reduction temperature. After 973-K reduction, the activity is almost the same as the activity after 1073-K reduction, suggesting that 973K might be sufficient to reduce the Pt back to its active form.

To present the rate data for all three perovskite-supported, thin-film catalysts in a more direct, comparable manner, the rates for samples at 453 K were measured as a function of reduction temperature. Because some of the conversions were below the detection limit of the GC, those rates were extrapolated using the activation energy from the Arrhenius plot shown above. Figure 8-7 shows the rate comparison without any normalization to account for dispersion. One can clearly see that the rates for these three samples were dramatically different, as was the effect of reduction temperature. I observed rates that were ten times higher on some samples, even when the particle sizes were found to be only slightly different, as shown in the STEM/EDS results. Again, this is potentially due to the different promotional effect from the different perovskite thin films.
Figure 8-7 Measured or extrapolated rates for CO oxidation at 453K with 25 Torr of CO and 12.5 Torr O₂ for (▲) Pt/CaTiO₃/MgAl₂O₄, (■) Pt/SrTiO₃/MgAl₂O₄, and (●) Pt/BaTiO₃/MgAl₂O₄ as a function of reduction temperature.

Figure 8-8 shows rates for each of the samples normalized to their rates after reduction at 1073 K in order to show how different the effect of reduction temperature is on the three samples. The rates after different pretreatments are reported as a percentage of the performance of that specific sample after reduction at 1073 K. For Pt/CaTiO₃/MgAl₂O₄, rates increased only after sample was reduced at 1073 K, suggesting that the activation of the sample is only possible at high temperatures. For the Pt/SrTiO₃/MgAl₂O₄ sample, there is a clear increase in catalytic performance at lower temperatures. Finally, for the Pt/BaTiO₃/MgAl₂O₄ sample, 80% of the ultimate performance can be achieved after reduction at 973 K. This suggests that Pt interacts less strongly with the BaTiO₃ thin film.
Figure 8-8 Normalized rates for CO oxidation at 453K with 25 Torr of CO and 12.5 Torr O₂ for (▲) Pt/CaTiO₃/MgAl₂O₄, (■) Pt/SrTiO₃/MgAl₂O₄, and (●) Pt/BaTiO₃/MgAl₂O₄ as a function of reduction temperature.
8.4 Discussion

Preparation of thin film perovskites has been demonstrated as an effective way of fully utilizing the concept of “intelligent” catalyst [130]. While specific metal-perovskite interactions have been largely ignored in the past, recent studies on the thin film samples have shown that perovskites with similar structure, when in their thin film forms, can have dramatic impact on the properties of the geometry and the catalytic performance of the supported metals. For example, as discussed in CHAPTER 6, Rh particles were found to have very different geometries when supported on different titanate thin films. The work shown here with Pt demonstrates that the interaction between metal and the perovskites can be combination specific. From the evidence listed in this chapter, the degree of interaction between Pt and ATiO₃ thin films can be ranked in this order: Pt/CaTiO₃/MgAl₂O₄ > Pt/SrTiO₃/MgAl₂O₄ > Pt/BaTiO₃/MgAl₂O₄.

The ultimate performance was also dependent on the particular perovskite composition, suggesting that there might be different support effects for Pt catalysts on with different titanates. Transition metals can catalyze the reduction of the host perovskite materials [122, 131, 132], and it is likely that the extra oxygen vacancies created by doped Pt enhances the catalytic performance. However, this effect is not large with Pt and the titanates, given that the activation energy for CO oxidation did not change and that no changes in reaction orders for CO or O₂ were observed.

Similar to the previous results on the Pt-LaFeO₃ thin-film system [118], huge and sharp peaks for Pt were observed on all three Pt/ATiO₃/MgAl₂O₄ samples. It was claimed that the strong interaction between Pt and the perovskite thin film leads to epitaxial growth of very small Pt clusters on the perovskite surface. While the STEM/EDS results in this chapter demonstrated existence of larger Pt particles on the Pt/ATiO₃/MgAl₂O₄ samples, and the Scherrer Equation would indicate
average Pt particle size of 19 nm, 22 nm and 30 nm on Pt/CaTiO$_3$/MgAl$_2$O$_4$, Pt/SrTiO$_3$/MgAl$_2$O$_4$ and Pt/BaTiO$_3$/MgAl$_2$O$_4$, respectively, we cannot rule out the possibility that these Pt particles were actually two-dimensional and in registry with the perovskite thin films. The fact that no CO adsorption can be found on these samples clearly suggested the unique interactions between Pt and the support materials.

Results in this chapter clearly demonstrate that there is much to learn about the exsolution process and its derivations. In collaboration with computational simulation, it is possible to have a better mechanistic understanding of different systems [133-136]. But one should realize that factors such as the different geometries of the perovskite materials and the additional strain introduced by the MgAl$_2$O$_4$ substrates could make the simulation results inconsistent with the experimental findings.

Although the difference in the Pt-perovskite interactions were not that significant, the reported results clearly suggested that tuning the A-site cations can be a potential route to tune the properties of Pt, thus achieving better selectivities for potential reactions. For example, Pt nanoparticles supported on SrTiO$_3$ perovskite nanocuboids were found to be able to convert plastic bags into high-quality liquid product such as lubricants and waxes, while Pt/Al$_2$O$_3$ can only over-hydrogenolyze polyethylene to undesired light hydrocarbons [137]. Changing A-site cations can potentially allow us to better understand the reaction mechanisms behind reactions similar to this one and provide guidance on future catalyst design.
8.5 Conclusions

In this chapter, I demonstrated the different degrees of interactions between Pt and three different titanate thin films. Under different reduction conditions, the samples showed different paths to reaching the ultimate performance. Pt/CaTiO$_3$/MgAl$_2$O$_4$ cannot be activated until 1073-K reduction. For Pt/SrTiO$_3$/MgAl$_2$O$_4$, partial activation was found possible at relatively lower temperatures. The reduction temperature for Pt/CaTiO$_3$/MgAl$_2$O$_4$ to achieve the ultimate performance is highest among the three perovskite-containing samples. Comparing to the results in the previous chapters for Rh-ATiO$_3$ and Ni-ATiO$_3$ interactions, the differences were found to be less significant. But changing A-site cations certainly provides an opportunity for tailoring the Pt properties.
CHAPTER 9. CONCLUDING REMARKS AND SUMMARY

This thesis focuses on preparing titanate thin films on high-surface-area substrates by Atomic Layer Deposition (ALD) and characterizing the resulting catalytic properties when using these materials as supports for transition-metal catalysts. The unique properties of the thin-film perovskite systems presented in this thesis provide guidance for future catalyst design.

First of all, ALD can be a powerful tool for thin-film perovskite preparations due to its self-limiting growth mechanism, the good mixing of the deposited materials, and the similar growth rates of different ALD processes. Successful preparation of CaTiO$_3$, SrTiO$_3$ and BaTiO$_3$ thin films on MgAl$_2$O$_4$ with a thickness of ~1nm were demonstrated in this thesis, and the ATiO$_3$/MgAl$_2$O$_4$ samples were proven to be thermally stable. Evidence from multiple characterization techniques suggested that the deposited materials remained a uniform film even after high-temperature redox treatments. X-Ray Diffraction confirmed the perovskite phase formation for all three samples. The presence of intense perovskite diffraction peaks for 1-nm films suggests formation of relatively large, two-dimensional crystals, randomly oriented with respect to the support. The high surface areas and the good thermal stability of these materials bring opportunities for fulfilling the potential of the “intelligent catalyst” concept.

Detailed investigation of metals deposited onto these ATiO$_3$/MgAl$_2$O$_4$ materials surfaces clearly suggested similarities between thin-film and bulk perovskite materials. In general, for the metal-perovskite pairs where the metal and perovskite interact strongly in the bulk form, I found that high-temperature reductions were also required to activate their thin-film counterparts. Specific to individual systems, connections between bulk and thin-film samples were observed. In CHAPTER 4, it was demonstrated that similar to bulk titanates, the Ni/ATiO$_3$/MgAl$_2$O$_4$ can be
coke-resistant when exposed to dry methane. In **CHAPTER 5**, it was shown that sintering of Pt is suppressed upon high-temperature redox cycles if Pt is deposited onto CaTiO$_3$/MgAl$_2$O$_4$. Similar to the bulk CaTi$_{0.95}$Pt$_{0.05}$O$_3$, the Pt/CaTiO$_3$/MgAl$_2$O$_4$ sample was active for CO oxidation while inactive for toluene hydrogenation reaction. Also, Pd does not interact with CaTiO$_3$/MgAl$_2$O$_4$, just like its bulk counterparts. All the evidence clearly suggested the close connection between thin-film and bulk samples. The concept demonstrated in this thesis can potentially overcome the disadvantages of bulk “intelligent catalysts”, including but not limited to the low surface areas and slow diffusion, but keep the similar metal-perovskite interactions and the desired properties.

While the thin-film and bulk samples show many similarities, one should realize that there are differences between these systems. In **CHAPTER 5**, I reported an unusual rhombohedral shape for Pt particles after high-temperature reduction for Pt/CaTiO$_3$/MgAl$_2$O$_4$. Results suggested the Pt particles were in registry with the underlying supports. No CO chemisorption could be detected on the Pt even though the Pt/CaTiO$_3$/MgAl$_2$O$_4$ was active for CO oxidation. Surface reconstruction was also identified for the Pt/CaTiO$_3$/MgAl$_2$O$_4$ sample, although no previous literature suggested similar findings for the bulk Pt-CaTiO$_3$ system. For the Rh/CaTiO$_3$/MgAl$_2$O$_4$ sample described in **CHAPTER 6**, the sample was not active even after high-temperature reduction, while the bulk Rh-doped CaTiO$_3$ can be quite active for CO oxidation after similar pretreatments. The different geometries of the perovskite materials, and the addition of a third component of MgAl$_2$O$_4$ could potentially lead to the discrepancies between bulk and thin-film samples. However, further investigation is required to get more precise answers.

Changing A-site cations in the ATiO$_3$/MgAl$_2$O$_4$ systems can clearly lead to the different degree of interactions between the metal and the perovskite thin films. The results in **CHAPTER 6** suggested that Rh particle sizes, reducibility, and catalytic properties can be greatly affected by
the A-site cations of the titanate systems. In **CHAPTER 7**, I showed that Ni oxidation equilibrium constant vary with the A-site compositions. **CHAPTER 8** suggested that upon different reduction pretreatments, the catalytic performance for CO oxidation were different for Pt deposited on the titanate thin films with different A-site cations. Interestingly, I found that, for all three transition metals (Rh, Ni and Pt) investigated, the ordering of support interactions was the same: CaTiO$_3$ interacts most strongly and BaTiO$_3$ least with the doped metals. While A-site cations certainly changed the properties of the Rh, Ni and Pt systems, the degrees of impact were different, Rh catalysts were affected the most by changing A-site cations, followed by Ni and Pt. Factors such as the surface terminations of the perovskites, the available oxidation states of the doped metals, and the free volumes of different perovskites can all potentially lead to the different properties.

In conclusion, ALD allows successful preparation of thin-film titanate perovskites. Metals deposited onto the thin-film perovskites show both similarities and differences compared to their bulk counterparts. A-site cations can be quite impactful in determining the metal-perovskite interactions on the thin-film samples, leading to changes in doped metal geometries, reducibility and catalytic properties.
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