

STUDY OF METAL CATALYSTS SUPPORTED ON THIN FILMS OF PEROVSKITES

PREPARED BY ATOMIC LAYER DEPOSITION (ALD)

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ABSTRACT

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Sintering is a severe problem for supported-metal catalysts in high-temperature applications, such as in automotive-emissions control, because it leads to a loss of catalytically active surface area. To stabilize the metal particles, in 2001, the Daihatsu group proposed using perovskite-supported metals, which they referred to as “intelligent” catalysts. The original goal was to regenerate sintered metals by driving the metal into the oxide lattice by high-temperature oxidation and releasing the metal as small particles by reduction. Unfortunately, the concept has not been entirely successful, partially because of the large crystallite size and low surface areas of typical perovskites. To achieve higher surface areas and reduce the length scale for any ingress-egress of metal particles, Atomic Layer Deposition (ALD) was used in this thesis to prepare thin films of perovskites on high-surface-area supports. These ALD films were shown to be uniform and thermally stable under high-temperature operating conditions. Metal catalysts, Pt, Ni, Pd, and Rh, were deposited onto the perovskite thin films, LaCoO_3 and LaFeO_3 , using ALD. The catalysts exhibited several key properties similar to bulk “intelligent” catalysts. First, the metal particles could be stabilized by the perovskite films under high-temperature

conditions. Second, the ALD platinum-group metal catalysts showed self-regenerative activity in CO oxidation upon oxidation and reduction at high temperatures. Third, like the Ni ex-solved from bulk perovskite materials, Ni supported by ALD perovskite films showed superior coking resistance towards methane. The metal particles in this thesis were likely very different from bulk intelligent catalysts because the film thickness was much smaller than the metal particle size. To understand their behaviors, this thesis focused on studying metal-perovskite interactions in the ALD samples of metals supported on LaFeO_3 films. It was found that metal-perovskite interactions could dramatically affect the preferential alignment of metal particles with the substrate, the metal dispersions, and catalytic activity. In the presence of the perovskite films, the equilibrium oxidation of the metals could also shift several order-of-magnitudes towards lower PO_2 . The changes in the thermodynamic properties would further cause different catalytic behaviors. Systems of different metals supported on LaFeO_3 films were studied and compared; it was found that the metal-perovskite interaction is specific for each system.

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CHAPTER 1. INTRODUCTION

1.1 Background: Sintering of Metal Catalysts

Supported-metal catalysts are widely utilized in industrial reactions ¹⁻³; however, many isolated metal sites or nanoparticles are not stable and seriously experience deactivation at high temperatures due to sintering ⁴⁻⁵. There are two known sintering mechanisms: Oswald ripening (OR) and particle migration and coalescence (PMC) ⁵⁻⁶. OR happens when the larger particles absorb atoms from small particles due to the difference in surface energy, while the route of PMC is that small particles migrate and collide with each other, followed by the formation of larger crystallites. It is generally believed that at the early stage of sintering, PMC dominates. Once the particle size reaches a certain level, the migration of large particles is less favored, and the growth is mainly due to OR ⁶. Sintering is one of the major reasons for catalyst deactivation because it leads to a loss in the active metal surface area, an increase in pore size, and a decrease in reaction activity ⁷.

One significant example of catalyst deactivation due to sintering is the platinum group metals used as the Three-Way Catalysts (TWC) in the automotive catalytic converter ⁸⁻¹⁰. To remove the unburned carbon monoxide (CO), hydrocarbons (HC), and nitric oxides (NO_x) released from the internal combustion engine, the catalytic converter that has Pt, Pd, and Rh catalysts is used to convert CO, NO_x, and hydrocarbons to CO₂, N₂, and water through a series of oxidation and reduction reactions ¹¹. However, the TWC needs to be exposed to the oxidizing and reducing environment periodically at high

temperatures (>1073 K), which can cause severe sintering of the metal particles. Fresh Pd particles with an average size of < 5 nm can grow to huge crystallites that are much larger than 100 nm after the high-temperature treatments ¹²⁻¹³. It has been reported that only 1-2% of Pd in the catalytic converter remained at the surface of the particles after 100 k equivalent miles of the catalyst aging ¹².

1.2 Motivation: Uniqueness of “Intelligent” Catalysts

To prevent sintering, researchers have been working on the supports that can stabilize the metal particles ¹⁴. The main approaches include the anchor of metal particles by the strong metal-support interaction, encapsulation of metal particles by a metal oxide layer, and fixation of metal particles in mesoporous materials and zeolite cages. Among all these studies, a unique solution, sometimes referred to as “intelligent” catalysts, was first proposed in 2001 by researchers at Daihatsu ¹⁵⁻¹⁷. The principle in developing this kind of material is that metal cations (Pt, Pd, and Rh) can incorporate into a perovskite lattice (ABO_3) under oxidizing conditions, then exsolve as reduced metal particles under reducing conditions. Because the exsolved particles are very small, the catalysts are self-regenerative upon redox cycling at high temperatures.

The most significant advantage of “intelligent” catalysts is that the dispersion of metal particles can be maintained high after high-temperature treatments. The example given by the Daihatsu group is that Pd exsolved from $LaFe_{0.95}Pd_{0.05}O_3$ lattice could be stabilized as 1-2 nm particles even after engine aging at 1173 K, while Pd supported on

conventional high-surface-area Al_2O_3 support would sinter to 120-nm particles after the same treatment. The same sinter-resistance performance was also observed on Pt and Rh particles exsolved from Titanate perovskites ¹⁶.

Following the ground-breaking Daihatsu work, many groups have investigated the ex-solution of transition metals from different perovskite hosts to synthesize stable catalysts for various applications. Besides simply stabilizing the dispersion, some other interesting catalytic properties were observed over these “intelligent” catalysts.

First, Ni particles exsolved from perovskite lattice showed excellent coking resistance when exposed to hydrocarbons at different conditions ¹⁸⁻²⁸. One possible explanation is that large Ni particles are more prone to whisker formation compared to small ones ²⁹⁻³³, and “intelligent” catalysts provide the opportunity to keep the Ni particles small under the harsh conditions of reforming reactions. Chai *et al.* demonstrated that metallic Ni could exist in 2.5-nm particles after a reduction of $\text{La}_{0.46}\text{Sr}_{0.34}\text{Ti}_{0.9}\text{Ni}_{0.1}\text{O}_3$ at 950 °C, showing no growth of carbon fiber under conditions of Methane Dry Reforming at 700 °C with $\text{CH}_4:\text{CO}_2=2:1$ ²⁵.

However, particle size alone cannot explain the coke resistance of exsolved Ni particles under some other conditions. For example, Neagu *et al.* reported that 20-nm Ni particles formed by high-temperature reduction of the $\text{La}_{0.4}\text{Sr}_{0.4}\text{Ni}_y\text{Ti}_{1-y}\text{O}_{3-y}$ also did not form carbon fibers when exposed to 20% CH_4/H_2 at 800 °C for 4 h, while similarly sized Ni particles prepared by vapor deposition on a $\text{La}_{0.4}\text{Sr}_{0.4}\text{TiO}_3$ substrate did form large amounts of carbon ²⁸. The authors believed that the strong interaction between the

exsolved Ni particles and the parent perovskite had anchored the particles and formed a socketed structure ³⁴. Since Ni particles were embedded into the perovskite, the growth of fibers from the interface between Ni and support appears to be suppressed. With increased reduction temperature, the authors reported the formation of larger particles (~80 nm) that did promote carbon growth, perhaps indicating that the interaction between exsolved particles and the parent oxide becomes less important at larger particle sizes. A similar observation was also reported by Otto *et al.* on Ni exsolved from $\text{La}_{0.5}\text{Ca}_{0.4}\text{Ni}_{0.2}\text{Ti}_{0.8}\text{O}_{2.95}$ ²³. In methane temperature-programmed reduction, carbon fibers started to grow on the Ni particles after reduction at 900 °C, which suggested that larger Ni particles were less affected by the support.

The other unique catalytic behavior found over “intelligent” noble metal catalysts is that there is a significant change in CO adsorption properties, which can change the reaction order for CO oxidation. For precious metal catalysts used for the TWC, CO oxidation is often examined as a probe reaction. On nonreducible supports, the reaction is structure insensitive; and the rate is known to be directly proportional to the surface dispersion of active metal particles, following a Langmuir-Hinshelwood mechanism. In excess CO, rates over Pt, Pd, or Rh supported on inert oxides show an inverse, first-order dependence on CO, with an activation energy close to 26 kcal/mol, a value that is equal to the heat of CO adsorption ³⁵⁻³⁶. It is well known that the CO poisoning of exposed metal surface in CO oxidation prevents the adsorption of O₂, further inhibits the reaction.

Singh *et al.* reported that a Pd-doped BaCeO₃ catalyst (BaCe_{0.90}Pd_{0.10}O_{3-δ}), in which Pd could reversibly enter the perovskite host, showed comparable rates for CO oxidation as dispersed Pd on Al₂O₃, even though it had a much lower surface area. The authors pointed out that Pd(II) in the lattice was the active phase for the reaction³⁷, but the most interesting observation from this work was that the reaction order in CO over BaCe_{0.90}Pd_{0.10}O_{3-δ} was zero under CO-rich conditions. This implies weaker adsorption of CO. The authors further argued that the oxygen storage capacity of BaCeO₃ increased dramatically when Pd was added so that the oxygen vacancies on the perovskite surface allowed independent O₂ activation without the competition of CO adsorption³⁸.

In another example, it was also reported that Pd-doped LaFeO₃ showed only half of the activation energy over Pd/Al₂O₃ for CO oxidation³⁹. For the doped sample, the reaction order in CO was found to be positive. Also, the activation energy was independent of the CO:O₂ ratio, whereas the order in CO was negative for the impregnated Pd on LaFeO₃. The activation energy increased monotonically as the CO partial pressure increased. The impregnated sample behaved more like a conventional Pd catalyst, while Pd doped in LaFeO₃ showed clearly different CO adsorption properties.

1.3 Limitations of Bulk “Intelligent” Catalysts

Although “intelligent” catalysts can exhibit such interesting behaviors, there are several significant limitations that prevent the potential of this kind of catalyst from being fully realized. Conventional bulk perovskite materials are usually synthesized using the

sol-gel method or other similar ways. To form pure crystallites of perovskite without contaminants of single-component oxides or carbonates, calcination at high temperatures is required at the final step of perovskite synthesis. Even when high-surface-area perovskites are prepared, they must remain catalytically and mechanically stable under very harsh conditions since they need to experience redox cycles at temperatures above 1273 K for TWC applications. However, such conditions usually cause the surface area of a perovskite material to drop to less than 1 m²/g. In contrast, conventional catalytic supports, such as Al₂O₃, MgAl₂O₄, and SiO₂, can have stable surface areas of more than 100 m²/g after calcination at 1173 K. Furthermore, these supports are less sensitive to redox cycles. Therefore, the low surface areas of bulk perovskite materials will, in turn, lead to lower activity of the “intelligent” catalysts.

Along with the low surface areas, the crystallite sizes of bulk perovskite materials are generally large, often more than 100 nm. As a result of that, the kinetics for metal particles to ingress into and egress out of the perovskite lattice will be slow. The mechanism of ex-solution has been carefully studied using Scanning Transmission Electron Microscopy (STEM) by the Pan group. They pointed out that metal atoms will first form particles in the bulk, then egress to the surface⁴⁰⁻⁴³. Because of this, they raised questions about the accessibility of reduced metal particles. For example, in a study of Pt doped in CaTiO₃, they showed that Pt cations could only move a few nanometers under reducing conditions at 1073 K. Most of the reduced Pt particles remained in the bulk without having access to gas phase reagents. This observation was later confirmed by Kim

et al. over the $\text{La}_{0.2}\text{Sr}_{0.7}\text{Ti}_{0.9}\text{Ni}_{0.1}\text{O}_{3-\delta}$ system. The majority of “exsolved” Ni particles were found in the bulk, even after reduction at 1173 K for 12 h, while only a few particles were on the surface available for reaction ⁴⁴.

In addition to slow kinetics, questions have been raised whether ex-solution is reversible. Indeed, unlike the original suggestion that metal atoms can reversibly go in and out of the lattice, it was found that the dissolution of particles is not 100% reversible for most of the systems. A good example of the irreversibility is Rh doped in CaTiO_3 ⁴³. After aging with a final step of oxidation, ~90 % of Rh was found on the surface of perovskite crystallites with an average size of 10 nm. Presumably, the particles that remain on the surface keep growing. With time, the advantages of an “intelligent” catalyst are lost as the aging time and the number of redox cycles increases.

1.4 High-Surface-Area, Thin-Film Supports Prepared by ALD

One possible solution to increase the perovskite surface area and decrease the length scale for ingress and egress of metal particles is to make thin films of perovskites on an inert, high-surface-area substrate. The thin films can then be used as the supports for the metal catalysts. The interaction between the metal particles and the perovskite films may stabilize the metal particles in the same way as occurs with bulk “intelligent” catalysts.

In this thesis, I used Atomic Layer Deposition (ALD) to grow thin films with precise control. ALD is unique among thin-film deposition techniques in that it can be

applied to porous materials. The principle behind ALD is that organometallic precursor vapors can react with sites on a substrate surface. Since the adsorption of precursor ligands is self-limiting, reaction stops at one monolayer. After removing excess precursor by evacuation or purging with an inert gas, the adsorbed precursor is oxidized. Films of varying thickness can be prepared by repeating the adsorption-oxidation cycle, and the loading of each oxide can be precisely controlled by the number of ALD cycles. In my work, this procedure resulted in uniform, conformal films for the oxides deposited.

Assuming the films are dense, the physical properties of the films should be the same as the bulk perovskites; therefore, film thicknesses can be determined from the weight loading of the perovskite. For example, a 1-nm, uniform film of LaFeO_3 (density of 6.65 g/cm^3) on a $120\text{-m}^2/\text{g}$ substrate results in a sample with 0.8 g of LaFeO_3 per gram substrate. The specific surface area of the sample is expected to drop from $120 \text{ m}^2/\text{g}$ to $67 \text{ m}^2/\text{g}$ ($120/1.8$) after the deposition due to the increased mass of the sample. Based on this simple calculation, one can also see that the film thickness is limited to $\sim 1 \text{ nm}$ in order to maintain a high surface area.

1.5 Scope of the Thesis

This thesis has 8 chapters. Chapter 2 describes the experimental methods used throughout the thesis, including catalyst synthesis methods and characterization techniques.

Chapter 3 talks about the preparation of six high-surface-area functional oxide supports using ALD. The resulted ALD films had similar surface area areas and surface morphologies, and I set out to study the support effects over Pd catalysts for CO and CH₄ oxidation reactions. The growth rates and physical properties of the ALD films investigated here provide a solid foundation for the preparation of perovskite thin films. The different support effects observed over the Pd-functional metal oxide systems indicated the importance of metal-support interactions for catalytic properties.

In Chapter 4, Pt supported on 0.5-nm LaCoO₃ films on MgAl₂O₄ was investigated, with a focus on catalytic properties. The ALD catalyst showed similar catalytic behavior to bulk “intelligent” catalysts. It exhibited self-regenerative activity for CO oxidation and Water-Gas-Shift (WGS) reaction upon high-temperature oxidation and reduction. The reaction order in CO was measured under conditions of different CO:O₂ ratios. Similar to what had been found over the bulk BaCe_{0.9}Pd_{0.1}O₃ sample, the reduced Pt/LaCoO₃/MgAl₂O₄ showed a reaction order near zero in CO and no CO chemisorption at room temperature. We also found unique selectivities for Pt/LaCoO₃/MgAl₂O₄, given that the reduced catalyst showed superior activity for CO oxidation but exceptionally low activity for toluene hydrogenation. The ability to turn on one class of reaction while turning off the other gives the ALD “intelligent” catalyst interesting potential for selective reactions in some catalytic applications.

Because LaCoO₃ itself is unstable to the high-temperature reduction, to further study the structure of the supported metal and the reasons behind the unique catalytic

behaviors of the ALD “intelligent” catalyst, a more stable LaFeO_3 perovskite support was prepared. In Chapter 5, Pt supported on 0.5-nm LaFeO_3 films was studied using X-Ray Diffraction (XRD), STEM, and XAS. A strong metal-support interaction was found between Pt and LaFeO_3 films, shown by an epitaxial registration of Pt with respect to the underneath LaFeO_3 lattice on the oxidized samples.

In Chapter 6, a study of Rh, Pt, and Pd on 1-nm LaFeO_3 films is reported. The metal-interaction strengths of the three systems were compared using metal dispersions, reduction kinetics, and thermodynamic measurements. The results demonstrated that Rh shows the strongest binding interaction with the LaFeO_3 films, followed by Pt and Pd.

Chapter 7 is an investigation of the thermodynamic properties of Ni supported on LaFeO_3 films. It was found that the equilibrium constant for oxidation of Ni to NiO is shifted significantly towards lower PO_2 in the presence of LaFeO_3 . This shift directly impacted the catalytic activity for Methane Dry Reforming by causing the catalyst to be oxidized under some reaction conditions.

Finally, all the conclusions are summarized in Chapter 8.

CHAPTER 2. EXPERIMENTAL METHODS

Summary

In this chapter, a general description is given of the experimental methods used throughout the dissertation research. The home-built setup and operational process for ALD are discussed in this chapter, as is the most critical synthesis method of the catalysts used in this thesis. Flow reactor setups with a gas chromatograph and a mass spectrometer are described, as are the apparatus used for reaction measurements throughout the thesis. Detailed theoretical and operational explanations are given for flow titration and coulometric titration, which were used to investigate the thermodynamic properties of the metal catalysts supported on ALD films.

2.1 Synthesis of High-Surface-Area MgAl_2O_4 support

A MgAl_2O_4 spinel was used as the support for ALD in order to achieve high-surface-area perovskite films. It was prepared by precipitating the mixed aqueous salt solution of magnesium nitrate hexahydrate (>99% purity, Sigma Aldrich) and aluminum nitrate nonahydrate (98%-102%, Sigma Aldrich) with an ammonium bicarbonate solution. Magnesium and aluminum nitrates were dissolved into DI water in a 1:2 molar ratio, and the final concentration of the solution was 0.15 M for Al^{3+} and 0.075 for Mg^{2+} . The concentration of the ammonium bicarbonate solution was selected as 1.5 M, and the initial pH value was adjusted to 11.5 with aqueous ammonia. Although Mg compounds have a relatively high solubility in pH-neutral solutions, alkaline conditions will favor their

complete precipitation. For the precipitation step, 400 mL of the mixed salt solution was added at a speed of 5 mL/min into 600 mL of ammonia bicarbonate solution under stirring at 323 K. The resulting precipitate was then filtered using suction filtration, rinsed with distilled water, and dried in the oven (343 K) overnight. The dried precipitate was then heated to 1173 K in a muffle furnace for 12 h to form a stable spinel structure. The resulting powders were washed in 10-mL concentrated HNO_3 (70 %, Fisher Scientific) for 1 h and rinsed in distilled water to remove any excess MgO that might form during the calcination. Finally, the resulting suspension was heated to 773 K to remove all nitrates. After this treatment, XRD was measured on the powders to ensure that only the MgAl_2O_4 phase existed. The BET surface areas of the MgAl_2O_4 powders varied slightly from batch to batch but were in the range of 120 m^2/g to 135 m^2/g .

2.2 Atomic Layer Deposition

ALD has been widely used in the semiconductor industry to grow films on flat surfaces with low surface areas ⁴⁵⁻⁴⁶. In order to grow relatively thick films, between 2 nm and 20 nm, at a reasonable rate, the precursor vapors and oxidant gases are typically passed through the sample chamber with a high-velocity carrier gas. The time for each of the four required ALD steps (precursor reaction with the surface, purging of the excess precursor vapors, oxidation of the adsorbed ligands, and purging of the oxidant) is typically around 0.5 s. Therefore, based on the typical growth rate for ALD, ~ 0.04 nm/cycle, a 10-nm film requiring 250 cycles requires 500 s to complete ⁴⁷⁻⁴⁸.

However, the flow system is not appropriate for deposition on porous materials for two main reasons. First, diffusion limitations in high-aspect-ratio pore structures would lead to large gradients in the film thickness. Due to the large aspect ratios of the pores, the time for precursor vapors and by-products to diffuse into and out of the pores would be much longer than 0.5 s, and the growth of films will not be uniform over the whole surface of the support. Second, most of the precursors used in conventional ALD pass through the system and are lost since most precursor vapors do not contact the substrate before leaving the chamber. This would result in a huge waste because the cost of precursor accounts for a significant part in manufacturing a catalyst. Finally, because the films for our application do not need to be more than ~1-nm thick, fast cycling is less important.

To fulfill the requirements of ALD on porous materials, a static ALD setup was used to prepare the samples in this thesis. A diagram of the equipment is shown below as **Figure 2.1**. This home-built system consists of three heated chambers with separate temperature controllers, one chamber for the substrate and two for the precursors. The temperature of the substrate chamber is maintained at a desired surface reaction temperature according to the reported ALD temperature window for each metal oxide. The precursor chamber is heated to generate ~5 Torr of vapor pressure, and the temperature is controlled below the decomposition point of the precursor. The precursor vapors are initially held in a sealed vessel. A roughing pump is used to evacuate the substrate vessel to ~100 mTorr. Next, the precursor vapors enter into the evacuated

substrate vessel. The substrate is exposed to 5 Torr of the precursor vapors for 60 s to perform the adsorption. It is important to note that because the surface area of the substrate, i.e., number of active sites, is large and adsorption of each precursor molecule generates by-products, the total pressure of the by-products is not trivial compared to the precursor vapor pressure. In order to solve the problem of back diffusion of by-products, the substrate vessel is evacuated after 60 s of exposure to purge the by-products, followed by a fresh exposure of the precursor vapors. The adsorption-purge step was typically repeated 5 times to ensure a saturated surface reaction.

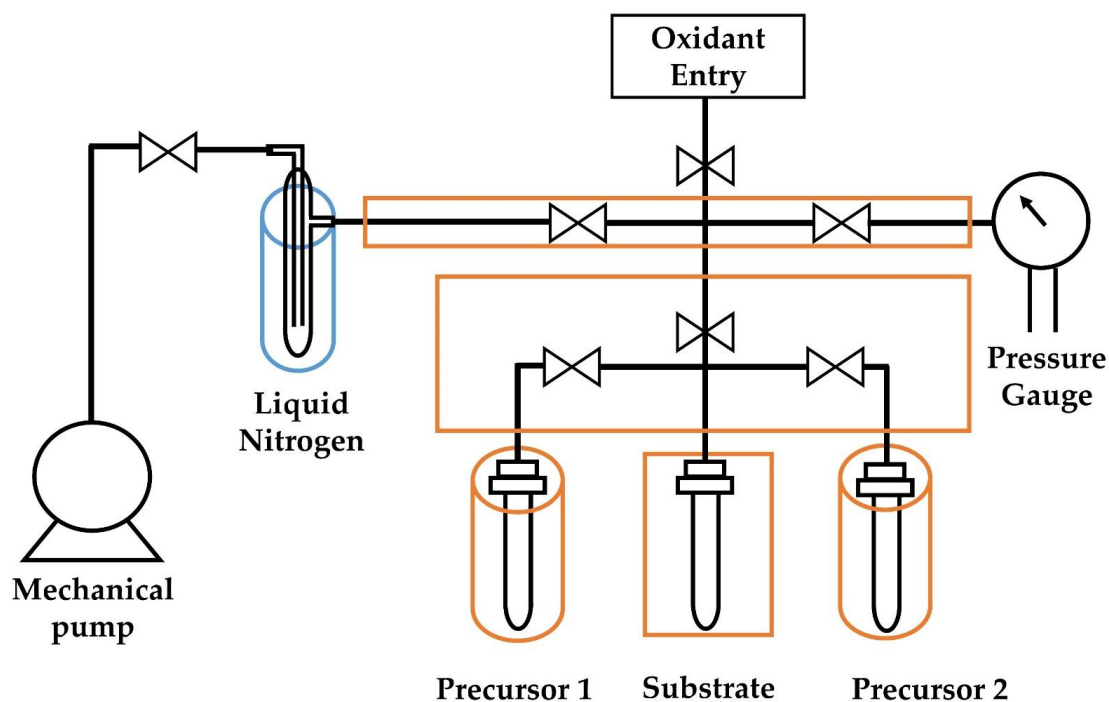


Figure 2.1: Scheme of the home-built static ALD system. The orange boxes represent heating chambers or other heating elements. The valves used here are “stainless steel secondary packed bellows sealed valve, welded, spherical stem tip, 1/4 in.” from Swagelok, and the Cajon fittings for tubes used here are “stainless steel bored-through ultra-torr vacuum fitting, reducing union, 1/2 x 1/4 in. tube OD” from Swagelok.

To complete one ALD cycle, the adsorbed precursors need to be oxidized to generate active sites for the next adsorption step. The selection of oxidant and oxidation temperature varied from precursor to precursor. For example, TiCl_4 can be oxidized using H_2O at 423 K ⁴⁹ and $\text{W}(\text{CO})_6$ can be oxidized using air at 473 K ⁵⁰, while $\text{La}(\text{TMHD})_3$ can only be fully oxidized by exposing to air at 673 K for 7 minutes. For precursors that are easily oxidized at lower temperatures, oxidant gases were pulsed into the ALD system. However, for precursors with TMHD ligands, the samples needed to be placed in a muffle furnace with a temperature higher than 773 K for ~5 minutes to ensure the removal of all the ligands. The valves and connections were maintained at 473 K to 523 K to avoid condensation of precursor due to cold spots. A liquid- N_2 cold trap was placed before the roughing pump to keep unused precursor from flowing into the pump and causing damage.

Table 2.1 lists the deposition conditions and growth rates of all the metal oxides that have been deposited using the static ALD equipment. The oxidant used for all these precursors was air, except for TiCl_4 , which used water.

Table 2.1: Deposition conditions and growth rates of metal oxides prepared by ALD.

Metal oxide	Precursor	Substrate	Pre T* (K)	Sub T* (K)	Oxi T* (K)	Oxi t* (min)	Grow R* (nm/cycle)
CeO ₂	Ce(TMHD) ₄	ZrO ₂	503	503	773	5	0.017
ZrO ₂	Zr(TMHD) ₄	ZrO ₂	503	503	773	5	0.030
WO ₃	W(CO) ₆	ZrO ₂	403	473	473	6	0.023
CeO ₂	Ce(TMHD) ₄	γ -Al ₂ O ₃	503	523	773	5	0.020
ZrO ₂	Zr(TMHD) ₄	γ -Al ₂ O ₃	503	523	773	5	0.015
Fe ₂ O ₃	Fe(Cp) ₂	γ -Al ₂ O ₃	433	573	573	5	0.019
MnO ₂	Mn(TMHD) ₃	γ -Al ₂ O ₃	523	503	773	5	0.019
Co ₃ O ₄	Co(TMHD) ₃	γ -Al ₂ O ₃	523	503	773	5	0.013
NiO	Ni(TMHD) ₂	γ -Al ₂ O ₃	523	503	773	5	0.019
La ₂ O ₃	La(TMHD) ₃	MgAl ₂ O ₄	523	503	873	3	0.015
Fe ₂ O ₃	Fe(Cp) ₂	MgAl ₂ O ₄	433	573	773	5	0.025
Co ₃ O ₄	Co(TMHD) ₃	MgAl ₂ O ₄	523	503	773	5	0.013
TiO ₂	TiCl ₄	MgAl ₂ O ₄	363	423	423	7	0.025

*: Pre T = precursor temperature; Sub T = substrate temperature; Oxi T = oxidation temperature; Oxi t = oxidation period; Grow R = growth rate.

2.3 Flow Reactor Setups

2.3.1 Flow reactor with a gas chromatograph

This setup consists of a 1/4-inch, quartz, tubular flow reactor connected to an on-line gas chromatograph (SRI8610C), which is equipped with a Hayesep Q column and a TCD detector. For each measurement of steady-state, differential reaction rates, 0.1-g samples were placed in the middle of the tube. A layer of granular quartz with a thickness of 1 cm was placed on the front and at the back of the catalyst bed to fix its position. The reactor was then heated by a Ceramic Radiant Cylinder heater, and the temperature was measured with a K-type thermocouple positioned at the catalytic bed. The mass flow controllers connected to a “four channel flow controller power supply and readout” (MSK instruments, Inc.) were used to control the gas flow rates. The flow conditions for each reaction are specified in each chapter.

2.3.2 Flow reactor with a mass spectrometer

Light-off reaction profiles and flow titration were measured over samples in a separate tubular flow reactor with an on-line quadrupole residual gas analyzer (SRS-RGA-100). The reactant and product compositions can be monitored continuously. Again, the flow rates are controlled by the mass flow controllers connected to a “four channel flow controller power supply and readout”. Switching between different gas streams was controlled by computer-controlled solenoid valves. Flow conditions for each measurement are specified in each chapter.

2.4 Thermodynamic Measurements

2.4.1 Flow Titration

An equilibrium PO_2 can be established by a fixed H_2 - H_2O mixture, assuming equilibrium for the H_2 oxidation reaction, $H_2 + \frac{1}{2}O_2 = H_2O$. The equilibrium PO_2 's established by H_2 and H_2O with different ratios are shown in **Table 2.2**, using Equation 1.

$$(PO_2)^{\frac{1}{2}} = K_{eqm}^{-1} \frac{PH_2O}{PH_2} \quad (Eq.1)$$

Flow-titration experiments were performed by placing 0.5-g samples in the flow reactor described in **Chapter 2.3.2**, reducing the catalyst in dry H_2 for 30 min, and then equilibrating the catalyst in a flowing H_2 - H_2O mixture (20 mL/min) for another 30 min. The partial pressure of H_2O in the H_2 - H_2O mixture was controlled by the temperature of a water bubbler through which the H_2 passed. After purging the reactor with dry He, the sample was exposed to dry, flowing air (5 mL/min) while monitoring the effluent products using the quadrupole mass spectrometer. The amount of oxygen required to re-oxidize the sample could be calculated by integrating the difference between N_2 and O_2 signals. The average oxidation state of the catalyst at that PO_2 was then determined by the amount of oxygen required to fully oxidize the sample.

Table 2.2: Equilibrium PO_2 's established by H_2 and H_2O at 973 K and 1073 K.

Temperature (K)	$\text{H}_2\text{O}/\text{H}_2$	Log PO_2
973	0.03	-23.9
	0.1	-22.8
	0.2	-22.2
	3	-19.9
	5	-19.4
	10	-18.8
	15	-18.5
	20	-18.2
1073	0.03	-21.4
	0.1	-20.4
	5	-17.0
	20	-15.7

2.4.2 Coulometric Titration

Because there is a limited range of $\text{H}_2\text{:H}_2\text{O}$ ratios that can be accurately measured in a flow system, coulometric titration was used for thermodynamic measurements on samples requiring higher PO_2 for oxidation. In coulometric titration, for which the apparatus is shown schematically in **Figure 2.2**, 0.5-g samples were placed in the center of a YSZ (yttria-stabilized zirconia, 1-cm diameter, 30-cm long) tube, which had Pt electrodes painted on both inside and outside. After placing the YSZ tube in a horizontal tube furnace, the center of the tube with the sample was heated to 1073 K at a heating rate of 1.0 K/min. The sample was then pretreated with flowing gases, either a mixture of 5% H_2O , 10% H_2 ,

and 85% He for experiments that started with a reduced sample or a mixture of 5% H₂O, 10% O₂, and 85% He for measurements starting with an oxidized sample. After the sample had equilibrated, the ends of the YSZ tube were sealed with Cajon fittings and grease. Known quantities of oxygen were then electrochemically pumped into or out of the YSZ tube by applying a known charge across the electrodes using a Gamry instruments potentiostat. After allowing the system to come to equilibrium with the electrodes at an open circuit, the equilibrium PO₂ could be calculated from open circuit potential across the Pt electrodes using the Nernst Equation, shown as Equation 2.

$$E = -\frac{RT}{nF} \ln \frac{PO_{2,inside}}{PO_{2,outside}} \quad (\text{Eq. 2})$$

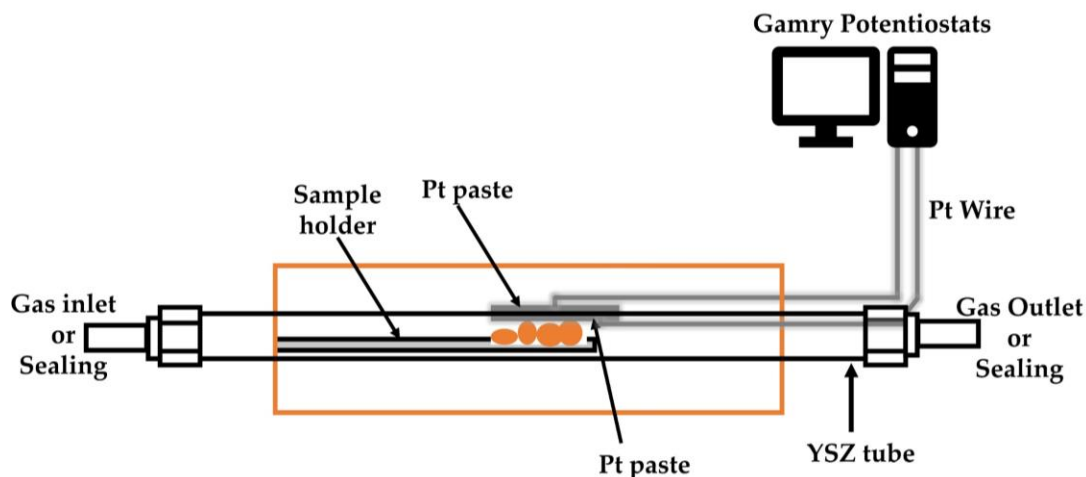
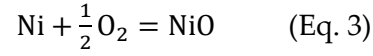


Figure 2.2: Scheme of the coulometric titration, which is used to study the thermodynamic properties of catalysts and supports. The orange box represents a horizontal Ceramic Radiant Cylinder furnace with a temperature controller. The Pt paste on two sides of the YSZ tube are used as electrodes, and a known amount of oxygen can be pumped into or out of the system using a Gamry Instrument Potentiostat.

2.4.3 Thermodynamic Equations

Equilibrium between a metal oxide and the metal can be calculated using the tabulated values of ΔH and ΔS . For example, the procedure for calculating equilibrium PO_2 between Ni and NiO is shown in Equations 3 to 5, where “a” represents the activity of a solid and is unity.



$$\Delta G = \Delta H - T\Delta S = -RT(\ln K_{NiO}) \quad (\text{Eq. 4})$$

$$K_{NiO} = \frac{a_{NiO}}{a_{Ni} \cdot PO_2^{\frac{1}{2}}} = PO_2^{-\frac{1}{2}} \quad (\text{Eq. 5})$$

Heats of formation can be calculated using Equation 6 if isotherms are measured at multiple temperatures. Since the heat of formation is relatively independent of temperature, the equilibrium PO_2 at a lower temperature can be estimated.

$$\Delta H = \left\{ \frac{-R\delta \ln(P_{eqm})}{\delta\left(\frac{1}{T}\right)} \right\}_x \quad (\text{Eq. 6})$$

CHAPTER 3. A STUDY OF SUPPORT EFFECTS FOR CH₄ AND CO OXIDATION OVER Pd CATALYSTS ON ALD-MODIFIED Al₂O₃¹

Summary

This study investigated the effect of support composition on Pd catalysts by preparing uniform films of NiO, Co₃O₄, Fe₂O₃, MnO₂, CeO₂, and ZrO₂ on γ -Al₂O₃ using ALD. Interactions between a metal and its oxide support can influence CO and CH₄ oxidation, but promotion by the support can be difficult to study because the various oxides have different surface structures and surface areas. ALD allowed the preparation of supports with different compositions but similar surface areas and pore sizes. The structure of the films was characterized by XRD and STEM, and catalysts with ~1-wt% Pd were examined for CO and CH₄ oxidation. CeO₂/ γ -Al₂O₃ was unique among the supports in greatly stabilizing the Pd dispersion to 1173 K. Rates for CO oxidation were enhanced by the presence of CeO₂, Fe₂O₃, and MnO₂, while the other oxides had no promotional effect. For CH₄ oxidation, only NiO and Co₃O₄ were modest promoters, while the other reducible oxides even showed a negative effect on rates. Possible reasons for the differences between CH₄ and CO oxidation activities are discussed.

¹ This chapter was reproduced from Catal. Lett. 2019, 149, 905-915.

3.1 Introduction

A primary challenge for emissions control from natural-gas engines is the difficulty of oxidizing CH_4 and CO at lower temperatures, preferably below 623 K⁵¹, in the presence of a high partial pressure of water. The catalyst must also be catalytically and mechanically stable under very harsh conditions, since it can experience temperatures above 1273 K, conditions which can lead to sintering of both the metal and the support⁵². Better materials are still needed.

CO oxidation over Pd catalysts is reasonably well understood, and the effect of metal-oxide/Pd interactions is clearly important. On non-interacting supports, the reaction is structure insensitive and rates are proportional to the exposed Pd surface area, limited by the rate of O_2 adsorption for higher $\text{CO}:\text{O}_2$ ratios on the CO -saturated surface⁵³⁻⁵⁴. With supports such as CeO_2 that can transfer oxygen at the metal-oxide/Pd interface, rates can be orders-of-magnitude higher than on $\text{Pd}/\text{Al}_2\text{O}_3$ ⁵⁵. The higher rates on Pd/CeO_2 are due to an additional rate process, which has a lower activation energy and is associated with oxidation of CO at the periphery of the Pd particles^{36,55}. The effect of other oxide supports is less well documented, but enhanced CO -oxidation activity has also been reported for Pd catalysts using Fe_2O_3 as a support⁵⁶.

The effects of Pd structure and support are not as well understood for CH_4 oxidation. While PdO_x is recognized as the best catalyst for CH_4 oxidation⁵⁷⁻⁶⁶, most Pd-based catalysts still require operating temperatures in excess of 773 K and tend to deactivate through a loss of active surface area because of sintering and by transformation

of PdO into metallic Pd at temperatures above 873 K ⁶⁷⁻⁶⁸. As with CO oxidation, there is also evidence that the activity and stability of Pd catalysts are affected by interactions with oxides that the Pd is in contact with and oxides that stabilize CH₄ oxidation appear to do so by stabilizing PdO ^{36, 67, 69}. Based on these observations, one might expect that there would be a good correlation between activity for CH₄ oxidation and activity for CO oxidation. For example, ceria is a well-known promoter for CO oxidation on Pd ⁵⁵; and it has been reported that a catalyst consisting of a Pd nanoparticle core surrounded by a thin, porous CeO₂ shell (i.e., a Pd@CeO₂ core-shell catalyst) is capable of exceptional methane-oxidation activities under dry conditions ⁵⁸. Other oxides (e.g., NiO and CoO_x) have also been reported to enhance the activity of Pd catalysts ^{61, 70-72}. Based on the fact that the best catalysts appear to have both metallic and oxidized Pd domains in contact with each other ⁷³⁻⁷⁴, promoters may have an optimal “oxidizing power”, if that is the role of the promoter.

While CO oxidation on Pd is commonly believed to be structure insensitive, the issue is less well resolved for CH₄ oxidation. While some researchers have argued that CH₄ oxidation on Pd is structure insensitive and that rates depend only on the surface area of the Pd ⁷⁵, others have reported specific rates vary strongly with Pd particle size ⁷⁶. A recent study of CH₄ oxidation over Pd/Al₂O₃ even reported that the form of the alumina can affect rates ⁷⁷. That work showed dramatically different turn-over frequencies - by as much as an order of magnitude - depending on whether the form of the alumina was α , θ , or γ , and also stated that the rates varied with Pd particle size on α - and θ -Al₂O₃ but not on γ -Al₂O₃. The authors argued that the support influences the shape of the Pd

particles, with Pd crystallites on some supports having a higher fraction of step and corner sites exhibiting higher activity.

Water is known to be a serious poison for CH₄ oxidation and a catalyst that shows excellent activity only in dry methane is not likely to be useful for natural-gas vehicle applications in which the exhaust will include a high partial pressure of water. Indeed, with the previously discussed, Pd@CeO₂ core-shell catalyst that showed promising activity under dry conditions ⁵⁸, the ceria shell was found to transform into a catalytically inert hydroxide in the presence of water vapor ⁷⁸. Even with more conventional catalysts, CH₄-oxidation light-off temperatures for Pd/Al₂O₃ catalysts are reported to shift upward by 50 to 100 K in the presence of water ⁷⁹. Therefore, minimizing the deleterious effects of water on catalytic activity is an important goal.

Water poisoning is most severe in the presence of high O₂ levels, a result that has been interpreted as demonstrating water deactivation is caused by formation of hydroxyls on the Pd. The hydroxyls are believed to suppress Pd reoxidation to PdO and prevent adsorption of methane ⁸⁰⁻⁸¹. Interestingly, it has been reported that “different oxide supported catalysts have different affinity for hydroxyls, thus different susceptibility to water inhibition” ⁷⁹. This conclusion was also reached by other groups ⁸², some of whom further hypothesized that increasing the oxygen mobility on the surface of the support could make the catalyst more resistant to poisoning by water ⁸³⁻⁸⁴. Based on this hypothesis, controlling the interface between Pd and its support could produce catalytic materials that remain highly active for methane oxidation in the presence of water vapor.

A significant problem in studying the effect of oxide promoters is ensuring contact between the Pd and the promoter. For example, in a WGS study over catalysts prepared by aqueous, co-impregnation of $\text{Pd}(\text{NO}_3)_2$ and $\text{Ce}(\text{NO}_3)_3$ onto Al_2O_3 , the activity was much lower than that of CeO_2 -supported Pd due to poor contacting between Pd and CeO_2 , even though the CeO_2 loading was more than 20-wt% ⁸⁵. In an attempt to improve contact between components, Willis *et al.* ⁷² prepared bimetallic alloys of Pd in which the alloying metal oxidized under reaction conditions. They reported that catalysts made by alloying Pd with Fe, Co, and Sn had improved resistance to sintering and that the intrinsic activities of catalysts made from Pd-Ni and Pd-Zn were somewhat higher than that for Pd alone. However, because the nanoparticle loadings in this study were targeted to give a Pd loading of 0.3 to 0.5-wt%, the promoter loadings were also low, so that contact between the promoter and the Pd may be limited after high-temperature oxidation.

A focus of recent work in our laboratory has been the preparation of high-surface-area, functional catalyst supports using ALD ⁸⁵⁻⁹². In the present study, we used this approach to prepare a series of catalyst supports which had similar surface areas and morphologies but differed in their surface composition. Using $\gamma\text{-Al}_2\text{O}_3$ as the substrate, we examined the effects of NiO , Co_3O_4 , Fe_2O_3 , MnO_2 , CeO_2 , and ZrO_2 . These promoters were chosen because previous reports had suggested that some of them could enhance activity or stability under some conditions.

For purposes of the present study and based on previous experience ^{85, 90}, we considered that 20-wt% of the added metal oxides would be sufficient to ensure contact

between Pd and the oxide promoter. Assuming that the oxide promoters uniformly cover the surface, that the promoters have properties similar to bulk Fe_2O_3 , and that the substrate has a surface area of $100\text{-m}^2/\text{g}$, 20-wt% corresponds to a film that is 0.5-nm thick⁸⁷. The catalytic effects of the films were then evaluated for CO oxidation and CH_4 oxidation under both dry and wet conditions.

3.2 Experimental Methods

The Al_2O_3 substrate in this study was initially stabilized by calcining fresh $\gamma\text{-Al}_2\text{O}_3$ (Strem Chemicals, Inc., $180\text{ m}^2/\text{g}$) in air at 1173 K for 24 h. After this treatment, the Al_2O_3 had a BET surface area of $110\text{ m}^2/\text{g}$. The thin films of the various metal oxides were then deposited onto this substrate by ALD using a home-built, static system that has been described in **Chapter 2.2**. The ALD precursors that were used included $\text{Ce}(\text{TMHD})_4$ (Tetrakis(2,2,6,6-tetramethyl-3,5-heptanedionato)cerium(IV), Strem Chemicals, Inc.), $\text{Zr}(\text{TMHD})_4$ (Strem Chemicals, Inc.), $\text{Mn}(\text{TMHD})_3$ (Strem Chemicals, Inc.), $\text{Co}(\text{TMHD})_3$ (Strem Chemicals, Inc.), $\text{Ni}(\text{TMHD})_2$ (Strem Chemicals, Inc.), and ferrocene ($\text{Fe}(\text{Cp})_2$, Sigma Aldrich).

Briefly, the ALD procedure involved exposing $\sim 0.3\text{ g}$ of the evacuated Al_2O_3 substrate to $\sim 5\text{ Torr}$ of precursor vapors for $\sim 5\text{ minutes}$, followed by the oxidation. The conditions for the deposition of each metal oxide were listed in **Table 2.1**. Growth rates for each oxide film were determined by measuring the sample weights after every five cycles. The number of ALD cycles was varied to achieve a final film loading of 20-wt%.

Pd-containing samples were also prepared using ALD to ensure good contact between the Pd and the surface and to avoid exposing the supports to liquid water, which could potentially break up the oxide films. The Pd was added in one ALD cycle, using Pd(TMHD)₂ (Strem Chemicals, Inc.). In all cases, Pd was deposited onto oxide films that had been calcined to only 773 K to ensure that the oxide film was intact. After adding Pd, the catalysts were then oxidized at either 773 K or 1173 K in the muffle furnace for 6 h.

To demonstrate that the ALD-prepared supports produced films that were more uniform than those prepared by conventional impregnation, the Al₂O₃ substrate was loaded with the same oxides to a loading of 20-wt% using conventional, aqueous impregnation. These samples were prepared using solutions of Ce(NO₃)₃·6H₂O (Sigma Aldrich), ZrO(NO₃)₂·6H₂O (Sigma Aldrich), Fe(NO₃)₃·9H₂O (Sigma Aldrich), Mn(NO₃)₂·6H₂O (Alfa Aesar), Ni(NO₃)₂·6H₂O (Alfa Aesar) and Co(NO₃)₂·6H₂O (Sigma Aldrich). The samples were prepared by incipient wetness, followed by overnight drying at 333 K. Finally, the samples were calcined at 773 K for 6 h.

STEM/Energy Dispersive Spectroscopy (EDS) were performed with a JEOL JEM-F200 STEM, operated at 200 kV. The powder specimen was diluted in methanol and put on lacey carbon films on copper grids (Electron Microscopy Sciences). The catalysts were also characterized by XRD using a Rigaku Smartlab diffractometer equipped with a Cu K α source (λ = 0.15416 nm). Specific surface areas of ALD-prepared supports were measured using BET isotherms with N₂ at 77 K with home-built adsorption equipment⁹⁰. The weight loadings of the ALD-prepared samples were checked using Inductively

Coupled Plasma-Optical Emission Spectrometry (ICP-OES), performed on a Spectro Genesis spectrometer with a Mod Lichte nebulizer. The Pd dispersions were determined by CO chemisorption, assuming adsorption of one CO molecule per surface Pd. For the chemisorption measurements, samples were first oxidized at 673 K in 200 Torr O₂ and reduced in 200 Torr H₂ at 473 K before measuring CO uptakes at room temperature.

Fourier transform infrared (FTIR) spectra were collected with a resolution of 4 cm⁻¹ on a Mattson Galaxy FTIR with a diffuse-reflectance attachment (Collector II™) purchased from Spectra-Tech Inc. Samples were first oxidized in a flowing 20% O₂-He mixture at 573 K for 10 min, then reduced in a 20% H₂-He mixture for 10 min at the same temperature. Spectra were obtained on samples after exposure to pure CO for 20 min at room temperature, followed by a He purge for 10 min.

Steady-state, differential reaction rates were determined for CO oxidation and CH₄ oxidation using the setup described in **Chapter 2.3.1**. For CO oxidation, the total flow rate was maintained at 100 mL/min using a He carrier, with partial pressures of CO (PCO) and O₂ maintained at 25 Torr and 12.5 Torr, respectively. For CH₄ oxidation, the partial pressures of CH₄ and O₂ were maintained at 3.8 Torr and 38 Torr, respectively, with the total flow rate again being 100 mL/min. To determine the effect of water vapor on CH₄ oxidation, rates were also measured in the presence of 76 Torr H₂O, achieved by passing the He component through a heated water bubbler.

To look for the possibility that CH₄-oxidation rates might be affected by water stored on the support, transient conversions were measured in a separate tubular flow

reactor that allowed switching the feed using solenoid valves. Products were then analyzed using an on-line quadrupole mass spectrometer. The reactions were carried out using 0.1-g of catalyst at 623 K, using a total flow rate of 100 mL/min and partial pressures of 7.6 Torr CH₄ and 38 Torr O₂. Every 15 min, the feed was changed to include or remove 10-vol% water vapor.

3.3 Results

3.3.1 Characterization of Metal-Oxide ALD Films

The individual film growth rates for CeO₂, Fe₂O₃, MnO₂, NiO, Co₃O₄, and ZrO₂ on the γ -Al₂O₃ substrate were determined by measuring the sample weights after every five ALD cycles. The specific coverage of metal atoms (metal atoms/m²) could then be calculated from the sample weights using the BET surface area of the alumina (110 m²/g) and the listed metal-oxygen stoichiometry. These specific coverages are shown in **Figure 3.1** as a function of the number of ALD cycles for each of the precursors. In each case, the specific oxide coverages increased linearly with the number of ALD cycles, varying between 4×10^{17} /m² cycle (for Co₃O₄) and 1×10^{18} /m² cycle (for NiO). These values are close to those reported in the classical work by Puurunen ⁹³, who also showed that the growth rates changed by only a small amount depending on substrate pretreatment conditions. The similarity in the growth rates for the various oxides is reasonable given that, with the exception of Fe(Cp)₂, the ligands were the same for the other precursors. The growth rates in nanometers/cycle can also be calculated assuming that the films were uniform over the

entire surface and packed with their bulk densities ⁸⁷. These are reported in **Table 3.1** and show that the growth rates varied from 0.013 to 0.02 nm/cycle. While these values are significantly lower than the 0.1-nm/cycle rate typically reported for alumina films formed by cycling $\text{Al}(\text{CH}_3)_3$ and water, the lower growth rates are reasonable for the precursors used in the present study, given the bulky nature of the ligands.

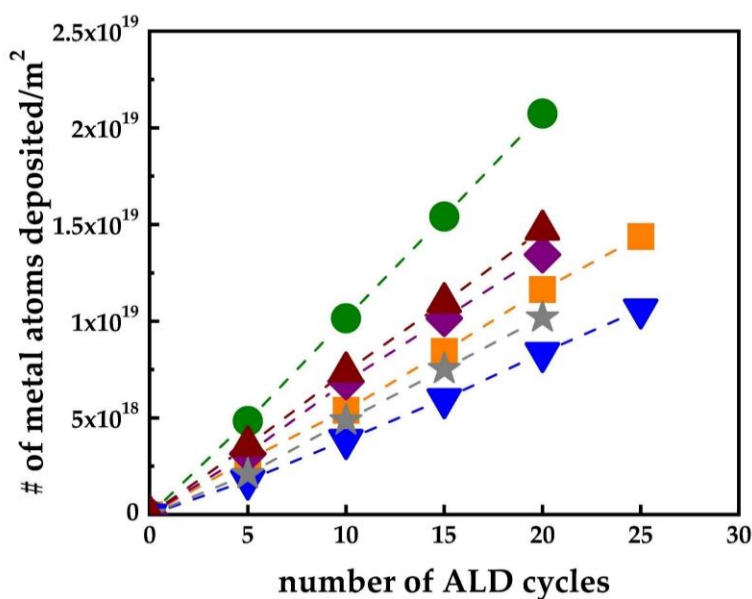


Figure 3.1: Metal atoms per area of $\gamma\text{-Al}_2\text{O}_3$ as a function of ALD cycles: $\text{CeO}_2/\gamma\text{-Al}_2\text{O}_3$ (■), $\text{Fe}_2\text{O}_3/\gamma\text{-Al}_2\text{O}_3$ (▲), $\text{MnO}_2/\gamma\text{-Al}_2\text{O}_3$ (◆), $\text{NiO}/\gamma\text{-Al}_2\text{O}_3$ (●), $\text{CoO}_x/\gamma\text{-Al}_2\text{O}_3$ (▼), and $\text{ZrO}_2/\gamma\text{-Al}_2\text{O}_3$ (★).

Table 3.1: Physical characteristics of ALD-modified γ -Al₂O₃.

	ALD growth rate (nm/cycle)	Metal oxide loading ± 0.50 (%)	BET S.A. (m ² /g)	
			773-K calcination	1173-K calcination
CeO ₂ / γ -Al ₂ O ₃	0.020	22	89	63
Fe ₂ O ₃ / γ -Al ₂ O ₃	0.019	21	90	80
MnO ₂ / γ -Al ₂ O ₃	0.019	19	87	60
NiO/ γ -Al ₂ O ₃	0.019	20	85	69
Co ₃ O ₄ / γ -Al ₂ O ₃	0.015	22	88	61
ZrO ₂ / γ -Al ₂ O ₃	0.013	23	83	65

In this study, we targeted a film loading of 20-wt% and varied the number of ALD cycles in order to achieve that loading. The numbers of ALD cycles required for CeO₂, Fe₂O₃, MnO₂, ZrO₂, Co₃O₄, and NiO were estimated to be 20, 25, 25, 20, 30, and 20 cycles, respectively. The final compositions were also measured by ICP-OES, shown in **Table 3.1**, and these agreed reasonably well with the gravimetric measurements. **Table 3.1** also reports the BET surface areas of the ALD-prepared composite supports after calcination at 773 K and 1173 K. The data demonstrate that the fresh supports calcined at 773 K have very similar surface areas, around 85 m²/g. The decreases in surface areas from that of the γ -Al₂O₃ substrate are primarily because of the added mass of metal oxides (i.e., The surface area of the sample remains constant but the mass increases.). After calcination, the specific surface areas decreased an additional amount to between 60 and 80 m²/g. Since the γ -Al₂O₃ had been calcined to 1173 K prior to adding the metal oxides, the decreases observed here must indicate some additional sintering caused by the metal-oxide films.

Previous work with CeO_2 ⁸⁵, ZrO_2 ⁹¹, and Fe_2O_3 ⁹⁰ ALD films on alumina showed that 0.5-nm films were difficult to observe by electron microscopy; however, because metal oxides added by ALD had a different morphology from impregnated metal oxides, XRD patterns of samples prepared by ALD were distinct. The two-dimensional films prepared by ALD were invisible to XRD for film thicknesses below 1 nm, likely because the films were thinner than the X-Ray coherence length^{85, 90-92}, while two-dimensional particles prepared by impregnation exhibited strong diffraction peaks⁹⁰. Therefore, in the present work, XRD patterns for each of the ALD-prepared samples were compared to those of samples prepared by impregnation to have the same metal-oxide loadings. **Figure 3.2** shows this comparison for each of the oxides, with each set of data displaying patterns for the unmodified $\gamma\text{-Al}_2\text{O}_3$, the ALD-prepared sample calcined at 773 K, the ALD-prepared sample calcined at 1173 K, and the impregnated sample calcined at 773 K. We attempted to normalize the diffraction patterns using peaks from the alumina substrate.

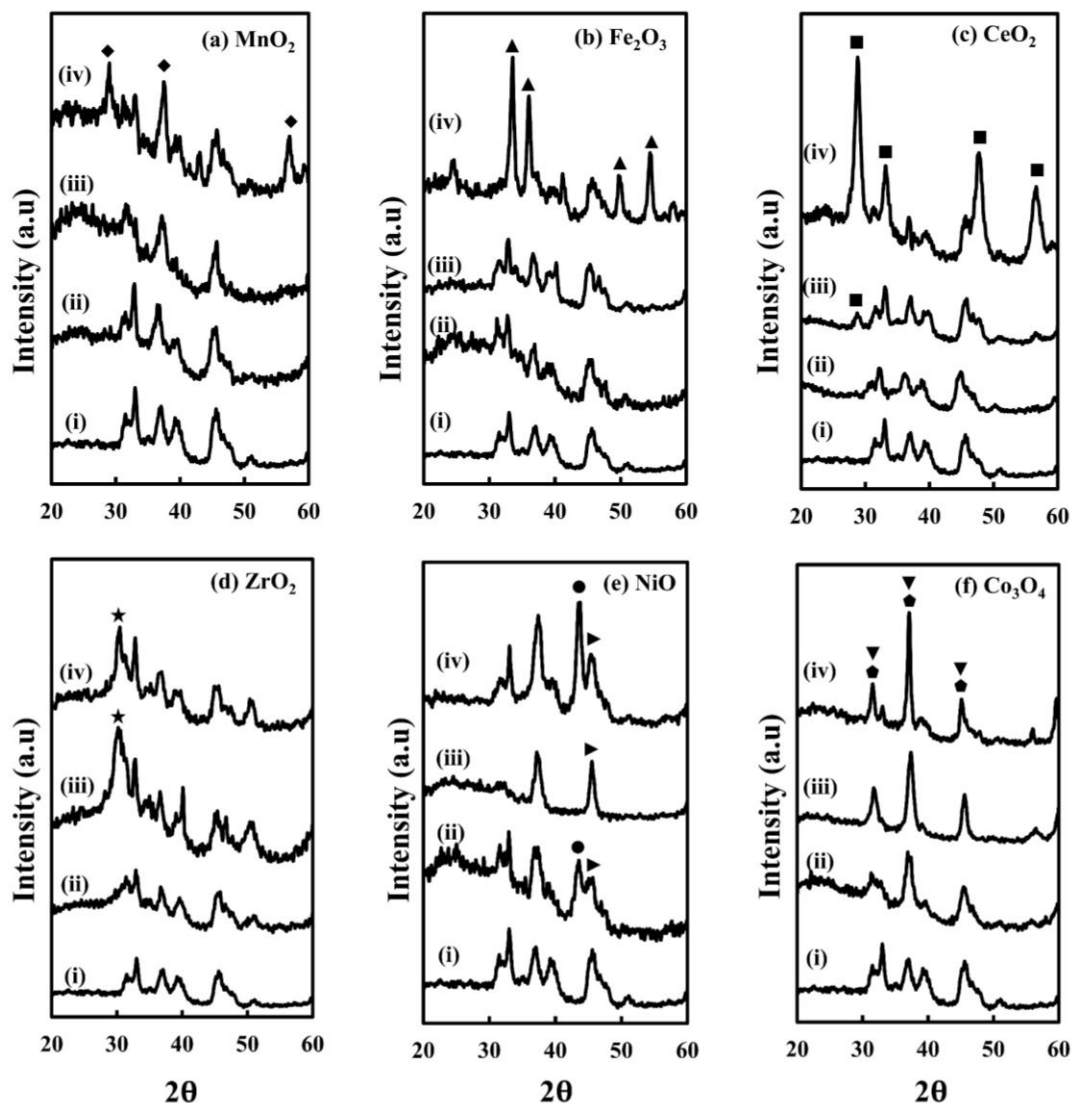


Figure 3.2: XRD patterns for (i) γ - Al_2O_3 ; (ii) ALD-modified sample after 773 K; (iii) ALD-modified sample after 1173 K; (iv) impregnated sample after 773 K. Characteristic peaks are marked as: α - MnO_2 (◆); α - Fe_2O_3 (▲); CeO_2 : (■); tetragonal- ZrO_2 (★); NiO (●); NiAl_2O_4 (►); Co_3O_4 (▼), and CoAl_2O_4 (◆). Peak intensities are normalized to peaks for γ - Al_2O_3 at either $2\theta=33^\circ$ or $2\theta=46^\circ$.

With the exception of $\text{Co}_3\text{O}_4/\gamma\text{-Al}_2\text{O}_3$, and $\text{NiO}/\gamma\text{-Al}_2\text{O}_3$ to a lesser extent, the XRD patterns of samples with ALD films calcined at 773 K did not change significantly from that of the $\gamma\text{-Al}_2\text{O}_3$ itself, even though the oxide loadings were relatively high. The XRD

patterns of the ALD samples with MnO_2 , Fe_2O_3 , and CeO_2 , showed only small features associated with the bulk oxides, even after calcination at 1173 K, suggesting that the films are quite stable. With ZrO_2 , features associated with the tetragonal phase did show significant growth, but only after heating to 1173 K. With NiO, the presence of diffraction peaks associated with the spinel phase and bulk NiO indicate that there is some mobility of the NiO to form particles and to undergo solid-state reactions already at 773 K. Heating to 1173 K completely converted this sample to the spinel phase, as indicated by the XRD pattern and by the fact that the sample turned from dark grey to sky blue in color. With Co_3O_4 , the diffraction peaks associated with the bulk oxide and the spinel phase overlap, making identification of the phases less definitive; however, the entire XRD pattern is dramatically different already at 773 K. We suggest that both phases are likely present after calcination at 773 K but that the sample is completely converted to the spinel phase by 1173 K. The evidence for this is twofold. First, the XRD pattern of the sample after calcination at 773 K exhibits peaks associated with alumina that disappear upon calcination to 1173 K. Second, calcination to the higher temperature caused the sample to turn from dark grey to bright blue, the color associated with tetrahedral Co^{+2} .

In all cases, the XRD patterns of the ALD-prepared samples differed significantly from those of the samples prepared by impregnation and calcined to 773 K. In each of the samples prepared by impregnation, relatively intense diffraction peaks associated with the bulk oxides are readily apparent at the lower temperature. In the Ni-containing sample, NiO dominates the spinel feature. While Co_3O_4 and CoAl_2O_4 are difficult to

distinguish ⁹⁴⁻⁹⁶, the intensity of the Co-associated peaks and the presence of γ -Al₂O₃ features on the sample prepared by impregnation, but not in the ALD sample heated to 1173 K, suggests that Co₃O₄ is the primary species.

Confirmation by STEM that our ALD procedures result in uniform films for CeO₂, ZrO₂, and Fe₂O₃ after calcination at 773 K has been reported previously ⁹⁰⁻⁹². In the case of ZrO₂ ⁹¹, there was some evidence that the film crystallized into very small particles at 1073 K; however, even in this case, the alumina remained uniformly covered, even at higher temperatures. The STEM and EDS results for the Co₃O₄/Al₂O₃ sample after calcination at 773 K, **Figure 3.3**, again show that Co uniformly covers the surface in this case as well. Because this sample turned a bright-blue color after heating to 1173 K, indicating the formation of CoAl₂O₄, it was not analyzed further.

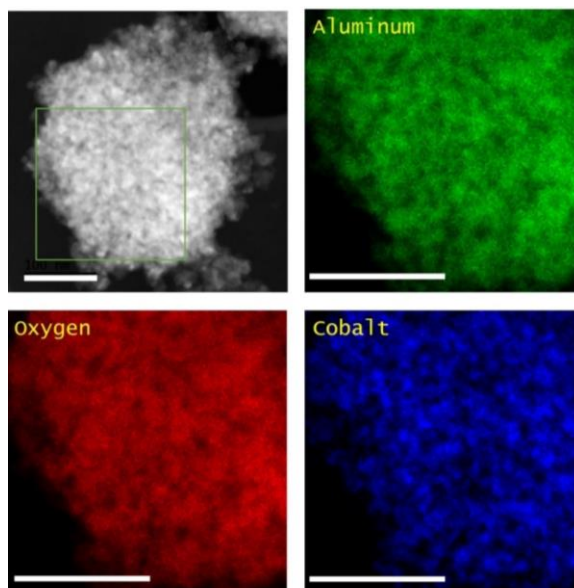


Figure 3.3: High-angle annular dark-field STEM image and EDS maps of Al, O, and Co on ALD $\text{CoO}_x/\text{Al}_2\text{O}_3$ after calcination to 773 K, taken from the region indicated by the green box. The scale bars represent 100 nm.

As will be discussed in the next section, Pd sintering was observed to be dramatically different for the $\text{Pd}/\text{CeO}_2/\text{Al}_2\text{O}_3$ and $\text{Pd}/\text{MnO}_2/\text{Al}_2\text{O}_3$ samples after calcination at 1173 K. Therefore, STEM and EDS measurements were performed on these two samples after calcination to 1173 K, with the data reported in **Figure 3.4** and **Figure 3.5**. With $\text{Pd}/\text{CeO}_2/\text{Al}_2\text{O}_3$, the absence of CeO_2 crystallites in STEM and the overlap in the EDS signals for Al and Ce demonstrate that the CeO_2 remains as a uniform film. Interestingly, the Pd also remained uniformly dispersed. With $\text{Pd}/\text{MnO}_2/\text{Al}_2\text{O}_3$, there is some evidence of non-uniformity in the MnO_2 layer since the EDS maps for Al and Mn do not match up perfectly; but Mn is still present over the entire surface, which is the main point for our purposes here. The fact that the alumina remained covered after 1173 K implies that it was almost certainly covered after calcination to 773 K. What is dramatically

different with MnO_2 is that the Pd has now formed into very large particles. This implies a much stronger Pd- CeO_2 interaction compared to that of Pd- MnO_2 .

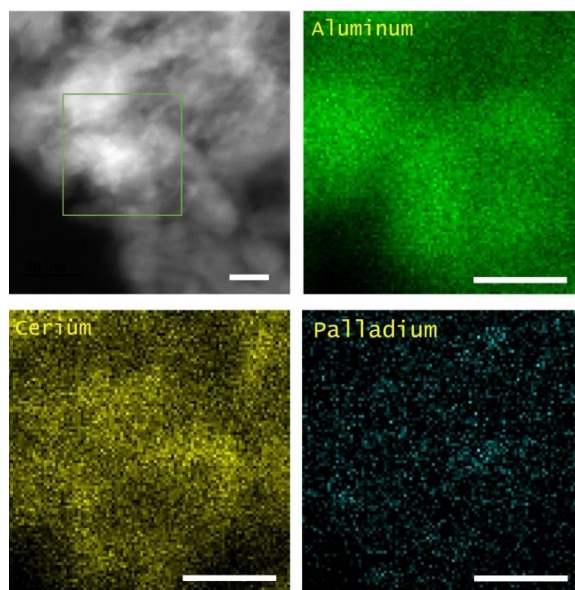


Figure 3.4: High-angle annular dark-field STEM image and EDS maps of Al, Ce, and Pd on ALD Pd/ CeO_2 / Al_2O_3 after calcination to 1173 K, taken from the region indicated by the green box. The scale bars represent 10 nm.

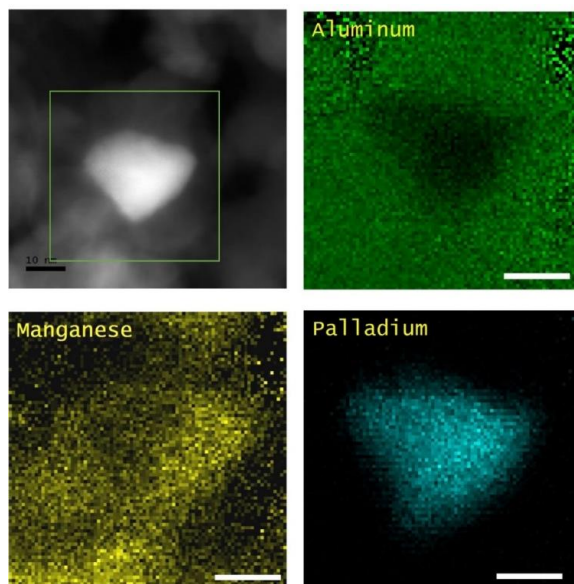


Figure 3.5: High-angle annular dark-field STEM image and EDS maps of Al, Mn, and Pd on ALD Pd/MnO₂/Al₂O₃ after calcination to 1173 K, taken from the region indicated by the green box. The scale bars represent 10 nm.

3.3.2 Pd Particle Characterization

As pointed out earlier, Pd was added to each of the ALD-prepared supports using one ALD cycle of Pd(TMHD)₂. The Pd loadings on each of the supports were determined by ICP-OES and are reported in **Table 3.2**, together with the Pd dispersions, measured by CO chemisorption. After calcination to 773 K, the dispersions were similar for each of the catalysts. With the exception of Pd/CeO₂/Al₂O₃, the dispersions ranged from 18 to 29%. The value on Pd/CeO₂/Al₂O₃, 35%, was higher, reflecting the strong interaction that exists between Pd and CeO₂. We also examined the Pd dispersions after calcination to 1173 K as a further measure of support interaction, recognizing that this higher calcination temperature may also affect the underlying oxide films. The dispersions dropped dramatically for all but the Pd/CeO₂/Al₂O₃ sample. In agreement with the STEM results in

Figure 3.4 and earlier literature reports that CeO₂ can stabilize single-atom catalysts ⁹⁷, Pd remains well dispersed, even after this very harsh treatment.

Table 3.2: Pd loadings and the dispersions as a function of calcination temperatures.

	Pd loading ± 0.2 (%)	Dispersion (%)	
		773-K calcination	1173-K calcination
Pd/ γ -Al ₂ O ₃	1.3	29	7
Pd/CeO ₂ / γ -Al ₂ O ₃	1.1	35	26
Pd/Fe ₂ O ₃ / γ -Al ₂ O ₃	1.3	19	3
Pd/MnO ₂ / γ -Al ₂ O ₃	1.3	26	6
Pd/NiO/ γ -Al ₂ O ₃	1.4	22	2
Pd/Co ₃ O ₄ / γ -Al ₂ O ₃	1.1	22	3
Pd/ZrO ₂ / γ -Al ₂ O ₃	1.0	18	4

To look for evidence that we had formed single-atom catalysts, FTIR spectra of adsorbed CO were obtained at room temperature on the Pd/CeO₂/Al₂O₃ and Pd/Al₂O₃ samples that had been calcined to either 773 or 1173 K. Prior to adsorption of CO, the catalysts were reduced at 573 K in flowing H₂. The spectra are reported in the supporting information of the original publication ⁹⁸. First, results for the Pd/CeO₂/Al₂O₃ and Pd/Al₂O₃ samples calcined at 773 K were very similar. Both samples exhibited peaks near 2090 cm⁻¹ and 1930 cm⁻¹, which can be assigned to on-top and bridged-bond CO, respectively. The intensities of the bands decreased dramatically on the Pd/Al₂O₃ sample after it had been calcined to 1173 K; but there were no major changes in the spectra of Pd/CeO₂/Al₂O₃ upon

high-temperature calcination, consistent with its high Pd dispersion. The similarity in the peak positions and the presence of bridged-bonded CO on all of the samples argues against the presence of single-atom species in our samples.

3.3.3 Reaction Rates

As discussed in the Introduction, CO oxidation on supported Pd catalysts is reasonably well understood. The reaction is structure insensitive on non-interacting supports but some reducible supports can promote reaction at the metal-oxide/Pd interface. **Figure 3.6** is an Arrhenius plot showing differential rates in 25 Torr CO and 12.5 Torr O₂ for each of the Pd-containing catalysts after they had been calcined to 773 K. For a numerical comparison, **Table 3.3** reports the Turnover Frequencies (TOF), normalized to the site densities obtained from the dispersions in **Table 3.2** and extrapolated to 423 K, for each of the catalysts.

Rates over Pd/ γ -Al₂O₃, Pd/NiO/ γ -Al₂O₃, Pd/CoO_x/ γ -Al₂O₃, and Pd/ZrO₂/ γ -Al₂O₃ were all approximately the same based on TOF and the Arrhenius plot, implying that interactions between the metal-oxide support and the Pd had minimal effect on the reaction. The small differences that are observed can be explained in part by small differences in the Pd loadings and the dispersions. On Pd/CeO₂/ γ -Al₂O₃, rates were more than an order-of-magnitude higher, and the activation energy significantly lower (50 kJ/mol, compared to 70 kJ/mol on Pd/ γ -Al₂O₃) due to reaction at the Pd-CeO₂ interface. Rates on Pd/Fe₂O₃/ γ -Al₂O₃ and Pd/MnO₂/ γ -Al₂O₃ were lower than that for the CeO₂-containing catalyst but higher than that for the other catalysts. Both MnO₂ and Fe₂O₃ are

reducible, and oxygen transfer between Pd and Fe_2O_3 has been invoked as an explanation for high WGS rates over Pd/ FeO_x catalysts^{90, 99}. Therefore, it is likely that the increased rates on these samples are again due to reaction at the metal-oxide/Pd interface, although these oxides are much less effective than CeO_2 for enhancing rates.

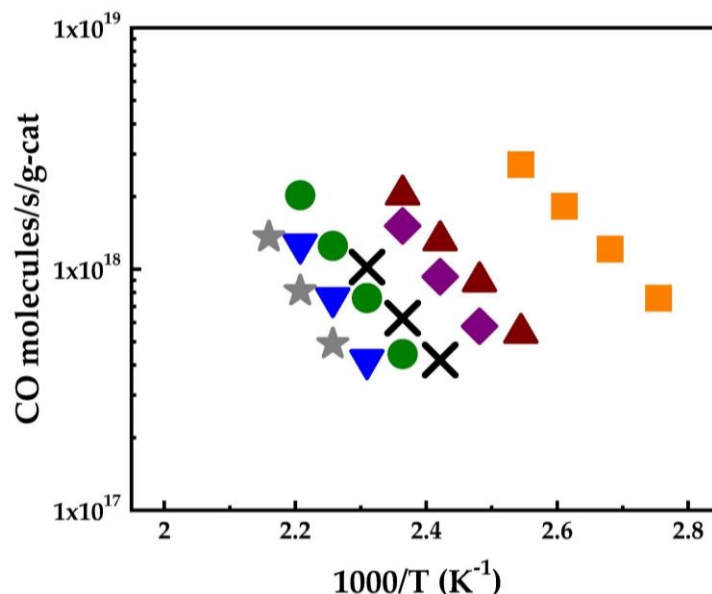


Figure 3.6: Differential, steady-state reaction rates for CO oxidation with PCO and PO_2 of 25 Torr and 12.5 Torr, respectively, on samples calcined to 773 K. Pd/ $\gamma\text{-Al}_2\text{O}_3$ (times), Pd/ $\text{CeO}_2/\gamma\text{-Al}_2\text{O}_3$ (■), Pd/ $\text{Fe}_2\text{O}_3/\gamma\text{-Al}_2\text{O}_3$ (▲), Pd/ $\text{MnO}_2/\gamma\text{-Al}_2\text{O}_3$ (◆), Pd/ $\text{NiO}/\gamma\text{-Al}_2\text{O}_3$ (●), Pd/ $\text{CoO}_x/\gamma\text{-Al}_2\text{O}_3$ (▼), and Pd/ $\text{ZrO}_2/\gamma\text{-Al}_2\text{O}_3$ (★).

Table 3.3: Turnover frequencies for CO oxidation and CH₄ oxidation in dry condition, and differences in temperatures required to achieve 10% conversion of CH₄ in dry condition and wet condition for CH₄ oxidation on samples calcined to 773 K.

	Turnover Frequencies (s ⁻¹)		Difference in temperatures required for 10% CH ₄ conversion in dry and wet conditions (K)
	CO oxidation at 423 K	CH ₄ oxidation at 573 K	
Pd/Co ₃ O ₄ /Al ₂ O ₃	1.9	4.5	75
Pd/NiO/ Al ₂ O ₃	1.9	2.6	80
Pd/Al ₂ O ₃	4.2	2.6	90
Pd/ZrO ₂ /Al ₂ O ₃	1.7	2.5	80
Pd/CeO ₂ /Al ₂ O ₃	31	1.5	100
Pd/Fe ₂ O ₃ /Al ₂ O ₃	16	1.7	100
Pd/MnO ₂ /Al ₂ O ₃	8	1.4	120

The Arrhenius plots for steady-state, differential reaction rates for CH₄ oxidation are shown in **Figure 3.7** for the ALD-prepared catalysts that were calcined at 773 K. **Table 3.3** also summarizes the TOF extrapolated to 573 K for each of the catalysts under dry reaction conditions. Because there are reports that some base-metal oxides, such as CoO_x, can exhibit reasonably high rates by themselves ¹⁰⁰⁻¹⁰¹, methane-oxidation rates were also measured on some of the supports without the addition of Pd (See supporting information of the original publication ⁹⁸.), but these rates were always at least two orders of magnitude lower than those of the Pd-containing catalysts. For calcination to 573 K, each of the Pd-containing, ALD-prepared catalysts must have very good contact between the Pd and the metal-oxide films, so that promotion by the support will be maximized for these materials. The variation in rates was much less than we observed with CO oxidation,

with the most active catalyst, Pd/CoO_x/γ-Al₂O₃, exhibiting rates that were only about five times that of the least active, Pd/FeO_x/γ-Al₂O₃ and Pd/MnO₂/γ-Al₂O₃. The extrapolated TOF varied by a factor of only about three between the most active, Pd/CoO_x/γ-Al₂O₃, and the least active, Pd/MnO₂/γ-Al₂O₃. Notably, there was no enhancement associated with CeO₂, ZrO₂, MnO₂, or FeO_x. In addition to the Co-containing sample, only the Pd/NiO/γ-Al₂O₃ catalyst exhibited an activity that was even equal to that of Pd/γ-Al₂O₃. The modest promotional effect of Co₃O₄ and NiO on CH₄ oxidation is in agreement with previous reports^{61-62, 71}.

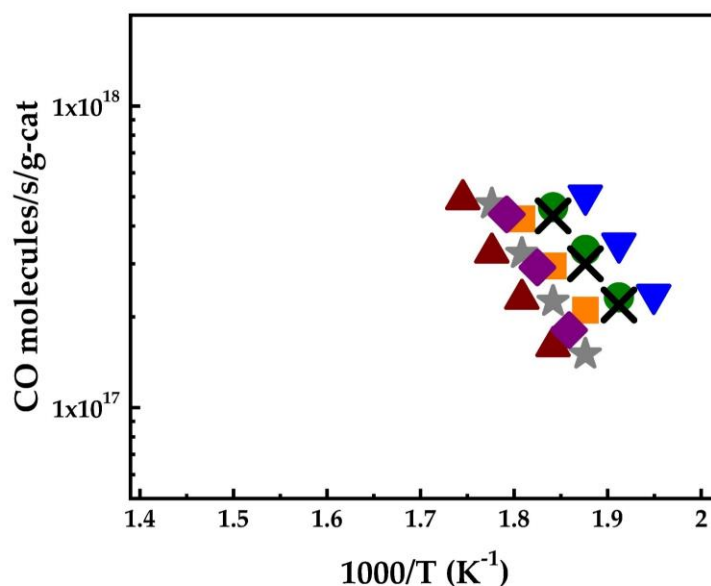


Figure 3.7: Steady-state differential rates for CH₄ oxidation, with PCH₄ and PO₂ of 3.8 Torr and 38 Torr, respectively, on samples calcined at 773 K. Pd/γ-Al₂O₃ (x), Pd/CeO₂/γ-Al₂O₃ (■), Pd/Fe₂O₃/γ-Al₂O₃ (▲), Pd/MnO₂/γ-Al₂O₃ (◆), Pd/NiO/γ-Al₂O₃ (●), Pd/CoO_x/γ-Al₂O₃ (▼), and Pd/ZrO₂/γ-Al₂O₃ (★).

Methane oxidation rates were also measured on these same catalysts in the presence of 10% water, with an Arrhenius plot of the data reported in **Figure 3.8**. The effect of water is also summarized in **Table 3.3**, where we have tabulated the temperature increases required to achieve the same rates under wet conditions as were obtained under dry conditions. The differences between the samples were slightly larger under wet conditions, and there were minor changes in the ordering of the activities; but Pd/CoO_x/γ-Al₂O₃ remained the most active, followed by Pd/NiO/γ-Al₂O₃. In general, **Table 3.3** indicates that there is a direct correlation between the TOF measured under dry conditions and the temperature difference for oxidation in the presence of water vapor. The one exception to this was Pd/ZrO₂/γ-Al₂O₃, which was one of the least active catalysts under dry conditions but was less affected by the presence of water vapor. This is in agreement with another recent report which suggested water poisoning was minimized on ZrO₂-supported catalysts⁸². However, the effect of ZrO₂ is certainly not large. Pd/CeO₂/γ-Al₂O₃, Pd/MnO₂/γ-Al₂O₃ and Pd/FeO_x/γ-Al₂O₃ were affected the most by water vapor. It may be significant that each of these oxides appears to promote CO oxidation activity, suggesting that there may be a relationship between the effects of water on methane oxidation and oxygen transfer at the metal-support interface.

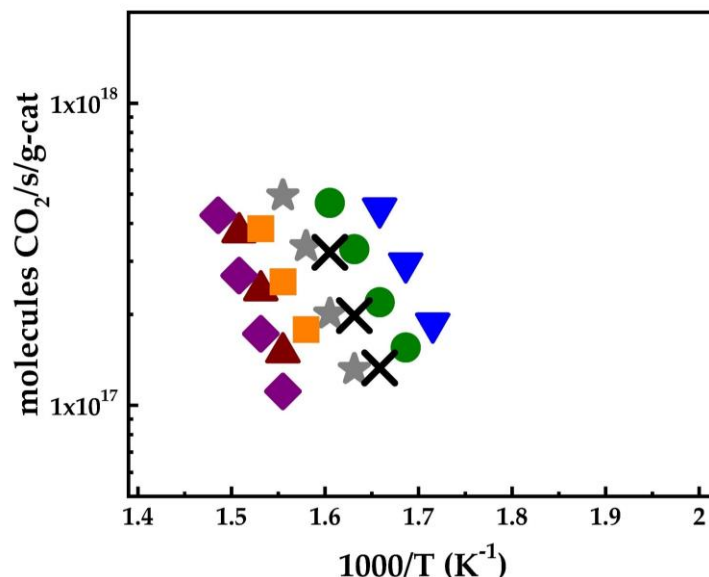


Figure 3.8: Steady-state differential rates for CH₄ oxidation in 10% water vapor with partial pressures of CH₄ and O₂ fixed at 3.8 Torr and 38 Torr, respectively, on samples calcined to 773 K. Pd/γ-Al₂O₃ (×), Pd/CeO₂/γ-Al₂O₃ (■), Pd/Fe₂O₃/γ-Al₂O₃ (▲), Pd/MnO₂/γ-Al₂O₃ (◆), Pd/NiO/γ-Al₂O₃ (●), Pd/CoO_x/γ-Al₂O₃ (▼), and Pd/ZrO₂/γ-Al₂O₃ (★).

Finally, there is some indication from the literature that the oxide supports can “store” water, leading to rates that change with time¹⁰². To determine whether a transient process of this sort could have affected our measurements, we measured the evolution of CH₄ conversion as a function of time after switching from dry-to-wet or wet-to-dry conditions (see Figure 9 in the original publication⁹⁸). For each catalyst, the time required to reach the new steady state was less than 2 min. There was no evidence for water storage on any of our samples, under the conditions of our study.

3.4 Discussion

Promotion of catalytic activity by contact between a metal catalyst and its support is well known for a number of important reactions, but it can be difficult to separate the effect that the support has on the structure of the metal particle from chemical effects associated with the metal-support interface. A good example of this is the case with supported Au catalysts, where the support composition and the metal particle structure can both influence rates ¹⁰³. While there is no perfect method for separating these effects, ALD modification of supports at least allows one to prepare supports in which the composition of the surface can be varied but the surface areas and pore sizes can be maintained a constant. For reactions in which the surface texture plays a role, maintaining that texture may not be possible.

For CO oxidation over Pd, the effects of support composition were significant in the ALD-modified Al_2O_3 , at least with CeO_2 , Fe_2O_3 , and MnO_2 . Consistent with earlier literature reports ⁸⁵, the interface between CeO_2 and Pd particles can promote the reaction rate; and contact between CeO_2 and Pd can be maintained to high temperatures when the CeO_2 is added by ALD. Results from the present study suggest Pd catalysts in contact with films of MnO_2 or Fe_2O_3 also demonstrate somewhat higher activities compared to other metal oxides, probably by transferring oxygen to Pd particles from the reducible metal oxides at the support/Pd interface. Unlike CeO_2 , these oxides did not stabilize the Pd dispersion. Although Co_3O_4 and NiO are also reducible, their presence actually seemed to decrease CO-oxidation rates slightly, perhaps because they are too easily reduced.

With CH₄ oxidation, the role of the support remains less obvious. In agreement with other literature reports, there is a modest promotional effect due to contact with Co₃O₄ and NiO^{61, 70-71} but the effect is not dramatic. What is perhaps most surprising is the fact CH₄ oxidation was not enhanced by contact between Pd and CeO₂. There is strong evidence from earlier work that CeO₂ can stabilize PdO by transfer of oxygen at the interface, and it was expected that this should enhance CH₄ oxidation. There are also previous publications which have reported enhanced oxidation rates for catalysts in which there is contact between Pd and CeO₂^{58, 104}. Because the structure of the catalysts in the earlier work was very different from that in the present study, one must conclude that structure must have played a role in the high rates reported in the previous work.

While we observed modest differences between the various promoters with water poisoning, the effects were again not large and seemed to scale with the TOF, with the most active catalysts affected less by water. This would argue against a direct role of the support in affecting rates, at least under the conditions of our measurements.

Finally, it is important to point out that oxides that promote CO oxidation on Pd do not necessarily promote CH₄ oxidation. Better catalysts are still required, particularly for CH₄ oxidation, and it is not yet clear how to prepare the best materials.

3.5 Conclusion

High-surface-area, functional oxides can be prepared as catalyst supports for Pd using ALD. For the CO oxidation reaction, CeO₂, Fe₂O₃, and MnO₂ films on γ -Al₂O₃ were shown to enhance rates compared to unmodified Pd/ γ -Al₂O₃, while the addition of NiO, Co₃O₄, and ZrO₂ had no effect on the rates. The situation with CH₄ oxidation is more complex, with only Co₃O₄ and NiO showing even modest promotion of the reaction. The results indicate clearly that the promotional effect of each oxide is different for CO oxidation and CH₄ oxidation.

CHAPTER 4. “INTELLIGENT” Pt CATALYSTS BASED ON THIN LaCoO_3 FILMS PREPARED BY ATOMIC LAYER DEPOSITION²

Summary

Bulk “intelligent” catalysts have been reported to exhibit self-regenerative properties upon redox cycling and changes in reaction order for CO oxidation. In this work, catalysts in which Pt is supported on 0.5-nm LaCoO_3 films were prepared using ALD. XRD patterns showed that the films exhibited a perovskite structure, and STEM/EDS data demonstrated that the films covered the substrate uniformly. The Pt remained well dispersed on the perovskite film, even after repeated oxidations and reductions at 1073 K. Despite the high Pt dispersion, CO adsorption at room temperature was negligible. Compared with conventional Pt on MgAl_2O_4 , the reduced forms of the LaCoO_3 -containing catalyst were highly active for the CO oxidation and WGS reactions, while the oxidized catalysts showed much lower activities. Surprisingly, the reduced catalysts were much less active than the oxidized catalysts for toluene hydrogenation, showing ability to turn on one class of reaction (oxidation) while turning off another one (hydrogenation). Catalysts prepared from thin films of Co_3O_4 or La_2O_3 exhibited properties more similar to Pt/ MgAl_2O_4 . Possible reasons for how LaCoO_3 affects properties are discussed.

² This chapter was reproduced from *Inorganics* 2019, 7 (9), 113.

4.1 Introduction

As discussed in the **Chapter 1.2**, the concept of “intelligent” catalysts was developed as a solution for sintering of precious metal catalyst under harsh operating conditions in automotive applications ¹⁵. The principle is that metal atoms can become part of the perovskite lattice for some perovskites under oxidizing conditions, then return to the surface under reducing conditions. This “ingress” of large metal particles into the perovskite and “egress” of smaller metal particles out of the lattice could allow re-dispersion of the catalyst and restoration of activity. However, there are two serious limitations that prevent practical application of the concept. First, the perovskites that are of interest for this application typically have low surface areas, at least after high-temperature cycling. Second, it has been shown that nucleation and subsequent formation of metal particles frequently occurs in the bulk of the perovskite, not at the surface, so that the metal particles that are formed are not accessible to reactants ⁴⁰⁻⁴³.

To avoid the problems associated with bulk perovskites, our group has been preparing thin-film perovskites, between 0.5 and 1.0 nm in thickness, on high-surface-area substrates using ALD. The deposited films retain a high surface area, and because the typical particle size for metal catalysts is greater than 1 nm, nucleation of particles in the bulk of the oxide can be avoided. In past published works, films of CaTiO_3 and LaFeO_3 were grown on MgAl_2O_4 and then used as catalyst supports for Pd ⁸⁶, Ni ¹⁰⁵, and Pt ⁴⁹. The CaTiO_3 and LaFeO_3 films were found to uniformly cover the MgAl_2O_4 support and to be

stable to cycling between oxidizing and reducing conditions (redox cycling) at temperatures as high as at least 1073 K.

Previous work with the thin-film versions of intelligent catalysts exhibited a number of interesting catalytic properties that are similar to what is observed on their bulk counterparts. For example, following an initial calcination at 1073 K, both CaTiO_3 - and LaFeO_3 -supported catalysts reduced at 773 K showed poor catalytic activity, but the same catalysts reduced at 1073 K were very active. This kind of behavior would be expected for bulk-perovskites supports, since high temperatures are required for egress of the metal cations following high-temperature oxidation. Similar to Ni catalysts formed by ex-solution, Ni supported on CaTiO_3 films showed extreme tolerance against coking in the presence of dry methane ¹⁰⁵. Finally, similar to what is observed with bulk perovskites ¹⁷, Pt, but not Pd, was found to interact strongly with CaTiO_3 ⁴⁹.

One of the more interesting perovskites to consider as a catalyst support is LaCoO_3 . LaCoO_3 is much more easily reduced than either CaTiO_3 or LaFeO_3 ¹⁰⁶, implying that there should be a much higher concentration of oxygen vacancies under even mild reducing conditions. This could impact the ease with which metals enter and leave the perovskite lattice. Co oxides are also known to be catalytically active for reactions like CO and methane oxidation ¹⁰⁷⁻¹⁰⁸, and can also promote the activity of Pt for other reactions ¹⁰⁹. Therefore, it is possible that LaCoO_3 could be a promoter for some reactions. Therefore, we set out to examine the properties of Pt on LaCoO_3 films and to compare those

properties to Pt on LaFeO₃. The LaCoO₃ films were again prepared by ALD on MgAl₂O₄ and characterized by catalyst testing and various physical characterization methods.

4.2 Experimental Methods

4.2.1 Sample Preparation

The MgAl₂O₄ support used in this study was prepared in our laboratory using a precipitation method that has been described in **Chapter 2.1**. The final MgAl₂O₄ powder had a BET surface area of 120 m²/g and exhibited only peaks that are characteristic of MgAl₂O₄ in XRD.

La₂O₃, Co₃O₄, and LaCoO₃ films were deposited onto the MgAl₂O₄ support by ALD using the home-built, static system that has been described in **Chapter 2.2**. The ALD precursors used in this study were La(TMHD)₃ (Strem Chemicals, Inc.,) and Co(TMHD)₃ (Strem Chemicals, Inc). The operational details and deposition conditions were also reported in **Chapter 2.2**. Growth rates for each oxide film were determined by measuring the sample weights every five cycles. The film thicknesses were estimated from the mass of the film, assuming it had the bulk density and formed a uniform coating over the entire surface.

For WGS studies, I prepared a Pt/CeO₂/γ-Al₂O₃ sample for comparison. CeO₂ was again added by ALD, using Ce(TMHD)₄ (Strem Chemicals, Inc.) as the precursor. The CeO₂/Al₂O₃ sample was identical to that used in last chapter. The CeO₂ loading was 20-

wt %, corresponding to a film thickness of roughly 0.3 nm, and the BET surface area of the sample was 89 m²/g after calcination to 773 K.

Pt was added to the supports using ALD to ensure good initial contact between the Pt and the surface. One ALD cycle using Platinum(II) acetylacetonate (Strem Chemicals, Inc.) was sufficient to achieve the desired loading. In all cases, the Pt was deposited onto the as-prepared oxide films. In other words, the CeO₂/γ-Al₂O₃ and Co₃O₄/MgAl₂O₄ (Co/MAO) films had been calcined to only 773 K and the La₂O₃/MgAl₂O₄ (La/MAO) and LaCoO₃/MgAl₂O₄ (LCO/MAO) to only 873 K prior to adding the Pt. After addition of the Pt precursor, the samples were oxidized at 573 K to remove the ligands.

4.2.2 Characterization Methods

XRD, BET, CO chemisorption, ICP-OES, and STEM/EDS were used to characterize the samples, with operational details in **Chapter 3.2**.

Steady-state, differential reaction rates for CO oxidation and WGS reaction were measured over 0.1-g samples in the setup described in **Chapter 2.3.1**. Prior to reaction measurements, the catalysts were pretreated in either oxidizing (10% O₂ in He) or reducing (10% H₂ in He) conditions for 1 h at 1073 K. For CO oxidation, the total flow rate was maintained at 100 mL/min using a He carrier. The dependence of the rates on temperature was determined using fixed partial pressures of 25 Torr CO and 12.5 Torr O₂, while reaction orders for CO were measured by varying the CO flow rate for fixed temperatures and O₂ partial pressures. For WGS reaction, the partial pressures of CO and

H₂O were both maintained at 25 Torr, using He as a carrier gas flowing through a water bubbler at 307 K.

Light-off reaction profiles for CO oxidation were measured over 0.1-g samples in the setup described in **Chapter 2.3.2**. The partial pressures of CO and O₂ were maintained at 25 and 12.5 Torr, respectively, in a total flow of 100 mL/min, with He as the carrier gas. For light-off profiles of toluene hydrogenation, the toluene partial pressure was kept at ~7 Torr, achieved by passing the H₂ component through a toluene bubbler that was kept at 273 K. The temperature ramp rate was maintained at 10 K/min from room temperature to 473 K for both reaction measurements.

4.3 Results

4.3.1 Catalyst Characterization

The growth rate for La₂O₃ on MgAl₂O₄ in our system was reported to be 3.4×10^{17} La atoms/cycle·m² (0.017 nm La₂O₃/cycle) in previous work ⁸⁶. The weight changes associated with deposition of Co₃O₄ films on MgAl₂O₄ is shown in **Figure 4.1 (a)**, which demonstrates that the amount Co₃O₄ that was added per cycle was independent of the number of cycles and equal to 5.0×10^{17} Co atoms/cycle·m² (0.013 nm Co₃O₄/cycle, assuming uniform film growth and a bulk density for the film). This growth rate is the same as that measured previously for Co₃O₄ on γ -Al₂O₃ ⁹⁸. Therefore, in order to grow LaCoO₃ films with the correct stoichiometry, we alternated between 3 ALD cycles of La₂O₃ and 2 ALD cycles of Co₃O₄. **Figure 4.1 (b)** shows the sample weight as a function of this

alternating set of ALD cycles and demonstrates that the weight changes for the mixed oxide are consistent with that predicted from the sum of the individual oxides.

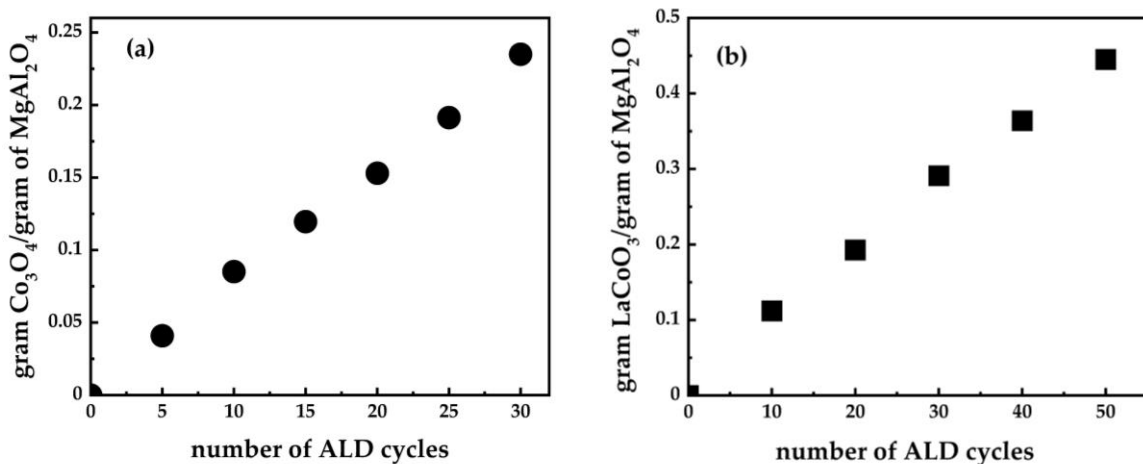


Figure 4.1: The mass gain of (a) Co_3O_4 and (b) LaCoO_3 on MgAl_2O_4 as a function of ALD cycles.

Samples were prepared with either 30-wt% LaCoO_3 (0.3 g of La_2O_3 and 0.15 g of Co_3O_4 on 1 g of MgAl_2O_4), 20-wt% La_2O_3 , or 20-wt% Co_3O_4 . After this, one ALD cycle of Pt was added to each of these materials to produce materials that were roughly 3-wt% Pt. A base-case sample was also prepared with one ALD cycle of Pt on MgAl_2O_4 (Pt/MAO). Each of the samples was then exposed to 5 oxidation-reduction cycles in which they were alternately oxidized in air at 1073 K for 1 h and then reduced in dry H_2 at 1073 K for 1 h. Each of these samples is listed in **Table 4.1**, along with its BET surface area and calculated film thickness.

Table 4.1: Physical properties of samples used in this chapter.

	BET S.A ($\pm 2 \text{ m}^2/\text{g}$)	Metal oxide loading ($\pm 1.5 \text{ wt}\%$)	Pt loading ($\pm 0.2 \text{ wt}\%$)	Film thickness (nm)
Pt/LCO/MAO	58	30	2.9	0.5
Pt/La/MAO	83	20	2.7	0.3
Pt/Co/MAO	81	20	2.8	0.3
Pt/MAO	118	-	3.1	-

XRD patterns of the oxidized and reduced Pt/LCO/MAO, Pt/Co/MAO, and Pt/MAO samples are shown in **Figure 4.2**, with the pattern for MgAl_2O_4 shown at the bottom of each set of patterns for comparison. In addition to the features associated with MgAl_2O_4 , the Pt/MAO sample, **Figure 4.2 (a)**, exhibited intense Pt peaks for both the oxidized and reduced samples. This is consistent with the fact that large Pt particles are formed by the high-temperature redox cycling ¹⁷. Because bulk Pt is difficult to oxidize, XRD patterns for the oxidized and reduced samples remain unchanged. The XRD patterns for Pt/Co/MAO, shown in **Figure 4.2 (b)**. The oxidized sample exhibits Pt features at $2\theta = 39^\circ$ and 46° , but it is difficult to compare intensities of these peaks with those of the substrate due to the overlap in peaks for Co_3O_4 and MgAl_2O_4 . However, when this sample was reduced, the features associated with Pt shift to 41.4° due to the formation of a Pt-Co alloy. There was also a small shoulder in the XRD pattern at 44.2° , which is likely associated with metallic Co.

XRD patterns for the Pt/LCO/MAO are shown in **Figure 4.2 (c)**. The most intense features are those associated with the perovskite phase. An estimate of the crystallite size

of the LaCoO_3 using the Scherrer equation and the peak at 33° gave a value of 11 nm for both the oxidized and reduced samples. The other big difference between this and the other two samples was that the Pt peak at 39° was very small on the oxidized sample and was only slightly larger on the reduced sample, despite the fact that all three samples had a similar Pt loading. Also, the reduced sample showed no evidence for Pt-Co alloy formation.

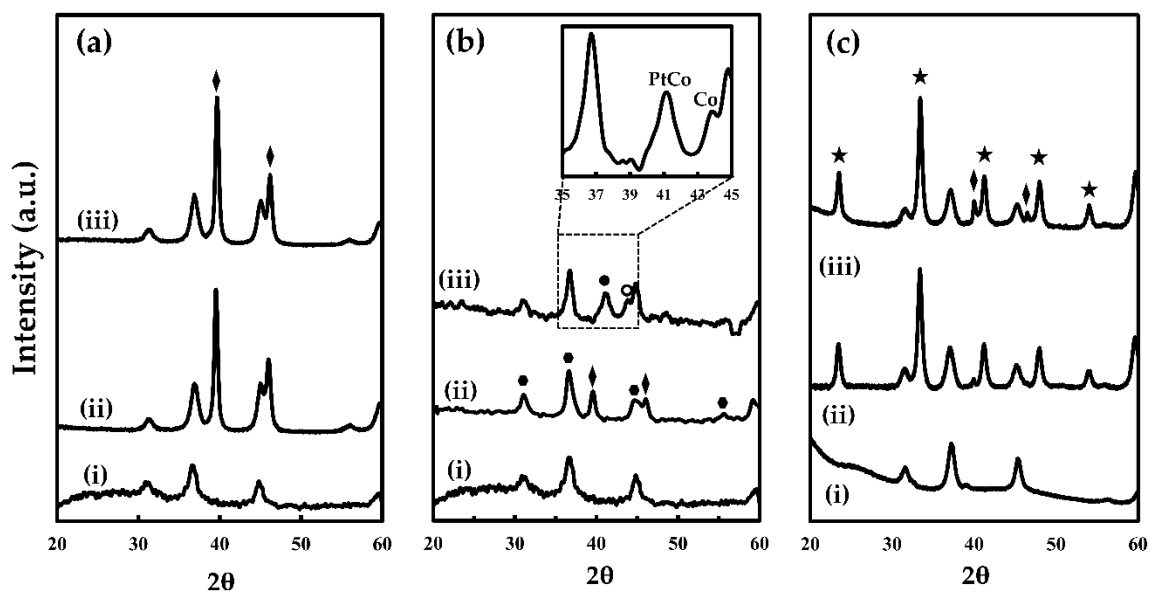


Figure 4.2: XRD patterns of (a) Pt/MAO, (b) Pt/Co/MAO, and (c) Pt/LCO/MAO: (i) unmodified MgAl_2O_4 ; (ii) oxidized Pt-containing sample after 5 redox cycles at 1073 K; (iii) reduced Pt-containing sample after 5 redox cycles at 1073 K. Metallic Pt features are marked with diamonds, Co_3O_4 with pentagons, PtCo alloy with solid circles, metallic Co with hollow circles, and perovskite with stars.

High-angle annular dark-field (HAADF) STEM images of the oxidized and reduce Pt/LCO/MAO sample are shown in **Figure 4.3**, **Figure 4.4**, and **Figure 4.5**, along with the

corresponding EDS mappings. Again, both samples had been oxidized and reduced five times at 1073 K before the final treatment. The image of the oxidized sample, shown **Figure 4.3**, is not easily distinguishable from that of the unmodified MgAl_2O_4 . There was no evidence for larger particles. The EDS maps show that Pt, La, and Co are uniformly present over most of the surface. With relatively few exceptions, the EDS intensities for these three elements follow those of the Mg and Al. The STEM image of the reduced sample in **Figure 4.4** was largely unchanged, but the EDS mappings showed differences in the elemental positions, with Co appearing to have agglomerated into 10-nm islands. Pt and La remain relatively well distributed over the surface. Although some regions of the sample also showed large Pt particles (**Figure 4.5**), the concentration of these particles was insufficient to account for the Pt content of the sample, but may account for the Pt XRD peak in **Figure 4.2 (c)**. That LaCoO_3 could at least partially decompose under harsh reducing condition is expected ¹¹⁰, but it is surprising this was not also observed in the XRD measurements. The XRD showed no change in the perovskite peak intensities and no evidence for new phases.

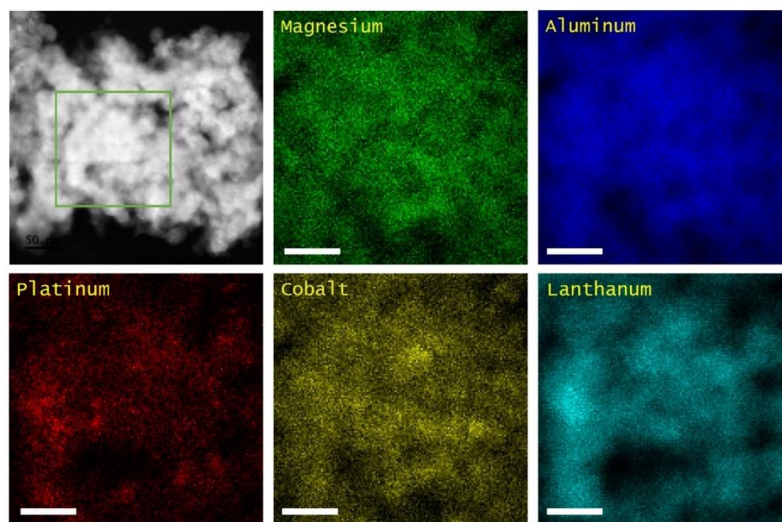


Figure 4.3: High-angle annular dark-field STEM image and EDS maps of Mg, Al, La, Co and Pt on oxidized Pt/LCO/MAO after 5 redox cycles, taken from the region indicated by the green box. The scale bars represent 25 nm.

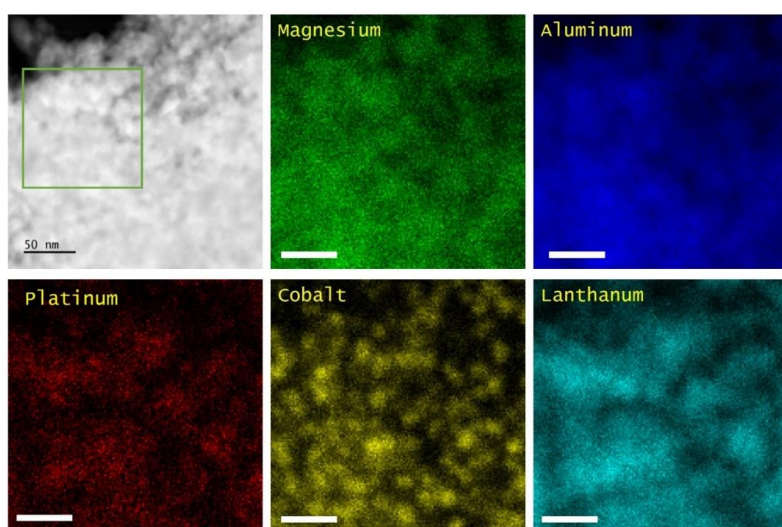


Figure 4.4: High-angle annular dark-field STEM image and EDS maps of Mg, Al, La, Co and Pt on reduced Pt/LCO/MAO after 5 redox cycles, taken from the region indicated by the green box. The scale bars represent 25 nm.

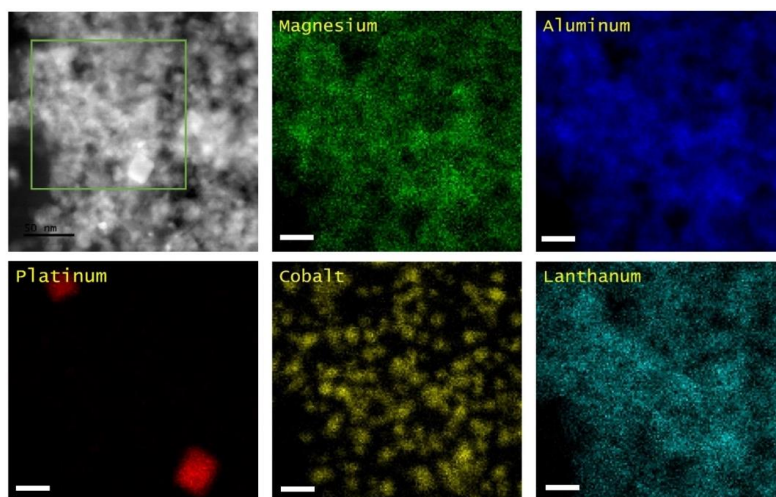


Figure 4.5: High-angle annular dark-field STEM image and EDS maps of Mg, Al, La, Co and Pt on reduced Pt/LCO/MAO after 5 redox cycles, taken from the region indicated by the green box. The scale bars represent 25 nm. Showing few large Pt particles.

4.3.2 CO Oxidation Rates

Past work with CO oxidation over perovskite-supported, ex-solution catalysts exhibited a high sensitivity to the pretreatment conditions ^{49, 86, 105}. Following high-temperature (1073 K) oxidation and relatively mild (773 K) reduction, the catalysts were inactive; but activity was restored upon high-temperature reduction. This behavior is unusual for supported metals and appears to be due to the high-temperature requirements for driving the metals into and out of the perovskite lattice. It is notable that this cycling between active and inactive states only occurs for those metal-perovskite pairs in which the metal can become part of the perovskite lattice ⁴⁹. Therefore, we employed similar CO oxidation measurements on the catalysts of this study to see whether these would also show evidence for ex-solution.

Figure 4.6 shows CO oxidation rates over Pt/LCO/MAO, Pt/La/MAO, Pt/Co/MAO, and Pt/MAO samples after various redox treatments. These samples were initially oxidized at 873 K to remove precursor ligands but were not otherwise redox cycled so that we could observe changes in the catalysts upon these various pretreatments. The rates were obtained under differential conditions with a constant Gas Hourly Space Velocity (GHSV) of $60000 \text{ mL}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$ (100 mL/min total flow rate, 100 mg catalyst). In order to maintain differential conditions, rates were measured at lower temperatures on the more active catalysts.

Initially, as shown in **Figure 4.6 (b)**, the rates over Pt/MAO were reasonably high due to the fact that the Pt dispersion was greater than 20% ⁴⁹. However, high-temperature oxidation caused a precipitous drop in the activity, and rates were not restored by high-temperature reduction. Additional redox cycling caused further drops in the activity; and, after 5 redox cycles, the rates had dropped by a factor of 50. Chemisorption measurements indicated that the loss in activity could be completely explained by a loss in Pt dispersion.

Rate data for Pt/LCO/MAO are shown in **Figure 4.6 (a)** and showed completely different characteristics. To begin these experiments, the catalyst was first reduced at 1073 K in 10% H₂-He. Similar to what has been observed on other ex-solution catalysts, this reduced catalyst showed very high activity, approximately five times higher than that observed on fresh Pt/MAO. When this catalyst was oxidized at 1073 K in 10% O₂-He, the activity dropped by almost a factor of 100. As shown in **Figure 4.7**, reduction at 773 K did not significantly restore activity, but reduction at 1073 K brought the rates back to their

initial value. The activity of this catalyst could be cycled between active and inactive states, with minimal changes, even after 5 redox cycles.

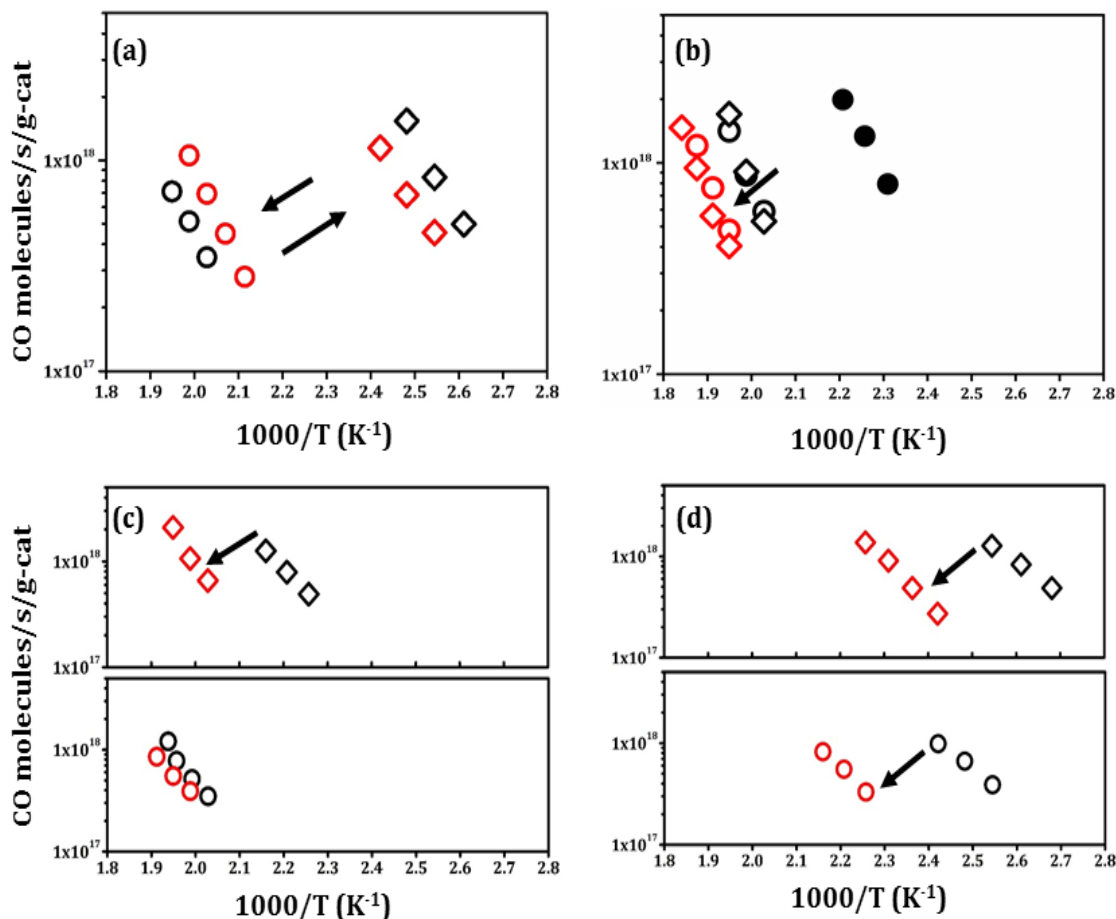


Figure 4.6: Steady-state, differential reaction rates for CO oxidation with 25 Torr of CO and 12.5 Torr O_2 for 0.1-g samples of (a) Pt/LCO/MAO, (b) Pt/MAO, (c) Pt/La/MAO, and (d) Pt/Co/MAO. Rates measured on samples that after oxidation in 10% O_2 -He at 1073 K for 1 h are marked in circles; rates measured on samples that after reduction in 10% H_2 -He at 1073 K for 1 h are marked in diamonds. Black symbols denote the first redox cycle, while red symbols denote the fifth cycle.

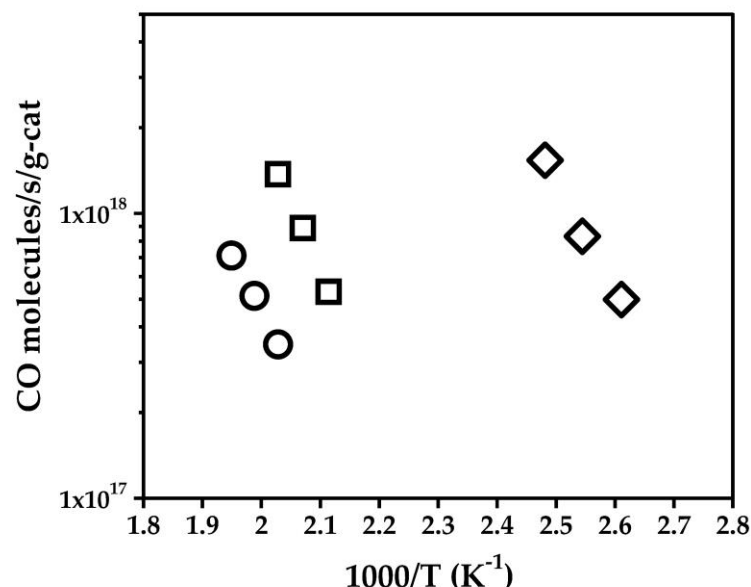


Figure 4.7: Steady-state, differential reaction rates for CO oxidation with 25 Torr of CO and 12.5 Torr O₂ for 0.1-g sample of Pt/LCO/MAO. Rates measured on sample that after oxidation in 10% O₂-He at 1073 K for 1 h are marked in circles; rates measured on sample that after reduction in 10% H₂-He at 1073 K for 1 h are marked in diamonds; rates measured on sample that after reduction in 10% H₂-He at 773 K for 1 h are marked in diamonds.

CO oxidation rates on Pt/La/MAO and Pt/Co/MAO are shown in **Figure 4.6 (c)** and **Figure 4.6 (d)**. Initially, the Pt/La/MAO exhibited properties similar to that of fresh Pt/MAO, and rates simply decreased after high-temperature treatments. After 5 redox cycles, Pt/La/MAO remained somewhat more active than Pt/MAO, suggesting that La₂O₃ suppresses Pt sintering to some extent. The Pt/Co/MAO sample was more interesting. The initial activity after 1073-K reduction was a factor of two times higher than even the reduced Pt/LCO/MAO. This agrees with previous work that has shown Co promotes Pt catalysts for CO oxidation¹¹¹. However, repeated oxidation-reduction cycles again caused

the activity of this catalyst to drop. Interestingly, the reduced catalysts were always somewhat more active.

In the absence of promoters (e.g., See the effects of ceria ⁵⁵), CO oxidation rates on Pt catalysts have been shown to be strictly proportional to Pt surface area ⁵³. Therefore, we performed CO chemisorption on the oxidized and reduced samples that had undergone 5 redox cycles in order to better understand the changes observed in **Figure 4.6**. Pt dispersions were also estimated from the normalized reaction rates reported in the literature ¹¹². These values are shown in **Table 4.2**. Similar to what was reported previously for Pt on CaTiO₃ films ⁴⁹, there was no CO chemisorption on either the oxidized or reduced Pt/LCO/MAO sample. Based on reaction rates, the Pt dispersion on the reduced Pt/LCO/MAO should have been 40%. In contrast to this, the agreement between Pt dispersions measured by CO chemisorption and estimated from the normalized reaction rates was very good for each of the other catalysts.

Table 4.2: Summary of Pt dispersion (%) measured by CO chemisorption or estimated based on dispersion and activity of Pt (111) in the literature for catalysts after 5th reduction and oxidation pretreatments at 1073 K.

	1073-K oxidized		1073-K reduced	
	measured	estimated	measured	estimated
Pt/LCO/MAO	-	2	-	40
Pt/MAO	0.1	0.1	0.1	0.4
Pt/Co/MAO	7	6.5	13	13
Pt/La/MAO	1.3	1.4	1.4	2.8

:- Not able to be measured.

The failure to observe CO chemisorption on the Pt/LCO/MAO sample suggests that the reaction rate expression should be very different. With non-interacting supports, CO oxidation on Pt is inversely proportional to the CO partial pressure due to the fact that the surface is saturated with CO. The rate-limiting step is O₂ adsorption⁵³, which in turn is limited by the availability of empty sites on the Pt. Based on the lack of CO chemisorption, the reaction order for CO on the reduced Pt/LCO/MAO sample is expected to be different. In **Figure 4.8**, differential rates are plotted at 393 and 423 K as a function of the CO partial pressure for a fixed O₂ pressure of 7.6 Torr. At both temperatures, there was a transition of slightly negative order to zeroth-order. The dependence on CO partial pressure was clearly much weaker on Pt/LCO/MAO than on conventional Pt catalysts, suggesting that the reaction mechanism is different.

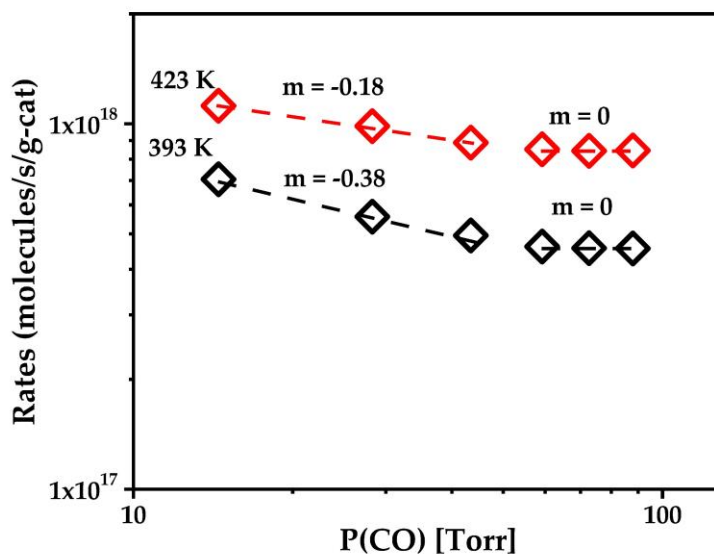


Figure 4.8: Dependence of CO oxidation rates at different temperatures, at constant $P_{O_2} = 7.6$ Torr, over 0.1-g sample of reduced Pt/LCO/MAO after 5 redox cycles at 1073 K.

4.3.3 WGS and Toluene Hydrogenation

Because changes in the adsorption properties could affect other reactions, we measured rates for toluene hydrogenation and WGS on the Pt/LCO/MAO catalyst as a function of the treatment conditions. These two reactions test the ability of the catalyst to activate H_2 and H_2O and are therefore complementary to CO oxidation, which is limited by O_2 dissociation. Pt-based catalysts are generally very active for hydrogenation of unsaturated organic molecules; however, a recent study of Pt on CaTiO_3 films showed surprisingly low rates for toluene hydrogenation⁴⁹. While Pt by itself is not a good WGS catalyst due to the inability of Pt to dissociate water, support interactions can lead to interfacial sites that are highly active. For example, ceria-supported Pt can be highly active for WGS and has received considerable attention for this application¹¹³⁻¹¹⁴.

Differential WGS rates are reported for Pt/LCO/MAO in **Figure 4.9** on samples that were again reduced or oxidized at 1073 K, after 1 or 5 redox cycles. Similar to what was observed for CO oxidation, the reduced catalysts were roughly 50 times more active than the oxidized catalyst, and redox cycling did not significantly affect the rates. It is also noteworthy that rates on the reduced catalysts approach those observed with ceria-supported Pt and are much more active than Pt on non-interacting supports. This is demonstrated in **Figure 4.10**, which compares rates on Pt/ $\gamma\text{-Al}_2\text{O}_3$, Pt/ $\text{CeO}_2/\gamma\text{-Al}_2\text{O}_3$, and the reduced Pt/LCO/MAO, all of which had similar Pt loadings and have been calcined at 1073 K. The fact that Pt/ $\text{CeO}_2/\gamma\text{-Al}_2\text{O}_3$ and reduced Pt/LCO/MAO are comparable implies that the LaCoO_3 phase is playing a role in the reaction.

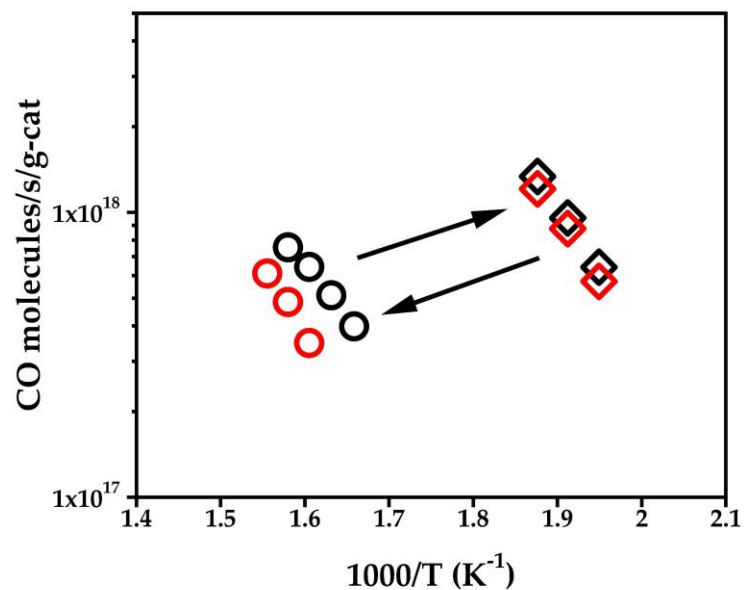


Figure 4.9: Steady-state, differential reaction rates over 0.1-g sample of Pt/LCO/MAO for WGS with partial pressures of CO and H_2O both kept at 25 Torr. Rates measured on sample that after oxidation in 10% O_2 -He at 1073 K for 1 h are marked in circles; rates measured on samples that after reduction in 10% H_2 -He at 1073 K for 1 h are marked in diamonds. Black symbols denote the first redox cycle, while red symbols denote the fifth cycle.

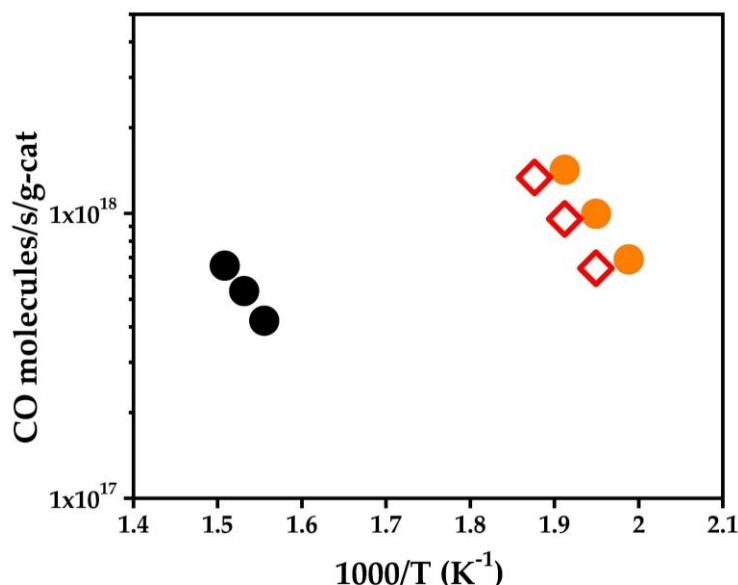


Figure 4.10: Steady-state, differential reaction rates over 0.1-g samples of (orange circles) 1073-K calcined Pt/CeO₂/γ-Al₂O₃, (black circles) 1073-K calcined Pt/γ-Al₂O₃, and (diamond) 1073-K reduced Pt/LCO/MAO after 5 redox cycles for WGS with partial pressures of CO and H₂O both kept at 25 Torr.

Light-off profiles for toluene hydrogenation are shown in **Figure 4.11** for the Pt/MAO and the reduced and oxidized Pt/LCO/MAO catalysts. The Pt/MAO catalyst used here was calcined and reduced at 1073 K prior to measuring the rates. This data is surprising for multiple reasons. First, rates on Pt/MAO were shifted to lower temperatures by nearly 50 degrees compared to rates on reduced Pt/LCO/MAO. For a typical reaction activation energy of 100 kJ/mol, a 50-degree temperature shift corresponds to a factor of 70 difference in rates. Second, the oxidized catalyst was more active for this reaction than the reduced catalyst. Because the STEM/EDS results suggested that the LaCoO₃ phase can at least partially decompose upon high-temperature reduction, which in turn could lead

to Pt-Co alloy formation, we also measured rates on the reduced Pt/Co/MAO sample, shown in the supporting information of the original publication ¹¹⁵. Rates on Pt/Co/MAO were comparable to that of Pt/MAO, showing that alloy formation cannot explain the low rates observed with Pt/LCO/MAO.

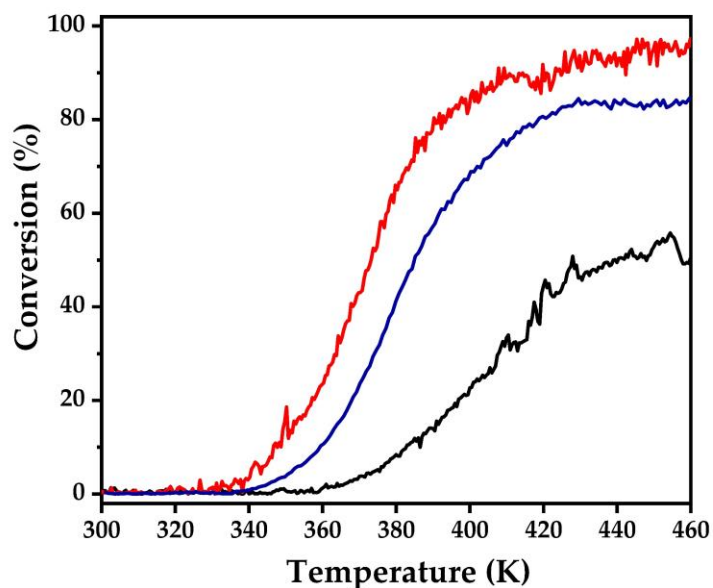


Figure 4.11: Light-off profiles for toluene hydrogenation for 0.1-g samples of (red) reduced Pt/MAO, (blue) oxidized Pt/LCO/MAO, and (black) reduced Pt/LCO/MAO. Samples have been pretreated with 5 redox cycles prior to measurements.

4.4 Discussion

The results of this study demonstrate that thin films of LaCoO_3 can be formed by ALD and that these films can exhibit interesting properties as supports for Pt catalysts. Catalysts prepared from these thin films retain a high Pt dispersion (as evidenced from the STEM/EDS data) following high-temperature redox cycling, and the reduced form of the catalyst is highly active for CO oxidation and WGS. However, many questions remain about the nature of the support interactions in these materials and they are clearly not a drop-in replacement for conventional Pt catalysts, given their low activity for hydrogenation reactions.

There are many similarities between the results shown here and those reported previously for Pt and Pd on CaTiO_3 and LaFeO_3 films ^{49, 86}. In each of these systems, high reduction and oxidation temperatures were required to transition the catalysts between their active and inactive states. For example, in each case, a catalyst placed in its inactive state by oxidation at 1073 K could not be restored by reduction at 773 K but could be restored by reduction at 1073 K. Furthermore, despite the fact that each of the perovskite-based catalysts was highly active for CO oxidation, CO adsorption was suppressed in each case. Unlike conventional Pt and Pd catalysts, each of the perovskite-based catalysts maintained their activity following many oxidation-reduction cycles. Similar to what was observed for Pt on CaTiO_3 , hydrogenation of toluene was strongly suppressed. Finally, the properties of Pt catalysts supported on the individual oxides (e.g., Pt/Co/MAO and Pt/La/MAO) were completely different from that observed for the mixed-oxide support.

The similarity between results for catalysts prepared from the thin-film perovskites and catalyst prepared by ex-solution of bulk perovskites strongly suggests Pt interacts with the thin films in a similar manner to that with the bulk perovskites.

It is interesting to ask why the perovskite phase is important in these systems. With a 0.5-nm film, bulk incorporation of the Pt seems unlikely. However, it is possible that the Pt could incorporate into lattice positions at the surface. These atoms would then be bonded strongly to the oxide cations making up the perovskite, so that they would still be present at the surface to catalyze reactions. The bonding to the perovskite would clearly affect their adsorption and reaction properties. It is somewhat surprising that perovskites as different as CaTiO_3 and LaCoO_3 would show such similar properties.

One question about the LaCoO_3 system is that the STEM/EDS results seemed to indicate that the LaCoO_3 decomposed and segregated into Co-rich islands. However, this is not consistent with either the XRD data or the reaction results. Regarding XRD data, not only did the perovskite peaks remain intense following high-temperature reduction, but we saw no evidence for the Pt-Co alloy formation that occurred with Pt on the Co_3O_4 films. The catalytic properties of the Pt/LCO/MAO catalyst were also distinctly different from that of Pt/La/MAO or Pt/Co/MAO. One possibility is that the Co-rich islands observed in the STEM/EDS result retain their perovskite structure, probably with a La deficiency since the La did not show similar segregation.

While the concept of “intelligent” catalyst is not new, the ability to prepare perovskite-supported catalysts with high surface areas and no remaining catalyst in the

bulk is new. While we do not fully understand what gives rise to their properties, these materials are clearly novel and interesting.

4.5 Conclusion

Thin films of LaCoO_3 were successfully deposited onto MgAl_2O_4 using ALD. When reduced at high temperatures, Pt catalysts prepared from thin-film supports are highly active for CO oxidation and WGS and remain highly stable to redox cycling at 1073 K. The properties of the LaCoO_3 -supported Pt catalysts showed important similarities to Pt on CaTiO_3 and LaFeO_3 films but were not similar to Pt on Co_3O_4 or La_2O_3 films, implying that the perovskite structure of the thin-film supports is important for determining their properties.

CHAPTER 5. EPITAXIAL BETWEEN Pt AND LaFeO₃ FILMS STABILIZE Pt DISPERSION³

Summary

This chapter focuses on the effects of strong metal-support interaction on metal dispersion, metal structure, and catalytic properties for Pt on LaFeO₃ films. We demonstrate that Pt particles can be maintained in the 1- to 2-nm range following multiple oxidation and reduction cycles at 1073 K when the particles are supported on 0.5-nm LaFeO₃ films that have been deposited onto MgAl₂O₄ using ALD. Characterization by XRD and STEM suggest that, when the catalyst is oxidized at 1073 K, the Pt crystallites are oriented with respect to the underlying LaFeO₃. X-Ray Absorption Spectroscopy also shows evidence for changes in the Pt environment. CO-oxidation rates for the reduced catalyst remain unchanged after five redox cycles at 1073 K. Epitaxial growth of Pt clusters and the consequent strong metal-support interaction between Pt and LaFeO₃ are suggested to be the main reasons for the enhanced catalytic performances.

³ This chapter was reproduced from J. Am. Chem. Soc. 2020, 142, 23, 10373-10382.

5.1 Introduction

In this work, I set to study metal-support interactions between Pt and LaFeO₃, prepared as a thin film on high-surface-area MgAl₂O₄ by ALD ⁸⁶. A 0.5-nm, uniform film of LaFeO₃ (density of 6.65 g/cm³) on a 120-m²/g substrate results in a material that is 28.5-wt% perovskite. Thus, we hypothesize that even at relatively high loadings of the perovskite lead to films that are so thin that the egress-ingress of large metal particles is not likely to occur. However, this work will show that strong chemical interactions between Pt and the LaFeO₃ films are able to dramatically stabilize small metal particles, even after multiple high-temperature, oxidation-reduction cycles. The chemical bonding in the oxidized samples is observed directly through the formation of Pt particles that are epitaxially aligned with respect to LaFeO₃ crystallites. The results suggest that perovskite-supported metals may provide a solution to the sintering problem in some applications.

5.2 Experimental Methods

5.2.1 Sample Preparation

MgAl₂O₄ was prepared using the method described in **Chapter 2.1**. The LaFeO₃ films were deposited onto the MgAl₂O₄ support by ALD. The ALD precursors were La(TMHD)₃ (TMHD = 2,2,6,6-tetramethyl-3,5-heptanedionato, Strem Chemicals, Inc.), and ferrocene (Fe(Cp)₂, Sigma-Aldrich). Operational details and deposition conditions were discussed in **Chapter 2.2**. The growth rates for the individual oxides were 3.4×10^{17} La atoms/cycle·m² (0.014 nm La₂O₃/cycle) and 1.0×10^{18} Fe atoms/cycle·m² (0.025 nm Fe₂O₃/cycle). Films with the correct perovskite stoichiometry were obtained by alternating between 3 ALD cycles of La₂O₃ and 1 ALD cycles of Fe₂O₃. The final loading of LaFeO₃ in this study, 30±1.5 wt%, was determined gravimetrically and confirmed by ICP-OES. The BET surface area of LaFeO₃/MgAl₂O₄ (LFO/MAO) after calcination at 873 K was 78 m²/g.

To ensure that there was good initial contact between the Pt and LaFeO₃ support, Pt was added by ALD using one cycle of platinum (II) acetylacetonate (Strem Chemicals, Inc.). The Pt was deposited onto the oxide films prior to the final calcination step (i.e., The LFO/MAO sample had been calcined to only 873 K prior to adding Pt. After adding Pt, the catalyst was oxidized in a muffle furnace at 573 K to remove the ligands. The Pt loading for the samples was measured by ICP-OES to be 2.9±0.2 wt% ($\sim 1.1 \times 10^{18}$ Pt/m²), which was comparable to the previous reported growth rate of Pt ALD¹¹⁶. Because our interest in the Pt/LFO/MAO catalysts was in understanding the stability of these catalysts following high-temperature oxidation and reduction, samples were exposed to five

oxidation and reduction cycles at 1073 K prior to the characterization shown in this paper. The oxidation cycles were carried out in 10% O₂-He for 1 h and the reduction cycles flowing 10% H₂-He mixtures for 1 h, and the total flow rate was maintained at 100 mL/min.

5.2.2 Characterization Methods

The ALD-prepared samples were characterized initially by XRD using a Rigaku Smartlab diffractometer equipped with a Cu K α source ($\lambda = 0.15416$ nm); but additional measurements were subsequently performed on a Philips X'Pert diffractometer equipped with a Cu K α source in the range 10 to 100° with a step of 0.02°. Rietveld analysis was performed using the PowderCell 2.4 program. Crystallite sizes were calculated applying the Scherrer's equation to the main reflections of each crystalline phase in the region 25 to 40°. For CO chemisorption measurements, samples were reduced in 200 Torr H₂ at 473 K before CO uptakes were measured at room temperature. ICP-OES was performed on a Spectro Genesis spectrometer with a Mod Lichte nebulizer. Initial STEM/EDS measurements were performed with a JEOL JEM-F200 STEM, operated at 200 kV; STEM images with high magnification were taken using a JEOL NEOARM STEM. Powder specimens were diluted in isopropanol and put on lacey carbon films on copper grids (Electron Microscopy Sciences).

Ex-situ XANES/EXAFS spectra were acquired on the SAMBA beamline at synchrotron SOLEIL (Gif-sur-Yvette, France) at the Pt L₃ edge (11563.7 eV)¹¹⁷. Spectra were collected by measuring the K α fluorescence line with a 36 pixels germanium detector (Canberra), whereas transmission data were simultaneously recorded with ionization

chambers (IC-SPEC, FMB-Oxford) for the sample and Pt foil as the standard. Data analysis was performed with the DEMETER software suite ¹¹⁸.

Simultaneous Temperature-Programmed Desorption/Thermogravimetric Analysis (TPD/TGA) measurements were performed using a home-built system consists of an evacuated CAHN 2000 microbalance equipped with an SRI Quadrupole mass spectrometer (RGA100). In the TPD-TGA experiment, 0.05-g samples were first heated in a vacuum to 823 K before being cooled to room temperature to remove water and any physisorbed contaminants. The samples were then exposed to the vapor from liquid 2-propanol at room temperature and evacuated for 1 h to a base pressure of 10^{-8} Torr. The TPD-TGA measurements were performed by ramping the sample temperature at 10 K/min while monitoring the partial pressures with the RGA100.

Differential, steady-state rates were measured over 0.1-g samples using the system described in **Chapter 2.3.1**. Most CO-oxidation rates were measured with the total gas flow rate maintained at 100 mL/min using a He carrier, and partial pressures of CO and O₂ maintained at 25 Torr and 12.5 Torr, respectively. To study the dependence of CO oxidation rates on the partial pressure of CO, the total flow rate and flow rate of O₂ were kept constant at 100 mL/min and 1 mL/min, but PCO was varied by changing the flow rates of He and CO. Before taking the measurements, the Pt catalysts were either oxidized or reduced in a 10% gas mixture of either O₂ or H₂ in He at a total flow rate of 100 mL/min.

Light-off reaction profiles of conversion versus temperature for CO oxidation were measured over 0.1 g samples in the system described in **Chapter 2.3.2**. The flow rates of

He, CO, and O₂ were kept the same as those for measurements of differential, steady-state rates. The temperature ramp rate was 10 K/min. The conversion of CO was calculated based on the ratio of the relative partial pressures of CO and CO₂.

5.3 Results

5.3.1 TPD/STEM/XRD

Assuming the LaFeO₃ uniformly covered the 120-m²/g MgAl₂O₄ support, a simple mass balance shows that a loading of 30-wt% would correspond to a film 0.56-nm thick if the LaFeO₃ has its bulk density of 6.65 g/cm³. Evidence for film uniformity came from multiple sources. First, HAADF-STEM/EDS measurements were performed to determine the morphology of the Pt/LFO/MAO samples. **Figure 5.1** and **Figure 5.2** provide images, together with the EDS maps, for an oxidized and reduced sample after the sample had already undergone five oxidation and reduction cycles at 1073 K. In both cases, the lower resolution HAADF-STEM images in the upper left-hand panels are indistinguishable from that of the MgAl₂O₄ support. More informative are the EDS maps, which show that La, Fe, and Pt each uniformly cover the surface after either oxidation or reduction. The EDS intensity variations for all three elements also overlap with intensity variations for Mg and Al from the support. STEM/EDS scans for the oxidized sample with lower magnification are shown as **Figure 5.3** and further confirm that La and Fe uniformly cover the support surface.

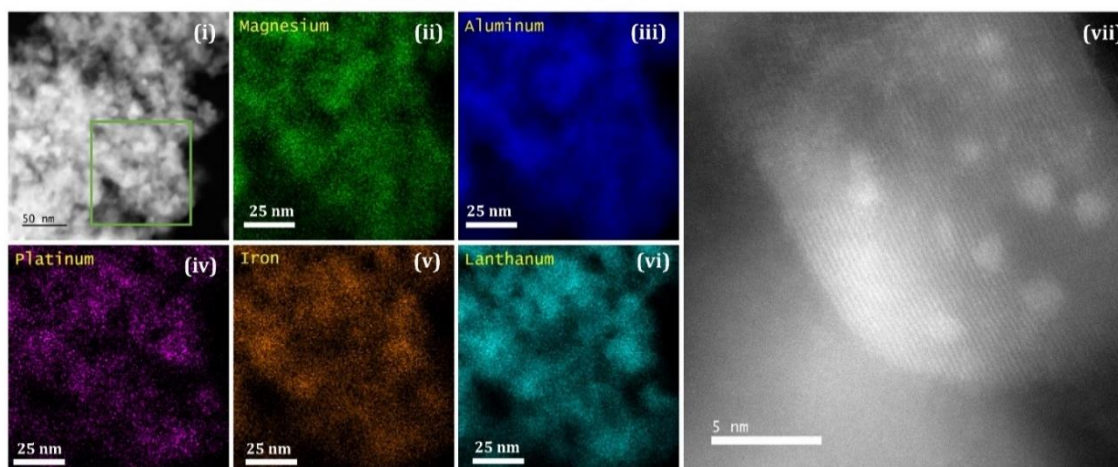


Figure 5.1: High-angle annular dark-field STEM image (i) and EDS maps (ii-vi) of Mg, Al, La, Fe and Pt on the oxidized Pt/LFO/MAO after 5 redox cycles, taken from the region indicated by the green box. High angle annular dark field STEM image with larger magnification (vii) on the same sample.

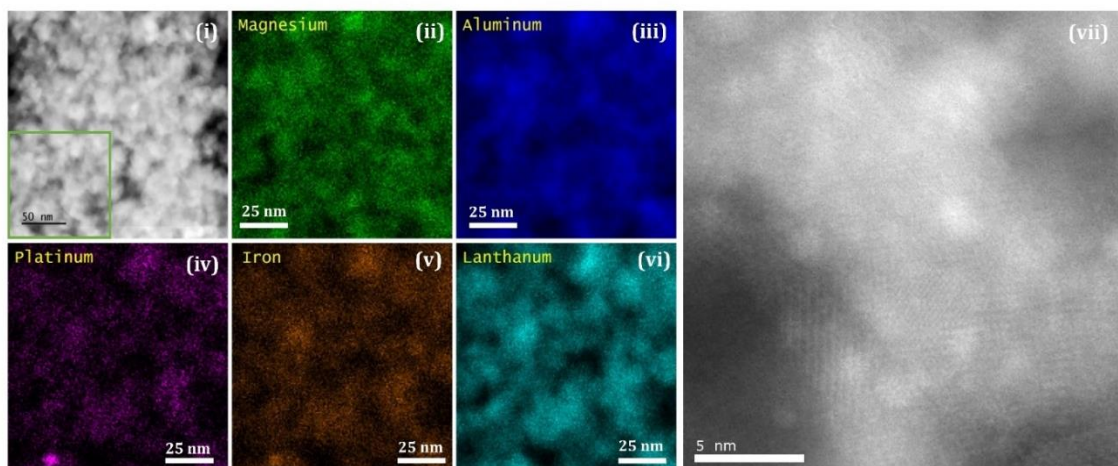


Figure 5.2: High-angle annular dark-field STEM image (i) and EDS maps (ii-vi) of Mg, Al, La, Fe and Pt on the reduced Pt/LFO/MAO after 5 redox cycles, taken from the region indicated by the green box. High-angle annular dark-field STEM image with larger magnification (vii) on the same sample.

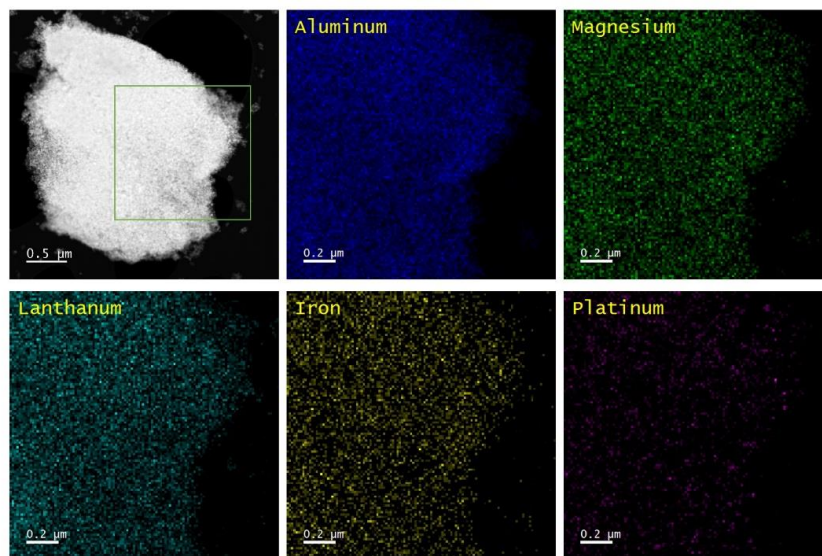


Figure 5.3: High-angle annular dark-field STEM image and EDS maps with lower magnification of Mg, Al, La, Fe and Pt on the oxidized Pt/LFO/MAO after 5 redox cycles, taken from the region indicated by the green box.

Additional evidence for film uniformity came from TPD-TGA measurements of adsorbed 2-propanol, performed on the unmodified MgAl_2O_4 and the oxidized Pt/LFO/MAO that had been treated with 5 redox cycles. These data are shown in **Figure 5.4**. MgAl_2O_4 exhibits Lewis-acid character and most 2-propanol that is adsorbed at room temperature undergoes dehydration to propene and water in a sharp reaction feature at 450 K in TPD. The MgAl_2O_4 feature is completely absent in the TPD-TGA results for Pt/LFO/MAO. Most of the adsorbed 2-propanol also reacted during TPD on this sample, but all the reaction occurred at a temperature higher than 450 K. Furthermore, a large fraction of the product was formed from 2-propanol was acetone. If any of the MgAl_2O_4 had been exposed, a feature at 450 K should have been observed. Given that the average

film thickness was only 0.56 nm, it is unlikely that there could be larger perovskite crystallites, with sufficient LaFeO_3 remaining to cover the surface of the MgAl_2O_4 .

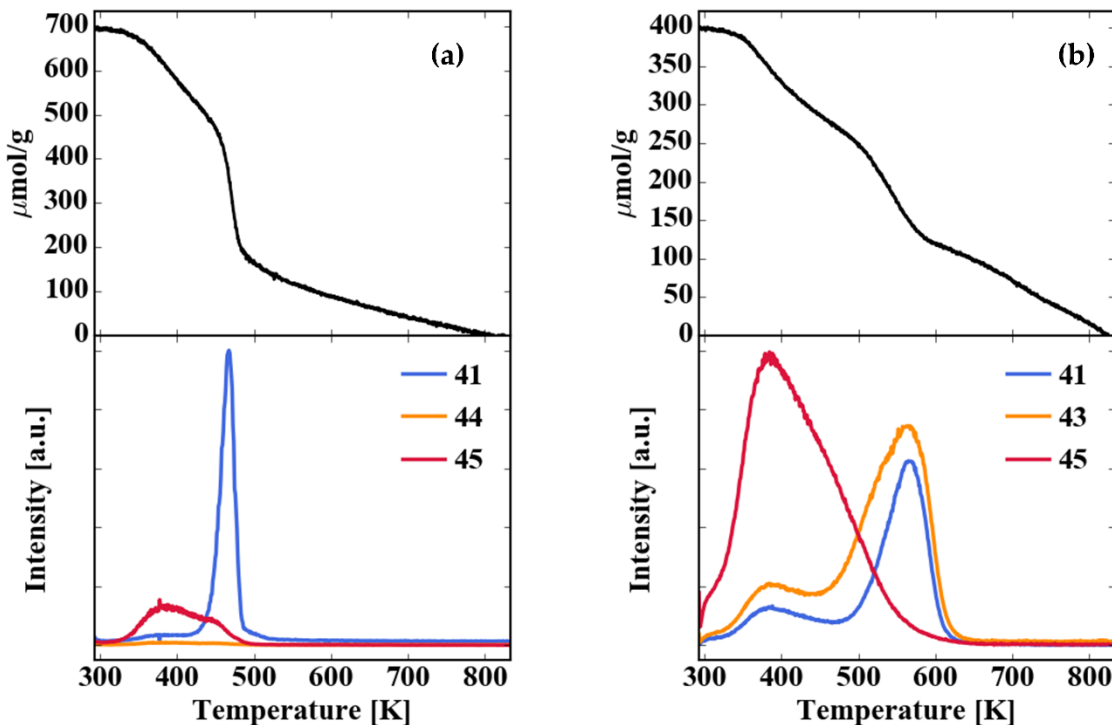


Figure 5.4: TPD-TGA of 2-propanol from (a) MgAl_2O_4 and (b) oxidized Pt/LFO/MAO after 5 redox cycles at 1073 K. Desorption features correspond to propene ($m/e = 41$), acetone ($m/e = 43$), and unreacted 2-propanol ($m/e = 45$). Before the TPD-TGA measurement, the samples were saturated with the vapor from liquid 2-propanol at room temperature and then evacuated for 1 h to a base pressure of 10^{-8} Torr. During the measurement, the temperature ramp rate was 10 K/min.

While the uniform coverage of LaFeO_3 over the MgAl_2O_4 surface had been established previously for ALD preparation⁸⁶, the fact that these films are stable to multiple redox cycles at 1073 K is encouraging. It is also encouraging to observe well-dispersed Pt following either oxidation or reduction at 1073 K. The higher-resolution

images in the right-hand panels of **Figure 5.1** and **Figure 5.2** indicate that Pt particles are present on both the oxidized and reduced samples, but they are irregular in shape and only 1 to 2 nm in size. That the STEM images are representative was demonstrated by the fact that the Pt calculated from the EDS signals varied from 2.7 wt.% to 3.1 wt.% on different regions with dispersed Pt, in good agreement with the ICP measurement.

To demonstrate that stabilization of the Pt particles on the Pt/LFO/MAO sample was due to the presence of LaFeO_3 , HAADF-STEM measurements were also performed on a reduced 3.0-wt% Pt/ MgAl_2O_4 (Pt/MAO) sample that had undergone 5 redox cycles. The Pt on this sample was again prepared by ALD and had an initial dispersion of 27%. As shown in **Figure 5.5**, the redox treatments caused a dramatic growth of the Pt on this sample, with crystallite sizes ranging from 50 to 100 nm. Pt/MAO has previously been reported to be relatively resistant to sintering ¹¹⁹, making the high dispersion of Pt/LFO/MAO sample even more noteworthy.

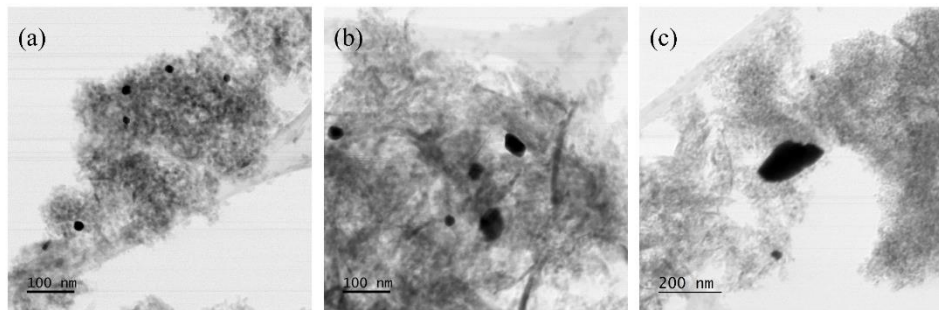


Figure 5.5: High-angle annular dark-field STEM image of the reduced Pt/MAO after 5 redox cycles at 1073 K.

A closer inspection of the high-resolution STEM/EDS images of the oxidized sample, shown in **Figure 5.6**, suggests that the small Pt particles on the oxidized sample are aligned with the underlying LaFeO_3 lattice. That these are indeed Pt crystallites was confirmed by the EDS maps and the signals of Pt M and Pt L emitted X-rays shown in **Figure 5.7**. The images show a distinct registry of the Pt atoms on top of the rows of LaFeO_3 . Other images of this sample, reported in **Figure 5.8**, also show very small Pt clusters that are oriented along the same direction with the LaFeO_3 lattice. Higher-resolution STEM images of the reduced sample are shown in **Figure 5.9**. The range of particle sizes is similar but slightly larger than that with the oxidized samples. What is different is that at least some of the Pt crystallites are not oriented with respect to the underlying perovskite lattice.

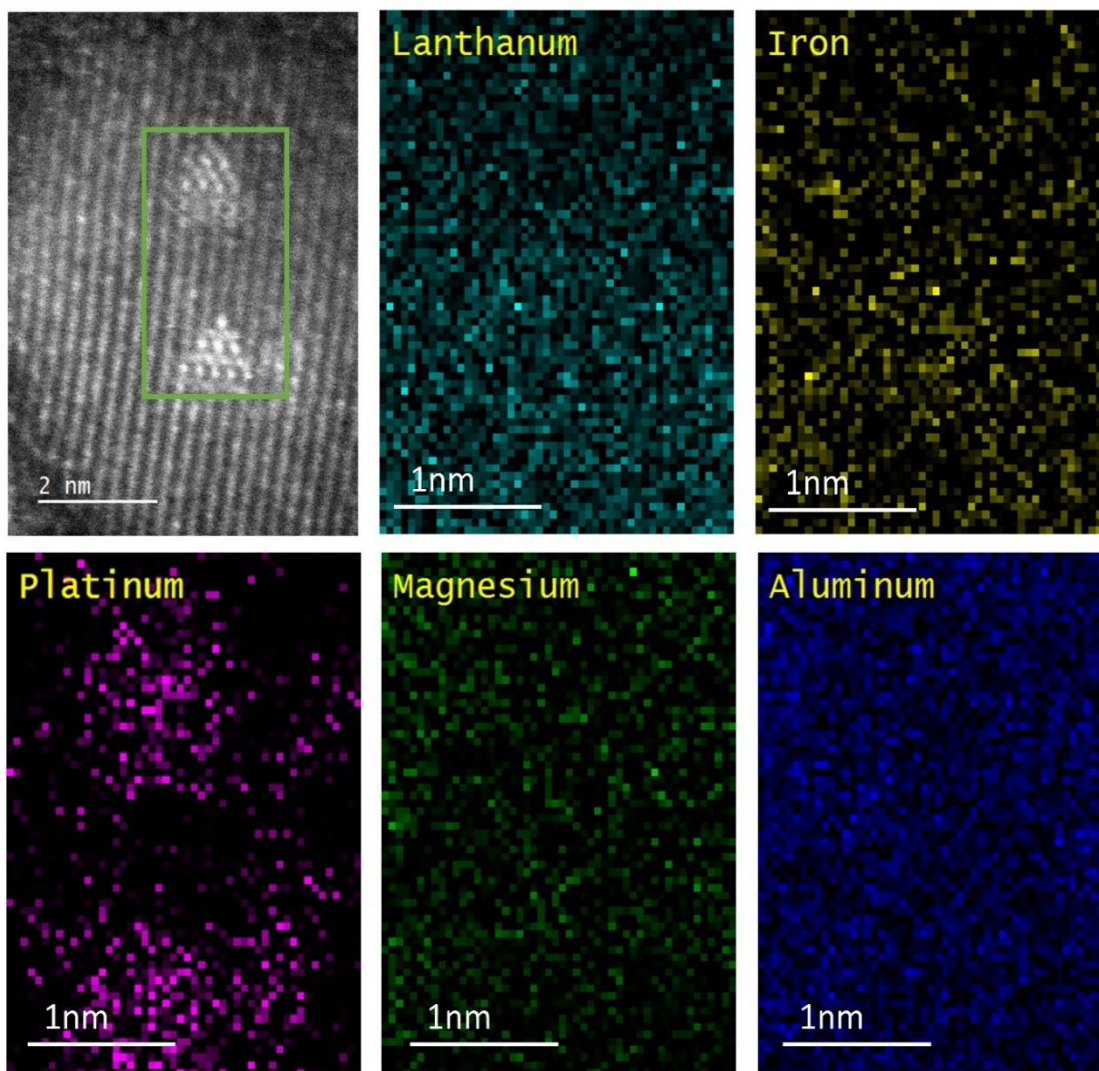
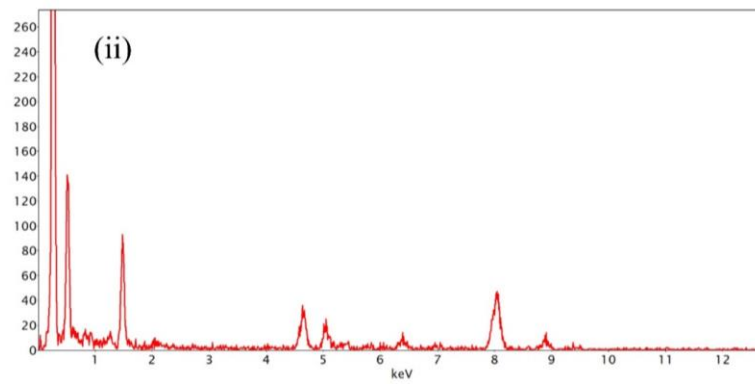
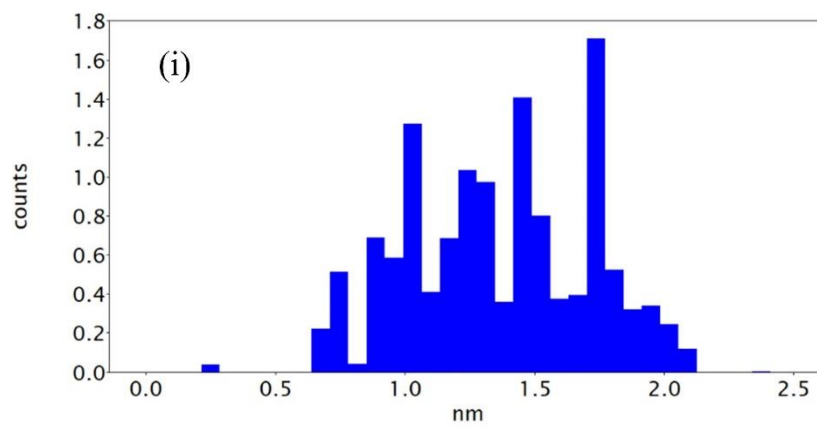
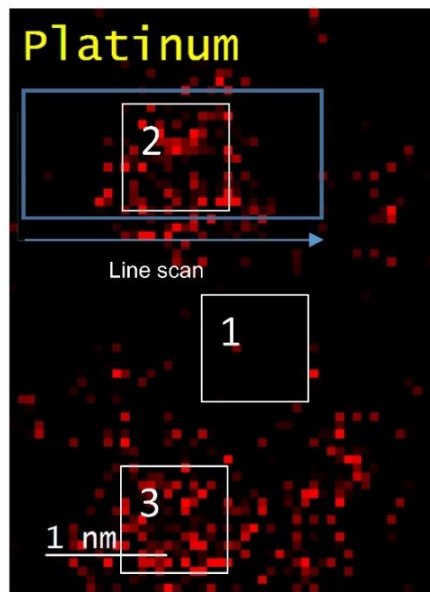


Figure 5.6: High-angle annular dark-field STEM image and EDS maps of Mg, Al, La, Fe and Pt on the oxidized Pt/LFO/MAO after 5 redox cycles, taken from the region indicated by the green box.



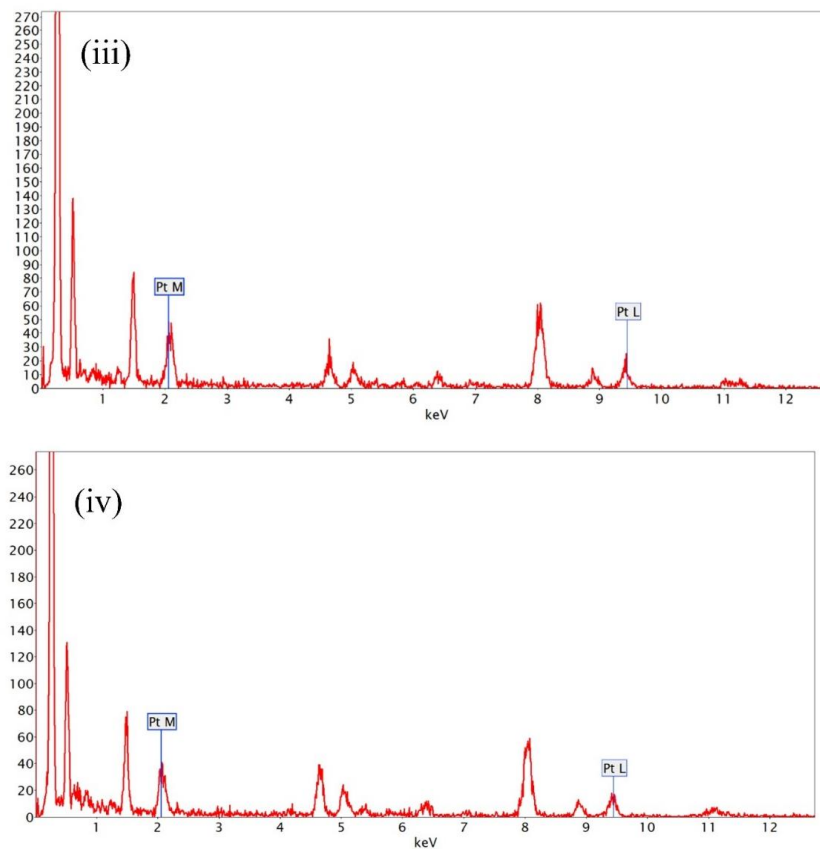


Figure 5.7: EDS map of Pt (same particles as in **Figure 5.6**), with (i) counts for Pt X-rays along the line scan of the region marked as the blue box, and EDS spectrum of regions marked as box 1 (ii), box 2 (iii) and box 3 (iv) in the EDS map.

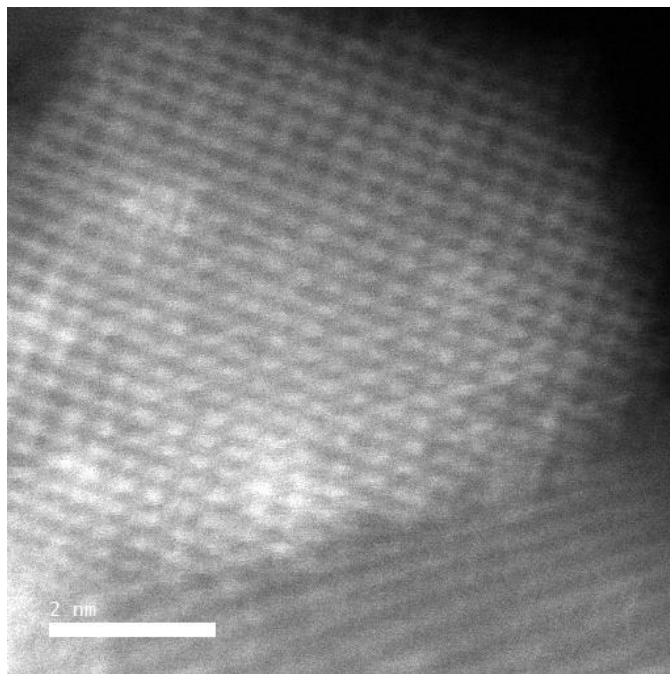


Figure 5.8: High-angle annular dark-field STEM image of the oxidized Pt/LFO/MAO after 5 redox cycles at 1073 K (same sample as the one in **Figure 5.6**).

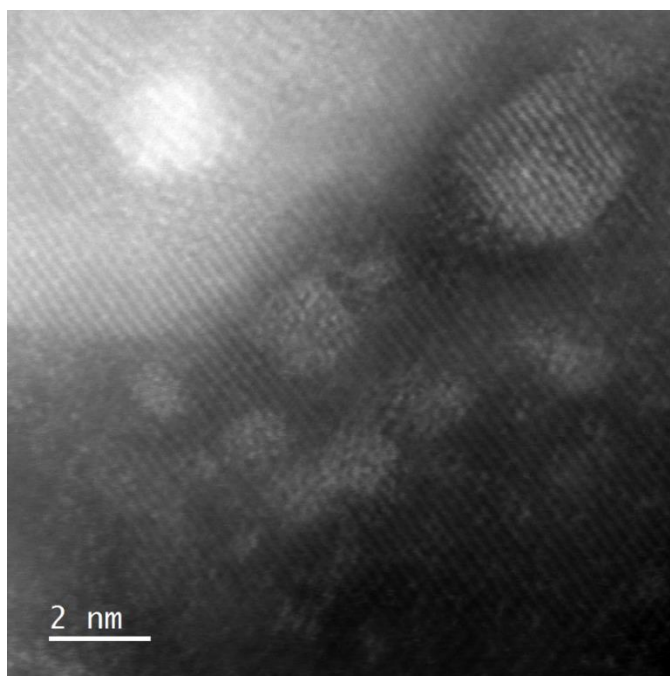


Figure 5.9: High-angle annular dark-field STEM image of the reduced Pt/LFO/MAO after 5 redox cycles at 1073 K.

XRD measurements were performed to determine the structure of the deposited films, with results reported in **Figure 5.10**. The bottom pattern, **Figure 5.10** (i), is that of the MgAl_2O_4 support, while the patterns for the oxidized (**Figure 5.10** (ii)) and reduced (**Figure 5.10** (iii)) samples with 2.9-wt% Pt and 30-wt% LaFeO_3 are shown above it. The XRD patterns in this figure were obtained on the same sample whose STEM images are shown in **Figure 5.1** and **Figure 5.2**. First, both the oxidized and reduced samples show intense peaks for the perovskite phase, without major changes due to pretreatment, indicating that the perovskite phase is reasonably stable. On the basis of the line widths, the crystallite size of the perovskite phase is on the order of 10 nm, which appears to contradict the earlier conclusion that the LaFeO_3 exists in the form of a 0.56-nm LaFeO_3 film. It is possible that a small part of LaFeO_3 films agglomerated into large crystallites that were not observed in STEM, leaving sufficient LaFeO_3 to cover the rest of the surface, but this would not explain the high intensity of the perovskite features. Two-dimensional crystallites could exhibit intense diffraction peaks but only in the directions perpendicular to the larger length scale ¹²⁰. Therefore, LaFeO_3 films in the form of two-dimensional crystallites, oriented in random directions, possibly with respect to the underlying MgAl_2O_4 grains, would be expected to exhibit a standard XRD powder pattern.

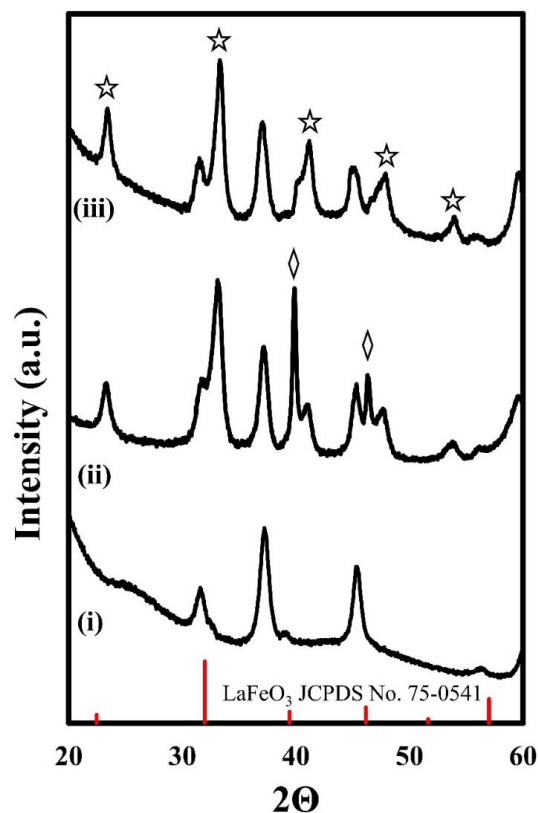


Figure 5.10: XRD patterns of: (i) unmodified MgAl_2O_4 ; (ii) oxidized Pt/LFO/MAO after 5 redox cycles at 1073 K; (iii) reduced Pt/LFO/MAO after 5 redox cycles at 1073 K. Perovskite features are marked with stars, metallic Pt with diamonds.

The major difference in the patterns for the oxidized and reduced samples is in the presence of very intense Pt features for the oxidized sample, which decrease dramatically in height after reduction. This result is surprising for multiple reasons. First, the intense, narrow Pt feature appears to be inconsistent with the observation of well-dispersed Pt in the STEM images. Second, high-temperature reduction would normally increase metal particle size, not decrease particle size; and this should cause the Pt peaks to sharpen and increase in height. Finally, it is important to recognize that this sample had been oxidized and reduced five times at 1073 K prior to acquiring the diffraction patterns; and the

transition between the patterns for the oxidized and reduced samples was completely reversible upon calcination or reduction at 1073 K.

To better understand the diffraction patterns, Rietveld analysis was performed on a separate sample batch prepared in the same manner. Conclusions from the analysis are summarized in **Table 5.1**. First, the Rietveld analysis indicates that the Pt content was approximately 4-wt% for both reduced and oxidized samples and that the change in the height and width of the Pt peaks upon reduction is due to an apparent decrease in Pt crystallite size from 22 nm to 10 nm. Obviously, the estimate of crystallite size does not agree with the STEM results in **Figure 5.1**. Since the estimates of the Pt content on both the oxidized and reduced samples agree reasonably well with the actual Pt content of 2.9-wt%, the XRD pattern cannot be associated with a small number of large Pt particles. Based on the size of the calculated unit cell for Pt, 0.38980 nm compared to 0.39231 nm for pure Pt, the amount of reduced Fe alloyed with Pt, if present, is very limited. There is no evidence for the formation of crystalline PtO₂ or of metallic Fe. The Rietveld analysis also suggests there may be an evolution of oxide phases during redox cycling. In particular, the analysis indicates that contact between the LaFeO₃ and MgAl₂O₄ may allow a reversible solid-state reaction between these two phases. The cell parameters determined for each oxide phase significantly differ from the theoretical values of the parent phases, suggesting the presence of doping ions in significant amounts. Based on the ionic radii of the various cations (Mg²⁺, Al³⁺, La³⁺, and Fe³⁺)¹²¹, the trends observed in the cell parameters are compatible with the mutual exchange between Mg²⁺ and La³⁺ and between Al³⁺ and

Fe³⁺. Notably, the relative amounts of the different phases differ depending on the thermochemical treatment applied to the materials and a new phase (La₃FeO₆) appears in the reduced sample. It should be noted that any MgO or FeO_x phases that must form in this reaction could not be distinguished, possibly due to being amorphous. Finally, considering the complexity of the XRD patterns and the high number of phases identified, a reliable determination of the exact composition of the different oxide phases is not possible.

Table 5.1: Results from Rietveld analysis of the XRD patterns of the oxidized and reduced Pt/LFO/MAO, in comparison with the cell parameters reported for the parent pure phases.

	Oxidized		Reduced		Parent pure phase
Phase (Space Group)	Amount (wt%)	Cell parameters (nm)	Amount (wt%)	Cell parameters (nm)	Cell parameters (nm)
Pt (Fm $\bar{3}$ m)	4.4%	a = 0.39172	4.1%	a = 0.38980	a = 0.39231
MgAl ₂ O ₄ (Fd $\bar{3}$ m)	64.2%	a = 0.80104	66.4%	a = 0.80517	a = 0.80806
LaFeO ₃ (Pnma)	16.0%	a = 0.56182 b = 0.76394 c = 0.54441	6.2%	a = 0.55398 b = 0.77324 c = 0.54456	a = 0.56619 b = 0.79447 c = 0.56008
LaAlO ₃ (R $\bar{3}$ c)	15.4%	a = 0.53967 c = 1.31445	21.8%	a = 0.54109 c = 1.31508	a = 0.53655 c = 1.31120
La ₃ FeO ₆ (Cmc2 ₁)	----	----	1.5%	a = 0.97279 b = 1.21087 c = 0.58461	a = 0.94443 b = 1.18767 c = 0.57373

For comparison, XRD patterns and Rietveld analysis were also performed on the Pt/MAO sample after 5 redox cycles, with results shown in the supporting information of

the original publication ¹²². The analysis indicates that the Pt particles supported on MgAl₂O₄ have an average size of ~20 nm, in good agreement with the STEM images. Unlike the case for Pt/LFO/MAO, no reversible changes in particle size or composition were observed upon redox cycling over samples of Pt/MAO.

5.3.2 XANES/EXAFS

To gain further insight into the nature of Pt interactions with the LaFeO₃, we acquired XAS spectra with a focus on Pt. The XANES spectrum at the Pt L₃ edge of the reduced Pt/LFO/MAO sample, **Figure 5.11**, is similar to that of a Pt foil, indicating that all of the Pt atoms are in the zero-valent state. Differences between the reduced sample and the Pt foil can be observed in the EXAFS part of the spectrum. The extracted EXAFS signal, **Figure 5.12 (a)**, resembles that obtained from a Pt foil but shows a lower intensity and a lower frequency. Attempts to model the EXAFS signal with a single Pt-Pt distance did not provide a reasonable fit of the experimental data. This was only achieved by introducing a Pt-Fe path at a distance slightly shorter than Pt-Pt distance. The obtained fit (R-factor = 0.0060) is presented in **Figure 5.13** while the contributions of each path to the FT-EXAFS signal are presented in **Figure 5.12 (b)**. The structural parameters extracted from this fitting are shown in **Table 5.2**. It is worth noting the absence of a relevant feature associated with a Pt-O distance near $R = 0.20$ nm ($R_{\text{eff}} = 0.16$ nm), as might be expected for Pt atoms on the surface of metal nanoparticles and interacting with the support. This fact may suggest the formation of a thin layer of reduced Fe atoms at the interface between the support and the small Pt nanoparticles. This is also consistent with there being an

important contribution from the Pt-Fe path (at a distance slightly shorted than Pt-Pt in Pt metal, see **Table 5.2** and **Figure 5.12**) and lack of a direct interaction between Pt particles and oxide support.

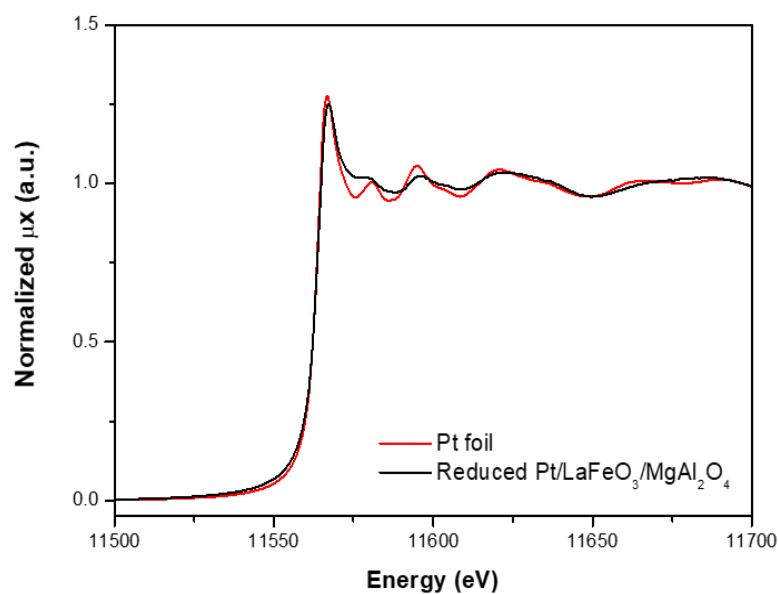


Figure 5.11: XANES spectrum for the reduced Pt/LFO/MAO samples, in comparison with the spectrum of Pt foil.

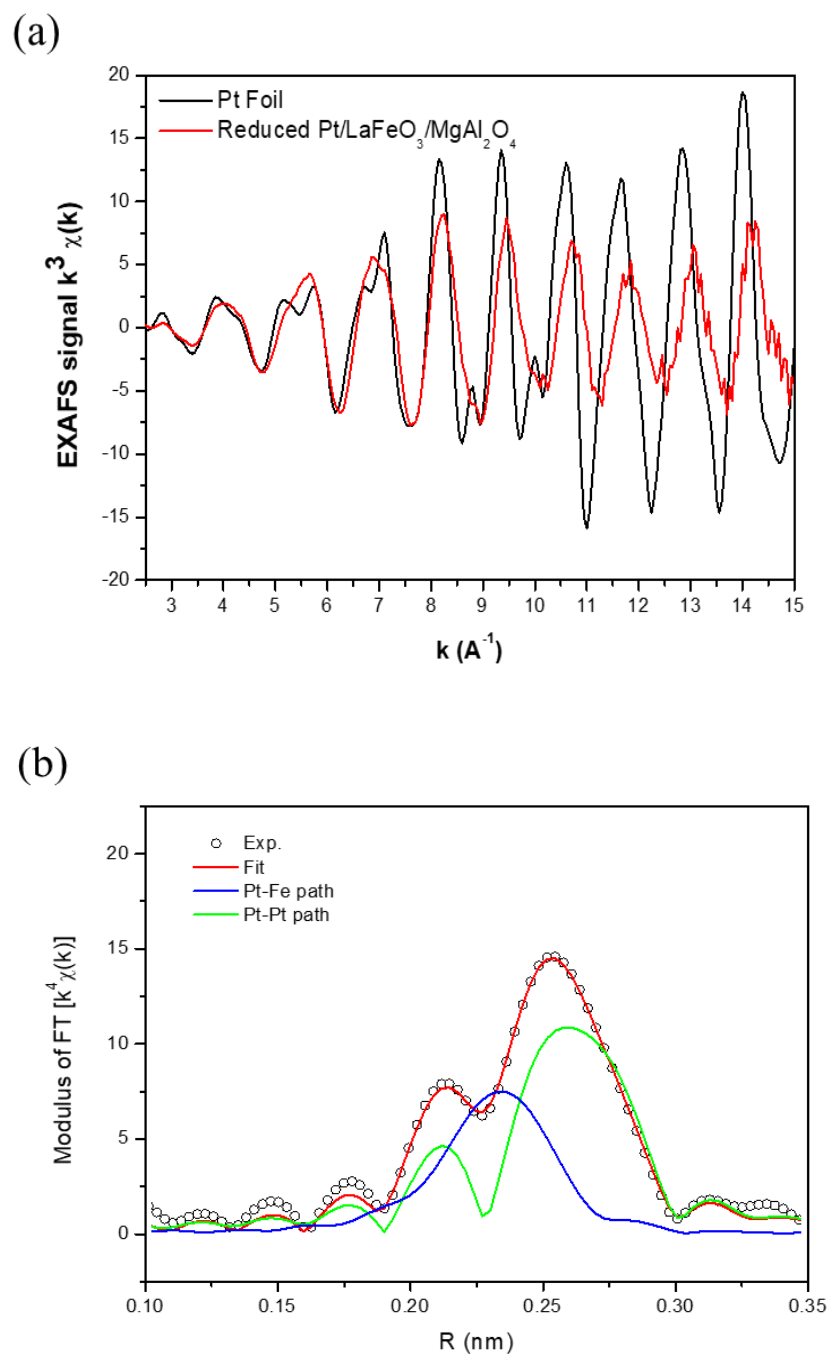


Figure 5.12: Extracted k^3 -weighted EXAFS spectrum for the reduced Pt/LFO/MAO sample, in comparison with the (a) spectrum Pt foil and (b) contribution of each path to fit of the k^3 -weighted FT-EXAFS spectrum.

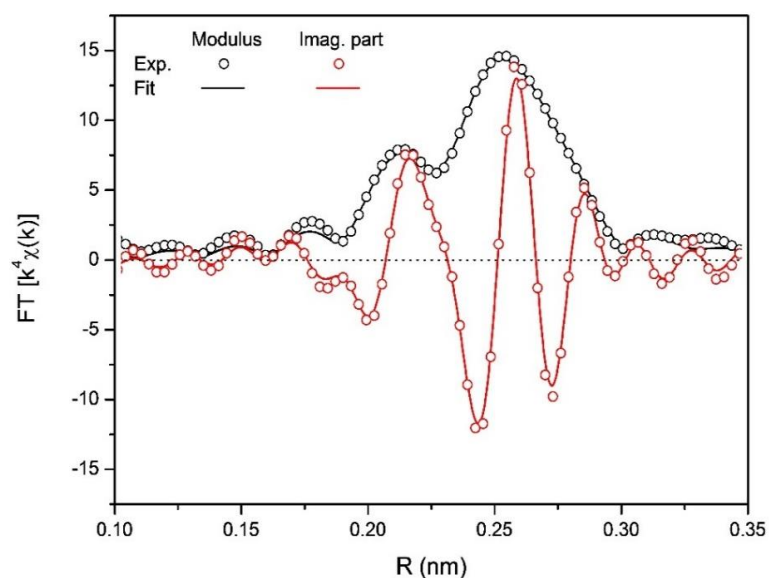


Figure 5.13: Fit of the experimental k^3 -weighted FT-EXAFS signals for the reduced Pt/LFO/MAO samples after 5 redox cycles at 1073 K.

Table 5.2: Fitting results from the ex-situ EXAFS analysis at the Pt L_3 edge for 1073-K oxidized and reduced samples.

Sample	Path	Coordination number (CN)	Distance R (nm)	$\sigma^2 \times 10^{-5}$ (nm ²)
Reduced Pt/LFO/MAO	Pt-Fe	3.3 ± 0.9	0.267 ± 0.001	6 ± 2
	Pt-Pt	4.7 ± 0.6	0.273 ± 0.001	4 ± 2
Oxidized Pt/LFO/MAO	Pt-O	1.8 ± 0.4	0.198 ± 0.001	2 ± 2
	Pt-Pt	8.3 ± 0.7	0.276 ± 0.001	5 ± 2

The XANES/EXAFS results for the oxidized Pt/LFO/MAO were significantly different. The white-line intensity in the XANES spectrum, **Figure 5.14**, was intermediate between that observed for Pt metal and PtO₂. Linear Combination Analysis indicated that 69% of Pt is in the zero-valent state, while 31% was present as oxidized Pt ions. The EXAFS signal at the Pt L_3 edge in the oxidized Pt/LFO/MAO sample, **Figure 5.15 (a)**, significantly

differs from that of the reduced sample, becoming more similar to (and being dominated by) a contribution from metallic Pt. Two contributions related to Pt-O and metal Pt-Pt paths can be clearly observed in the FT-EXAFS signal, **Figure 5.15 (b)**. Modeling of the EXAFS signal included these 2 paths, with the result presented **Figure 5.16** (R-factor = 0.0070) and the structural parameters reported in **Table 5.2**. The combination of XANES and EXAFS results on the oxidized Pt/LFO/MAO indicates that the Pt exists primarily in the reduced state, even if some re-oxidation occurs by passivation of the surface and/or at the interface with the support. It is noteworthy that the Pt-Fe path is lost after re-oxidation of the sample, consistent with changes in the Fe-containing phases observed by XRD analysis. It is noteworthy that the calculated coordination number for Pt was 8.3, suggesting a Pt particle size in the same range observed in STEM, 1 to 2 nm assuming a cuboctahedral morphology ¹²³.

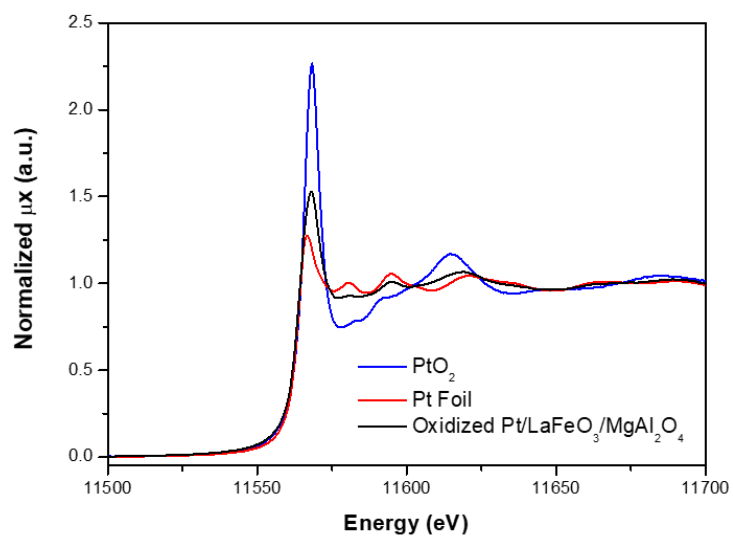


Figure 5.14: XANES spectrum for the oxidized Pt/LFO/MAO samples, in comparison with the spectra of Pt foil and PtO_2 .

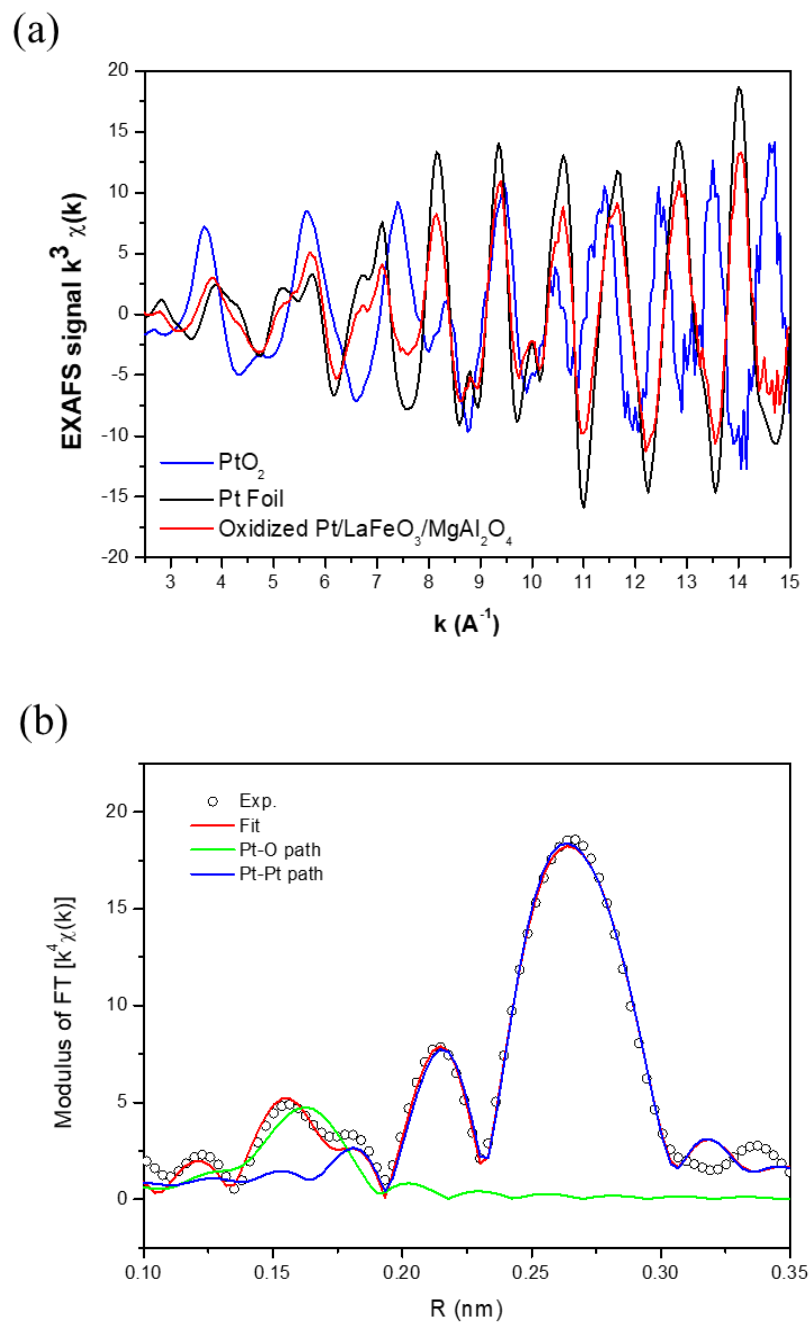


Figure 5.15: Extracted k^3 -weighted EXAFS spectrum for the oxidized Pt/LFO/MAO sample, in comparison with (a) the spectrum Pt foil and (b) contribution of each path to fit of the k^3 -weighted FT-EXAFS spectrum.

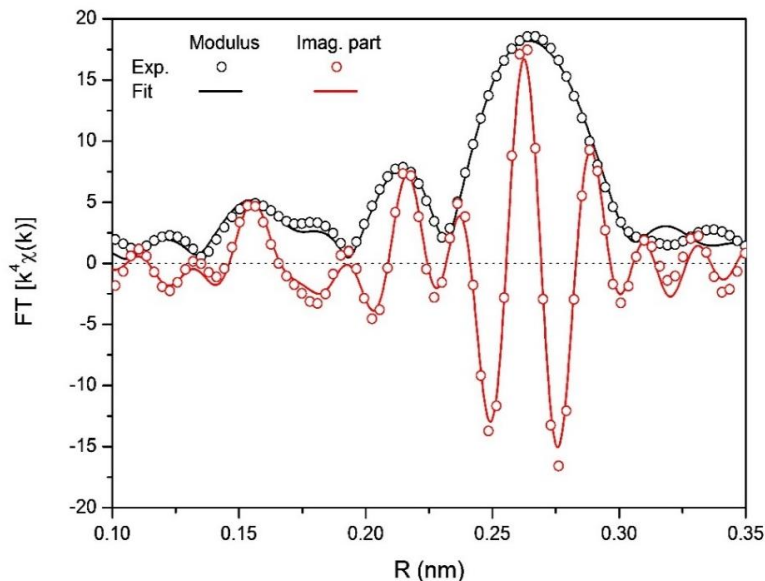


Figure 5.16: Fit of the experimental k^3 -weighted FT-EXAFS signals for the oxidized Pt/LFO/MAO samples after 5 redox cycles at 1073 K.

There is an obvious discrepancy between the Pt particle sizes obtained from XRD, from STEM, and from XAS. This can be rationalized only by considering differences in what the techniques measure. XRD is sensitive only to that fraction of the sample that has a high degree of crystallinity, and small particles would not contribute to the pattern. If there is a distribution of Pt particle sizes, XRD could therefore overestimate the actual mean crystallite size. Furthermore, the preferential orientation of particles could modify the intensity and width of the various reflections ¹²⁰. EXAFS, on the other hand, is particularly sensitive to smaller nanoparticles, and the coordination number can change dramatically for even minor changes in size ¹²³. This can result in the crystallite size being underestimated. Although the STEM measurements in this study showed only very small

particles, it must be acknowledged that the images sample only a fraction of the sample and may not be representative of the overall composition.

Several different scenarios can be used to explain the results. The first is that the Pt particles exist in a bimodal distribution. In this picture, the Pt XRD peaks for the oxidized sample are due mainly to the fraction of larger Pt particles, whereas the STEM and EXAFS over-represent smaller particles. This model is compatible with the epitaxial registration observed for the small Pt nanoparticles but would require reversible sintering of the Pt upon oxidation and spreading of Pt particles upon reduction. The Pt coordination number of 8.3 observed for the oxidized sample would be an average of that for small and large particles. Indeed, if only 69% of the oxidized catalyst has Pt in the metallic form, the actual CN of Pt in the metal nanoparticles is close to 12, the value for bulk Pt. The scenario would require 69% of the Pt to be present in the form of large metal particles and 31% in the form of isolated Pt atoms, neither of which was observed in HAADF-STEM. A second possible model is that the intense Pt diffraction feature observed in XRD on the oxidized sample is due to scattering from collections of small Pt clusters, oriented with respect to each other, on much larger, two-dimensional perovskite crystallites. After reduction, the epitaxy is partially lost, accounting for the increased width and decreased height of the Pt peaks in the XRD patterns of the reduced sample. We attempted to introduce preferential orientations for both the metallic Pt and the LaFeO_3 - and LaAlO_3 -related phases in the Rietveld analysis of the XRD patterns; however, the quality of the fit did not improve.

5.3.3 CO Oxidation Rates

Differential CO-oxidation rates were measured in 25 Torr CO and 12.5 Torr O₂ on Pt/LFO/MAO (2.9-wt% Pt, 30-wt% LaFeO₃), Pt/FeO_x/MAO (3.0±0.2-wt% Pt, 10±1-wt% Fe₂O₃), Pt/MAO (3.1±0.2-wt% Pt) samples. All the samples were prepared by ALD, with the Pt loadings achieved by the amount of Pt added in one ALD cycle. To determine the effect of pretreatment conditions, the initial measurements were performed on each catalyst prior to any redox treatments. After ALD deposition of Pt, the catalysts were calcined to only 573 K to remove the ligands on the Pt precursor before measuring the “as-prepared” rates. Rate measurements were then obtained on each of the catalysts after oxidation at 1073 K, after reduction at 1073 K, and after five redox cycles. Arrhenius plots for the Pt/LFO/MAO are shown in **Figure 5.17**. Light-off profiles for Pt/LFO/MAO are shown in the original publication ¹²² and are consistent with data in **Figure 5.17**. Rates on the as-prepared Pt/LFO/MAO were high, and it was necessary to obtain the data at relatively low temperatures in order to achieve differential conditions for the catalyst loading and flow rates that were used. When not promoted by a reducible oxide ¹²⁴, CO-oxidation rates on Pt are dependent only on metal surface area ¹²⁵. Using these rates from the literature ¹¹², the Pt dispersion of the as-prepared catalyst is estimated to be 26%, in good agreement with room-temperature CO chemisorption measurements, as shown in **Table 5.3**. When this catalyst was calcined to 1073 K, the rates decreased a factor of about 25; but the rates returned to their initial value after reduction at 1073 K. Repeated

oxidation and reduction cycles at 1073 K caused the catalyst to go between the active and inactive states.

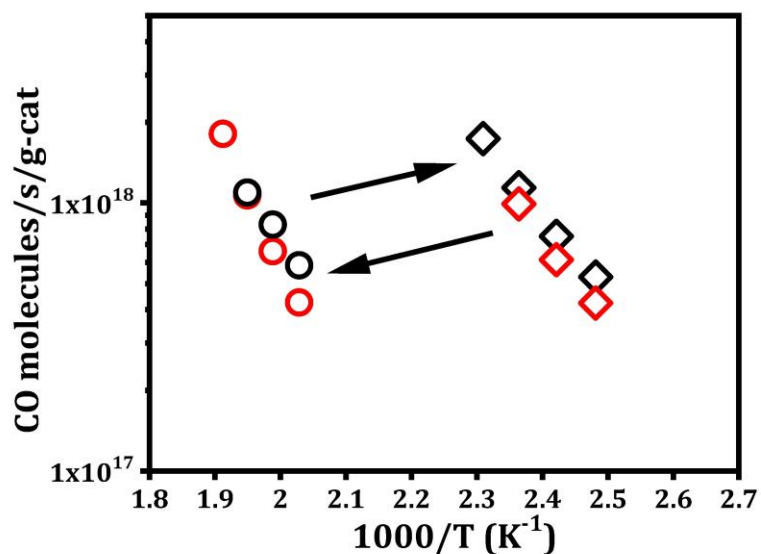


Figure 5.17: Steady-state, differential reaction rates for CO oxidation with 25 Torr of CO and 12.5 Torr O₂ for 0.1-g sample of Pt/LFO/MAO. Rates measured on the as-prepared sample are marked in solid squares. Rates measured on the sample that after oxidation in 10% O₂-He at 1073 K for 1 h are marked in circles; rates measured on the sample that after reduction in 10% H₂-He at 1073 K for 1 h are marked in diamonds. Black symbols denote the first redox cycle, while red symbols denote the fifth cycle.

Table 5.3: Summary of Pt dispersion (%) measured by CO chemisorption or estimated based on dispersion and activity of Pt (111) in the literature for catalysts after 5th reduction and oxidation pretreatments at 1073 K.

	as prepared		1073-K oxidized		1073-K reduced	
	measured	estimated	measured	estimated	measured	estimated
Pt/LFO/MAO	23	26	-	0.2	-	30
Pt/FeO _x /MAO	24	>100	0.9	0.3	1.1	0.6
¹¹⁵ Pt/MAO	27	23.5	0.1	0.1	0.1	0.4

:- Not able to be measured.

Activation and deactivation of the Pt/LFO/MAO cannot be due simply to oxidation or reduction of the Pt. First, as shown in **Figure 5.18**, reduction at 773 K did not restore activity in a catalyst that had been oxidized at 1073 K, and oxidation at 773 K did not deactivate a catalyst that had been reduced at 1073 K. Furthermore, deactivation of the oxidized catalyst cannot be due to reversible formation of Pt single atoms, as has been reported in other studies ^{97, 126}, since that would be inconsistent with the STEM and XRD data. There was also a major change in the catalyst after the first high-temperature oxidation cycle in that we were not able to measure dispersion by CO chemisorption. As shown in **Table 5.3**, adsorption of CO at room temperature was negligible after high-temperature treatments, even though dispersions estimated from the reaction rates were very high. This suggests that the CO-oxidation reaction on Pt/LFO/MAO is significantly different from that which occurs on normal Pt catalysts. In agreement with this, reaction orders for CO on the Pt/LFO/MAO, shown in **Figure 5.19**, were almost zero, whereas the reaction is normally inverse-first-order on conventional Pt ¹²⁷. Also, the activation energy

for CO oxidation over reduced Pt/LFO/MAO, 60 ± 5 kJ/mol, was significantly lower than the activation energies calculated for Pt/MAO, 100 ± 5 kJ/mol.

The failure to observe CO chemisorption, and the weaker dependence of the reaction on CO partial pressure over Pt/LFO/MAO, suggests that the reaction mechanism is different. It is likely that the reaction occurs at the interface between Pt and the LaFeO_3 support, similar to what has been observed on Pt- CeO_2 catalysts⁵⁵. In addition to the change in reaction order, reaction at the metal–oxide interface could also explain the decreased activation energy compared to that of the conventional Pt catalyst.

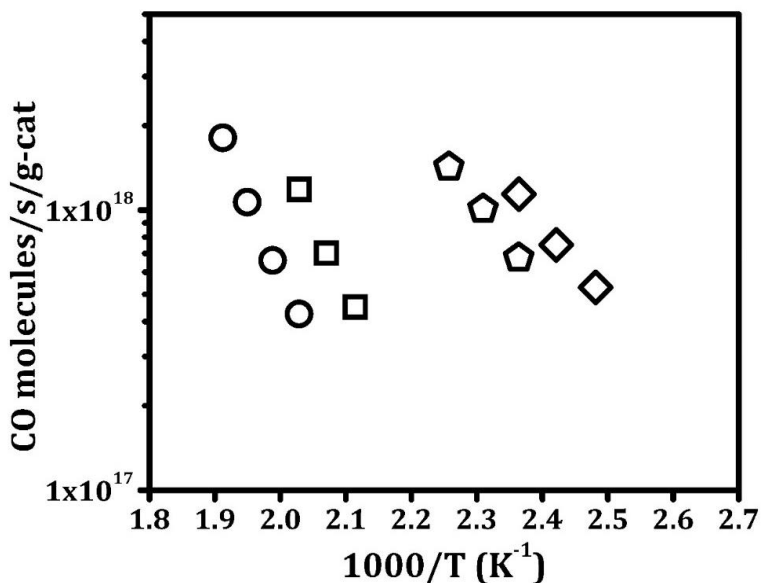


Figure 5.18: Steady-state, differential reaction rates for CO oxidation with 25 Torr of CO and 12.5 Torr O_2 for a 0.1-g sample of Pt/LFO/MAO. Rates were measured on a sample that had been oxidized in 10% O_2 -He at 1073 K for 1 h are marked in circles; rates measured after reduction in 10% H_2 -He at 773 K for 1 h are marked in squares; rates measured after reduction in 10% H_2 -He at 1073 K for 1 h are marked in diamonds; rates measured on a reduced sample after oxidation in 10% O_2 -He at 773 K for 1 h are marked in pentagons.

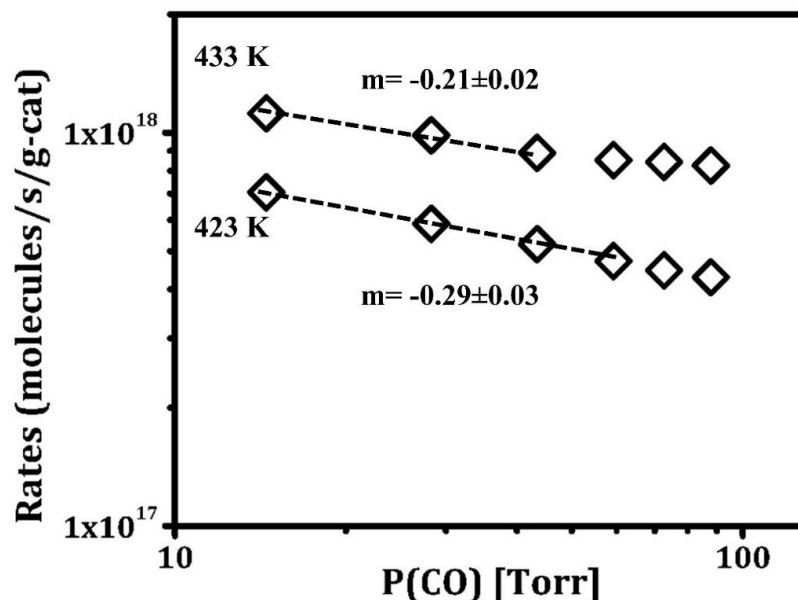


Figure 5.19: Dependence of CO oxidation rates at 423 K and 433 K, with PO₂ kept at 7.6 Torr, over 0.1-g sample of reduced Pt/LFO/MAO after 5 redox cycles at 1073 K.

To ensure that the reaction results on Pt/LFO/MAO are not due to the ALD preparation or the presence of FeO_x, reaction measurements were also performed on the Pt/MAO (Chapter 4) and Pt/FeO_x/MAO catalysts, with results shown in **Figure 5.20**. The as-prepared Pt/MAO exhibited similar rates to those observed on as-prepared Pt/LFO/MAO. The rates again decreased dramatically upon high-temperature calcination but were not restored by high-temperature reduction. As shown in **Table 5.3**, the dispersions estimated from the specific reaction rates agreed well with dispersions determined by CO chemisorption and the STEM measurements reported earlier (**Figure 5.5**). Rates on the as-prepared Pt/FeO_x/MAO were very high. Promotion of CO-oxidation rates on Pd catalyst due to contact with FeO_x has been reported previously⁹⁸ and is likely responsible for the high rates reported here. However, high-temperature redox cycling

again resulted in a dramatic decrease in rates that could not be restored. STEM images of the Pt/FeO_x/MAO catalyst, shown in **Figure 5.21**, demonstrated a large growth in the Pt particles and segregation of the FeO_x. Finally, a previous report of Pt/La/MAO also showed strong deactivation of the catalyst following redox cycling (Chapter 4).

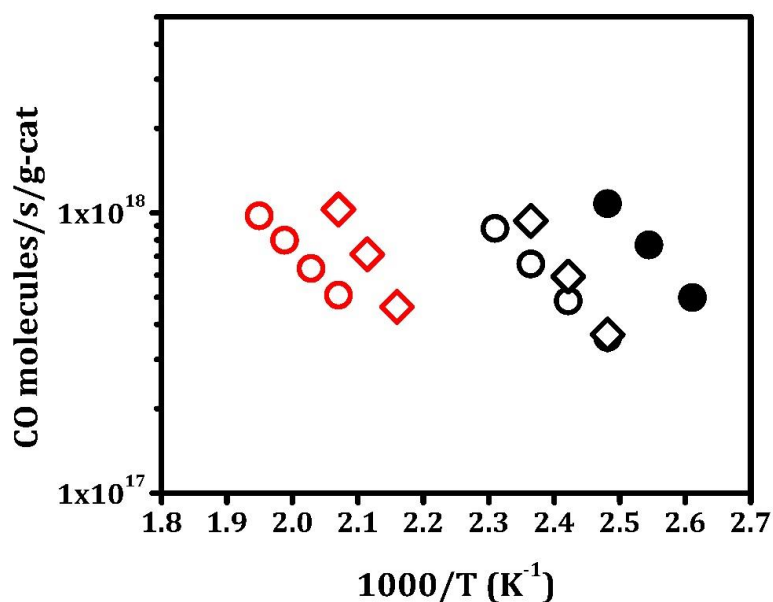


Figure 5.20: Steady-state, differential reaction rates for CO oxidation with 25 Torr of CO and 12.5 Torr O₂ for 0.1-g sample of Pt/FeO_x/MAO. Rates measured on the as-prepared sample are marked in solid squares. Rates measured on the sample that after oxidation in 10% O₂-He at 1073 K for 1 h are marked in circles; rates measured on the sample that after reduction in 10% H₂-He at 1073 K for 1 h are marked in diamonds. Black symbols denote the first redox cycle, while red symbols denote the fifth cycle.

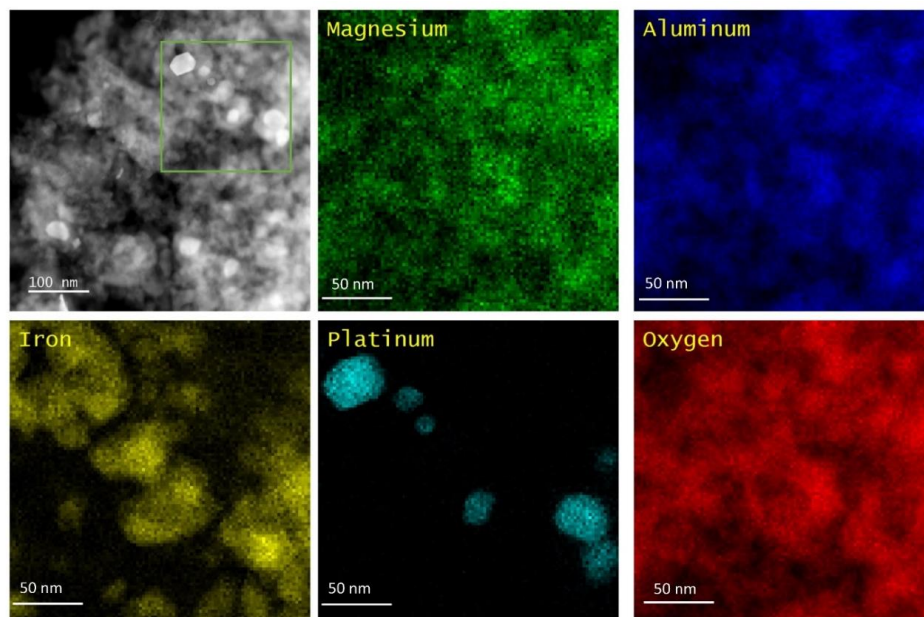


Figure 5.21: High-angle annular dark-field STEM image and EDS maps of Mg, Al, Fe, Pt and O on the reduced Pt/FeO_x/MAO after 5 redox cycles, taken from the region indicated by the green box. The image and maps were measured using a JEOL NEOARM STEM.

5.4 Discussion

Maintaining high metal dispersions in supported-metal catalysts upon high-temperature redox cycling is extremely challenging and could have important implications for catalysts operating under harsh conditions, such as those experienced by automotive emissions-control catalysts. The present work demonstrates that thin LaFeO₃ films may be capable of achieving this important goal. This could have important commercial consequences by allowing the use of reduced amounts of precious metals in these applications.

The observation that metal particles are oriented with respect to the perovskite film indicates that there must be strong bonding interactions between the metal and

perovskite. It is likely that similar bonding interactions are present with bulk perovskites and that these are at least partially responsible for the ex-solution phenomenon observed in some bulk perovskites. These bonding interactions are specific to the particular metal and perovskite. For example, it has been reported that Pt can enter the perovskite lattice for both the CaTiO_3 and LaFeO_3 , while Pd can only enter the LaFeO_3 lattice, not that of CaTiO_3 ¹⁷. Related to this, recent work also found evidence for strong support interactions with Pt, not with Pd, on thin CaTiO_3 films⁴⁹. The perovskite structure must be important since we did not observe similar stabilities for Pt particles when La_2O_3 or FeO_x were deposited individually. Finally, the strength of the bonding interactions varies with the specific metal and perovskite. While there was evidence for strong support interactions for Pt on thin CaTiO_3 films, relatively large Pt particles were still formed upon high-temperature redox cycling.

The properties of the Pt are clearly affected by interactions with the LaFeO_3 film, as demonstrated by the fact that CO adsorption is suppressed, and both the reaction order and activation energy for CO oxidation are affected. Since electronic interactions can extend a few atomic distances, this may be related to the fact that the Pt particles are very small in the present work, so that the Pt atoms at the surface of the particles must be close to the support interface. However, we cannot rule out the possibility that Pt can go beneath the surface of the perovskite, especially following oxidation. This could help explain the large difference in activity between the oxidized and reduced samples. The fact that such high temperatures are required to cycle the perovskite-containing catalysts

between “activated” and “deactivated” states suggests that oxidation and reduction cause a major restructuring of the catalyst, beyond simply oxidizing and reducing the Pt surface.

There is obviously still much to learn about these perovskite-supported metals. The catalytic properties of these materials are clearly very different from that of conventional supported-metal catalysts. The fact that they can exist in a deactivated state following high-temperature oxidation also implies that they can be pretreated and used in an appropriate manner. However, the fact that one can maintain very high dispersions under very harsh conditions makes the materials very intriguing and worth additional consideration.

5.5 Conclusion

In this work, we successfully prepared a high-surface-area LaFeO_3 thin film on MgAl_2O_4 support using ALD. We demonstrated that, following high-temperature reduction, Pt on the $\text{LaFeO}_3/\text{MgAl}_2\text{O}_4$ was able to exhibit superior activity for CO oxidation, even following harsh pretreatments. $\text{Pt}/\text{LaFeO}_3/\text{MgAl}_2\text{O}_4$ was found to switch between “active” and “inactive” states for CO oxidation after high-temperature reduction or oxidation. Stabilization of Pt particle size results from strong interactions between the Pt and the support, as evidenced by the appearance of Pt particles that are epitaxially aligned with respect to the perovskite support.

CHAPTER 6. A COMPARISON OF Rh, Pd, AND Pt CATALYSTS SUPPORTED ON LaFeO_3 FILMS PREPARED BY ATOMIC LAYER DEPOSITION⁴

Summary

Metal-support effects were studied for Rh, Pd, and Pt deposited onto 1-nm LaFeO_3 films prepared by ALD on MgAl_2O_4 . Significant differences were observed for how the three metals interact with LaFeO_3 . Although STEM showed that Rh remained well-dispersed after multiple oxidation and reduction steps at 1073 K, both reduced and oxidized catalysts showed low activity for CO oxidation. STEM data for the Pd/ LaFeO_3 / MgAl_2O_4 showed reversible formation of larger Pd particles and evidence for Pd-Fe alloy upon high-temperature reduction. CO-oxidation rates on Pt/ LaFeO_3 / MgAl_2O_4 could be cycled between inactive and active states by oxidation or reduction at 1073 K. In the absence of metal catalysts, reduction of LaFeO_3 at 1073 K was negligible but between 1.5 and 2 oxygens per metal atom could be removed on the supported catalysts. Coulometric titrations demonstrated that each of the metals was more difficult to reduce when supported on LaFeO_3 .

⁴ This chapter is in preparation, and will be submitted to a journal as a manuscript.

6.1 Introduction

An interesting aspect of support effects with perovskites is that they are specific to the specific metal and perovskite compositions. This was demonstrated early on by the fact that Pt cations, but not Pd cations, can enter the CaTiO_3 lattice, while the cations of both metals can become part of LaFeO_3 ¹⁷. In a comparison of Pt and Pd particles on $\text{CaTiO}_3/\text{MgAl}_2\text{O}_4$ ⁴⁹, the Pt/ $\text{CaTiO}_3/\text{MgAl}_2\text{O}_4$ catalyst exhibited characteristics associated with strong support interactions while the properties of Pd/ $\text{CaTiO}_3/\text{MgAl}_2\text{O}_4$ were similar to those found with Pd on noninteracting supports. A recent comparison of Rh on $\text{CaTiO}_3/\text{MgAl}_2\text{O}_4$, $\text{SrTiO}_3/\text{MgAl}_2\text{O}_4$, and $\text{BaTiO}_3/\text{MgAl}_2\text{O}_4$ reported significant differences between these catalysts ¹²⁸, with Rh bonding much more strongly to CaTiO_3 than to BaTiO_3 . The compositional specificity in each of these examples is similar to what would be expected if there were chemical bonding between the metals and the perovskite.

The initial application for “intelligent” catalysts was for automotive-emissions control and involved the precious metals, Pt, Pd, and Rh, with LaFeO_3 as the support ¹⁶⁻¹⁷. Each of the metals was shown to enter the lattice of LaFeO_3 upon high-temperature oxidation ¹⁷, but each metal exhibited different extents of ex-solution as particles upon reduction. These experimental observations were later supported by two computational studies using Density Function Theory (DFT). The calculations showed that bonding was different for these three metals ¹²⁹⁻¹³⁰; surface segregation was most favorable for Pd, followed by Pt, while Rh would prefer to remain in the perovskite over a wide range of PO_2 .

In the present study, we examined the Rh-LaFeO₃ system by preparing and characterizing Rh/LaFeO₃/MgAl₂O₄, denoted as Rh/LFO/MAO. In order to provide a better comparison with Pt and Pd, Pt/LaFeO₃/MgAl₂O₄ (Pt/LFO/MAO) and Pd/LaFeO₃/MgAl₂O₄ (Pd/LFO/MAO) were re-investigated using the same supports and preparation procedures. In agreement with the previous calculations¹²⁹⁻¹³⁰, our experimental results indicate that metal interactions with LaFeO₃ are different for the three metals. Based on differences with the more conventional metals MgAl₂O₄, interactions are strongest for Rh, followed by Pt and Pd.

6.2 Experimental Methods

6.2.1 Sample Preparation

The MgAl₂O₄ was prepared using the method described in **Chapter 2.1**, having a BET specific surface area of 120 m²/g. The LFO/MAO supports were prepared in the same manner to that described in the **Chapter 5.2.1**. The LaFeO₃ film thicknesses were calculated from the mass of LaFeO₃ and the BET surface area of the MgAl₂O₄, assuming a bulk density for the perovskite phase. Most samples in this study had an average perovskite film thickness of 1.0 nm, but one Pt-containing sample was prepared with a 0.5-nm film in order to examine the effects of LaFeO₃ thickness. The final calcination temperature for the films prior to metal deposition was 873 K.

Pt, Pd, and Rh were also added to the LaFeO₃ films by ALD using platinum(II) acetylacetonate (Pt(acac)₂, Strem Chemicals, Inc.), Bis(2,2,6,6-tetramethyl-3,5-

heptanedionato) palladium(II) ($\text{Pd}(\text{TMHD})_2$, Strem Chemicals, Inc.), and Rhodium(III) acetylacetonate ($\text{Rh}(\text{acac})_3$, Strem Chemicals, Inc.). Again, deposition procedures for each metal have been described in previous publications, and growth rates were shown to be $1.3 \times 10^{18} \text{ Rh/m}^2\text{-cycle}^{128}$, $\sim 1.0 \times 10^{18} \text{ Pt/m}^2\text{-cycle}^{122}$, and $1.0 \times 10^{18} \text{ Pd/m}^2\text{-cycle}^{98}$. The samples were calcined at 773 K for 10 minutes to remove the precursor ligands of the deposited metals. Samples that received only this treatment are referred to as “as-prepared” samples. Each of the samples was then oxidized and reduced five times at 1073 K by alternately flowing 10% O_2 -He and 10% H_2 -He mixtures over the sample in 1-h cycles.

The physical properties of all the samples in this investigation are listed in **Table 6.1**. The La:Fe ratios of LaFeO_3 for 0.5-nm and 1-nm films were 1.02 and 1.04, respectively, as determined by ICP-OES. Characterization of the 0.5-nm LaFeO_3 films was reported in the **Chapter 5.3**. Unless otherwise stated, all samples in this study were prepared with a 1-nm LaFeO_3 film.

Table 6.1: Physical properties of samples used in this chapter.

	Metal loading (Metal moles) ^a (± 0.2 wt.%)	LaFeO ₃ loading (± 0.5 wt.%)	BET S.A. ^b (± 5 m ² /g)
0.5-nm LFO/MAO	-	28.0	78
LFO/MAO	-	44.0	67
Rh/MAO	2.3 (224)		120
Rh/LFO/MAO	1.8 (175)		65
Pd/MAO	1.7 (160)		
Pd/LFO/MAO	1.5 (141)		
Pt/MAO	3.3 (170)		
Pt/0.5-nm LFO/MAO	3.1(159)		
Pt/LFO/MAO	2.9 (149)		

a: Loadings were measured by weight gains and ICP-OES.

b: Surface areas were measured on samples that was calcined at 873 K.

6.2.2 Sample Characterization

ICP-OES was performed on a Spectro Genesis spectrometer with a Mod Lichte nebulizer. The XRD patterns of ALD-samples were measured using a Rigaku Smartlab diffractometer equipped with a Cu K α source ($\lambda = 0.15416$ nm). Surface areas of samples were measured using BET isotherms from adsorption of N₂ at 78 K. Scanning Transmission Electron Microscopy (STEM) and Energy Dispersive Spectroscopy (EDS) were taken using a JEOL NEOARM STEM.

Differential, steady-state rates were measured over 0.1-g samples using the system described in **Chapter 2.3.1**. CO-oxidation rates were measured with a total gas

flow rate maintained at 100 mL/min using a He carrier, and partial pressures of CO and O₂ maintained at 25 and 12.5 Torr, respectively. Light-off reaction profiles for CO oxidation were measured over 0.1-g samples in the setup described in **Chapter 2.3.2**.

Catalyst redox properties were measured using flow titration and coulometric titration, and the operational details were reported in **Chapter 2.4**.

6.3 Results

Characterization of 0.5- and 1.2-nm LaFeO₃ films prepared by ALD has been reported in more detail in **Chapter 5.3** and previous publication ⁸⁶. Based on EDS mapping and 2-propanol adsorption studies, it was demonstrated that the LaFeO₃ forms a uniform film over the MgAl₂O₄ support. Although the film thicknesses in these two studies were less than the coherence length of the X-Rays, XRD showed intense peaks associated with a perovskite phase, apparently due to the presence of two-dimensional crystallites, randomly oriented on the MgAl₂O₄ surface ¹²². The LFO/MAO supports used in the present study showed essentially identical properties.

6.3.1 Rh/LFO/MAO

Rh was deposited onto the LFO/MAO support using one ALD cycle of Rh(acac)₃ to give a Rh loading of 1.8-wt%. This loading corresponds to 1.6x10¹⁴ Rh atoms/cm², a value that is nearly identical to the Rh loading reported after one ALD cycle of this same precursor on other supports ¹²⁸. This coverage is close to the expected monolayer coverage

of the precursor, which implies that the Rh is uniformly distributed over the surface of the support, at least prior to calcination.

The sample was characterized by XRD and STEM-EDS measurements after it had been oxidized and reduced 5 times at 1073 K. The diffraction patterns for the oxidized and reduced samples are shown in **Figure 6.1**, together with patterns for MgAl_2O_4 and for the LFO/MAO supports without Rh. Peak intensities in **Figure 6.1** were normalized to that of the MgAl_2O_4 spinel phase. The peaks associated with the perovskite phase dominate the pattern for the LFO/MAO support. No additional peaks were observed for Rh on either the oxidized or reduced samples and the treatment conditions did not alter the pattern of the perovskite phase. Rh particles could not be observed in the STEM images of the oxidized sample, **Figure 6.2 (a)**; but the EDS map showed that the Rh remained highly dispersed, uniformly covering the surface of the support. Upon reduction, **Figure 6.2 (b)**, 1- to 2-nm Rh particles were observed over the entire surface. Because the images of both the oxidized and reduced samples were taken after 5 redox cycles, the changes observed in **Figure 6.2** should be considered reversible. In a previous study of Rh on MgAl_2O_4 ¹²⁸, similar pretreatments resulted in significantly larger Rh particles, ~5 nm, implying that the LaFeO_3 had a stabilizing effect on the Rh dispersion.

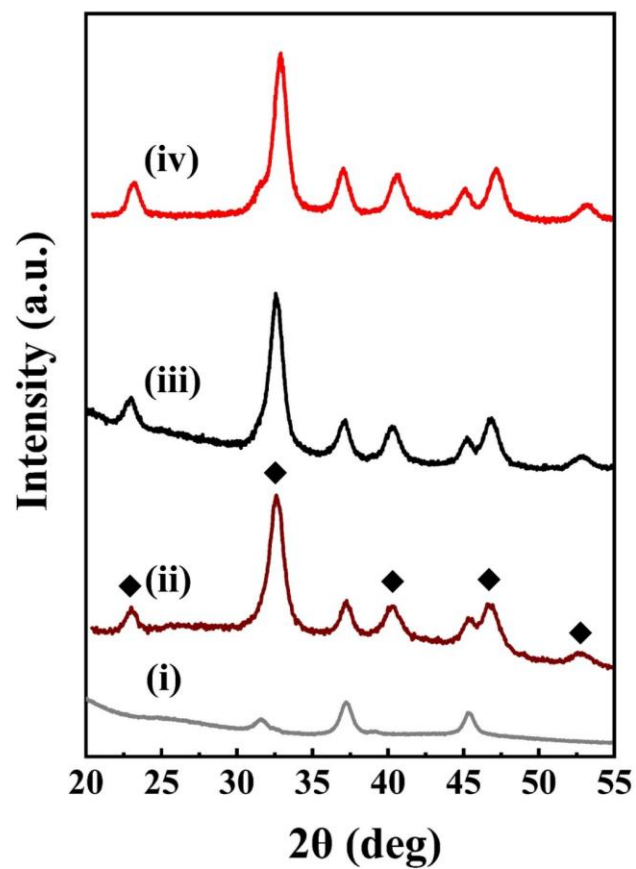


Figure 6.1: XRD patterns over Rh/LFO/MAO: (i) MgAl_2O_4 ; (ii) oxidized LFO/MAO after 5 redox cycles at 1073 K; (iii) oxidized Rh/LFO/MAO after 5 redox cycles at 1073 K; (iv) reduced Rh/LFO/MAO after 5 redox cycles at 1073 K.

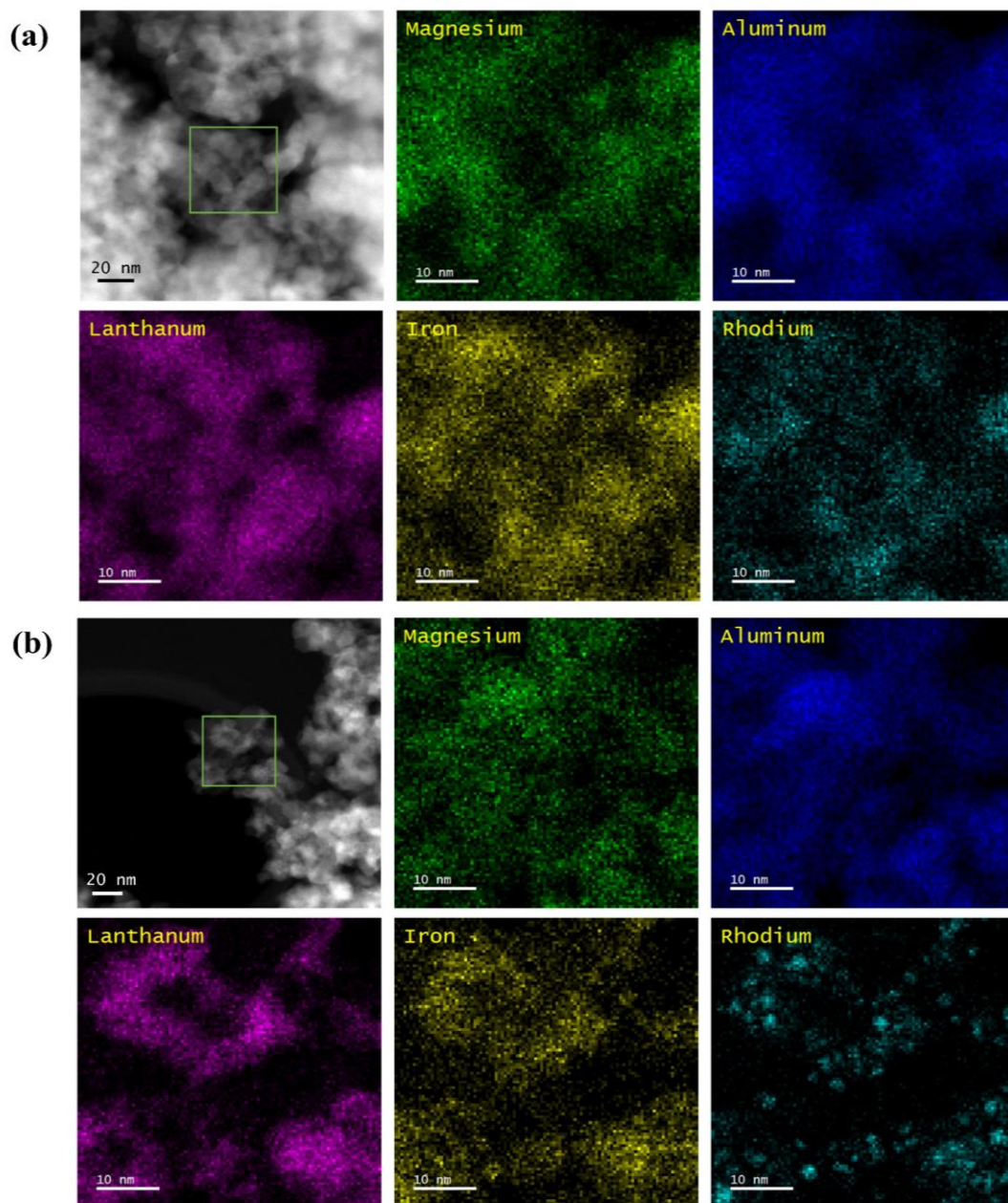


Figure 6.2: Representative STEM/EDS results for Rh/LFO/MAO after five 1073 K redox cycles with the final treatment being **(a)** 1073-K oxidation; **(b)** 1073-K reduction. EDS maps taken from the region of green box.

Steady-state, differential CO-oxidation rates were measured over Rh/LFO/MAO and Rh/MAO as a function of reduction temperature, with results shown in **Figure 6.3**. The samples were again oxidized and reduced five times at 1073 K prior to determining the rates, with oxidation as the last step. Rates on Rh/MAO increased steadily with increasing reduction temperature; on Rh/LFO/MAO, rates were higher after reduction at 573 K but did not change with increased reduction temperatures. After reduction 1073 K, rates on Rh/LFO/MAO were at least a factor of ten lower than those on Rh/MAO, despite the apparently higher dispersion observed in STEM measurements. The Rh dispersion for 1073-K reduced Rh/MAO, reported in **Table 6.2**, measured using CO adsorption, indicated a Rh dispersion of 21%, assuming a coverage of one CO molecule per surface Rh; however, CO adsorption on Rh/LFO/MAO indicated a dispersion of less than 2%, independent of reduction temperature. The low CO-oxidation rates and low CO chemisorption on Rh/LFO/MAO both suggest that Rh is either encapsulated in the LaFeO₃ or strongly bonded to the LaFeO₃.

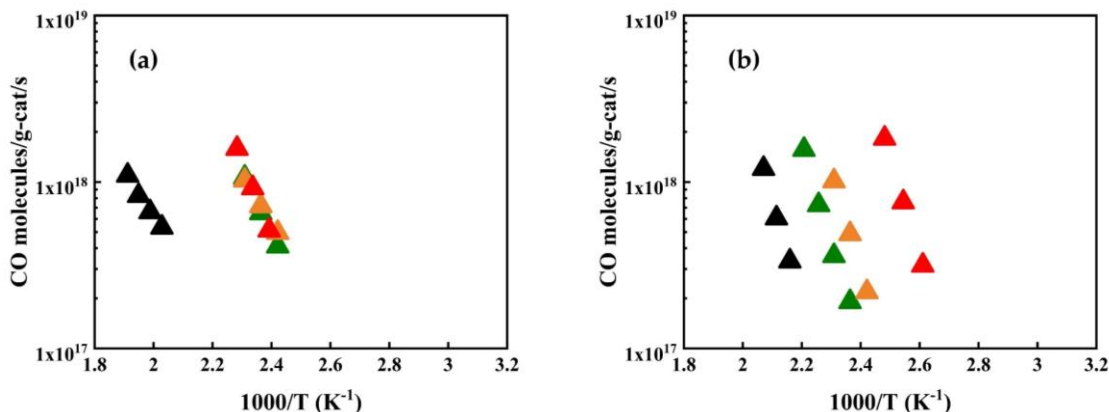


Figure 6.3: Steady-state, differential reaction rates for CO oxidation with 25 Torr of CO and 12.5 Torr O₂ for **(a)** Rh/LFO/MAO and **(b)** Rh/MAO as a function of reduction temperature. The samples had undergone 5 redox cycles with the final state of oxidation (black). Reduction pretreatment temperature: 573-K reduction (green), 773-K reduction (orange) and 1073-K reduction (red).

Table 6.2: Metal dispersion measured by CO chemisorption at room temperature^a.

	as-prepared ^b	573-K reduced (1 st redox cycle)	1073-K reduced (1 st redox cycle)	1073-K reduced (5 th redox cycle)
Rh/MAO	29	5.6	26	21
Rh/LFO/MAO	24	-	1.3	1.9
Pd/MAO	36	23	18	6.4
Pd/LFO/MAO	25	8.0	1.3	1.4

a: All the samples had been reduced in the CO chemisorption setup at 473 K before measurements.

b: Metals deposited on the films that after calcined at 873 K.

One possibility is that the Rh atoms interacting with the perovskite remain oxidized. To investigate this possibility, flow-titration measurements were performed on the Rh/LFO/MAO, Rh/MAO, and LFO/MAO samples. After each sample was reduced at either 573, 773, or 1073 K, the amounts of oxygen required for complete re-oxidation were

measured at 1073 K and reported in **Table 6.3**. MgAl_2O_4 is not reducible, and there was no oxygen uptake after heating in H_2 at 1073 K ⁴⁹. Reduction of LaFeO_3 was also negligible at 573 and 773 K but reached a value of 170 $\mu\text{mol O/g}$ at 1073 K. Based on the bulk composition and assuming the stoichiometry of the completely oxidized sample was LaFeO_3 , the LFO/MAO sample reduced at 1073 K had a stoichiometry of $\text{LaFeO}_{2.91}$. Oxygen uptakes on Rh/MAO were also dependent on the reduction temperature. To achieve the value close to that expected for oxidizing Rh to Rh_2O_3 , 336 $\mu\text{mol O/g}$, it was necessary to reduce the sample at 1073 K. Even at this high temperature, the oxygen uptake was only 320 $\mu\text{mol O/g}$. It is possible that some Rh on Rh/MAO remains in the oxidized state due to compound formation with the MgAl_2O_4 . The oxygen uptakes for Rh/LFO/MAO were significantly greater than the sum of uptakes for LFO/MAO and Rh/MAO, reaching values 360 $\mu\text{mol O/g}$ after reduction at 773 K and 560 $\mu\text{mol O/g}$ after reduction at 1073 K. The extent of reduction after 1073 K is particularly noteworthy because it is more than twice that expected for reduction of Rh_2O_3 in that sample (e.g., 175 $\mu\text{mol Rh/g}$ corresponds to 263 $\mu\text{mol O/g}$). Reduction of the Rh and LaFeO_3 components are clearly dependent on each other.

Table 6.3: Oxygen uptakes at 1073 K, measured over the samples reduced at 573 K, 773 K, and 1073 K.

	Metal moles (± 10 μmol/g)	573 K	773 K	1073 K	O:M (excludes LaFeO ₃)
		(± 20 μmol O/g)			
0.5-nm LFO/MAO	-	-	-	90	-
LFO/MAO	-	<10	30	170	-
Rh/MAO	224	75	140	320	1.4:1
Rh/LFO/MAO	175	220	360	560	2.2:1
Pd/MAO	160	140	150	165	1:1
Pd/LFO/MAO	141	145	180	440	1.9:1
Pt/MAO	170	-	-	3	-
Pt/0.5nm- LFO/MAO	159	-	-	385	1.8:1
Pt/LFO/MAO	149	<10	110	440	1.8:1

To gain additional insights into the nature of Rh-LaFeO₃ interactions, coulometric titrations were performed at 1073 K on Rh/MAO and Rh/LFO/MAO, with results shown in **Figure 6.4**. As shown in **Figure 6.4 (a)**, the total amount of oxygen uptake on reduced Rh/MAO agreed well with that expected for oxidation of Rh to Rh₂O₃. The oxidation occurred over a narrow range of PO₂, between 10⁻⁴ atm and 10⁻¹ atm, which is in good agreement with that expected for bulk Rh. Tabulated data indicate that, at 1073 K, Rh is oxidized to Rh₂O at PO₂=10^{-4.77} atm, to RhO at PO₂=10^{-1.27} atm, and to Rh₂O₃ at PO₂ = 10^{-0.69} atm.

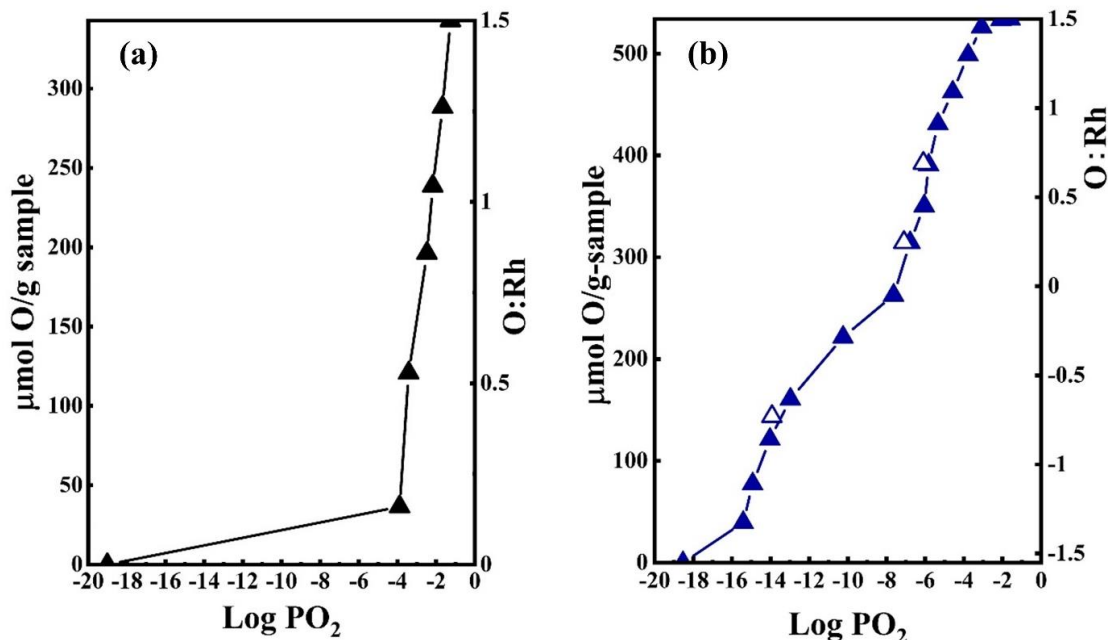


Figure 6.4: Oxidation isotherm obtained using coulometric titration at 1073 K for (a) Rh/MAO and (b) Rh/LFO/MAO. The sample had undergone 5 redox cycles before the measurement. The initial equilibrium is set by flowing 10% H_2 and 5% H_2O for 1h for the reduced sample.

Results for Rh/LFO/MAO in **Figure 6.4 (b)** were significantly different. First, the isotherms for Rh/LFO/MAO were independent of whether the measurements started from the oxidized or reduced states, demonstrating that these are equilibrium values. In agreement with the flow-titration data, the oxygen uptake was almost twice that which can be explained by oxidation of the Rh to Rh_2O_3 in this sample. The oxidation occurs in two general regions. The oxygen uptakes at the highest PO_2 values, between 10^{-8} and 10^{-4} atm, have the correct stoichiometry for Rh oxidation to Rh_2O_3 and must be associated with that process. This oxidation of Rh on Rh/LFO/MAO occurs at a much lower PO_2 than was observed on Rh/MAO, implying that the Rh on LFO/MAO is much harder to reduce. The

oxidation of the sample that occurs at PO_2 between 10^{-16} and 10^{-13} atm must be associated with the LaFeO_3 , and it is close to the range of PO_2 observed for reduction of 0.5-LFO films in a previous study¹³¹; however, because the amount of reduction observed here does not occur in the absence of the precious metal, interactions with the Rh must be important. The stoichiometry of 1.5 O per Rh is likely significant and will be discussed more later.

6.3.2 Pd/LFO/MAO

Previous work on Pd/LFO/MAO demonstrated that the catalytic activity of this material changes dramatically with oxidation and reduction pretreatments⁸⁶. In order to provide a proper comparison with Rh/LFO/MAO, new Pd/LFO/MAO samples were prepared and some of the critical experiments were repeated. One potentially significant difference for the samples used in this study is that the Pd was added by ALD and had a somewhat higher loading, 1.5- versus 1.0-wt% that in earlier study. Addition of Pd by ALD likely resulted in a more uniform initial distribution of Pd. The sample was again redox cycled at 1073 K five times prior to the measurements reported here.

Similar to what was observed for Rh/LFO/MAO, XRD patterns for both the oxidized and reduced Pd/LFO/MAO samples, shown in **Figure 6.5**, were indistinguishable from that of the LFO/MAO support. However, STEM/EDS maps of the Pd/LFO/MAO again showed evidence for reversible sintering of the Pd and possible changes in the support. After oxidation at 1073 K, **Figure 6.6 (a)**, EDS maps showed that Pd was present over the entire sample; but there were clearly regions where the Pd was more concentrated. After relatively mild reduction at 773 K, **Figure 6.6 (b)**, the Pd

segregated into particles that were 5- to 10-nm in diameter. The high concentration of these large particles for a catalyst that was only 1.5-wt% Pd suggests that the particles may be relatively flat. Reduction at 1073 K, **Figure 6.6 (c)**, gave rise to bigger regions of concentrated Pd but these regions were still relatively diffuse. It is also noteworthy that the EDS maps of La and Fe, which matched with each other after oxidation and mild reduction, are no longer similar in **Figure 6.6 (c)**. The EDS maps for Pd and Fe do correspond to each other, implying formation of a Pd-Fe alloy and some decomposition of the LaFeO_3 , although there was no clear evidence for this in XRD. Since all of these measurements were performed on samples that were redox cycled, the changes observed in **Figure 6.6** must be reversible.

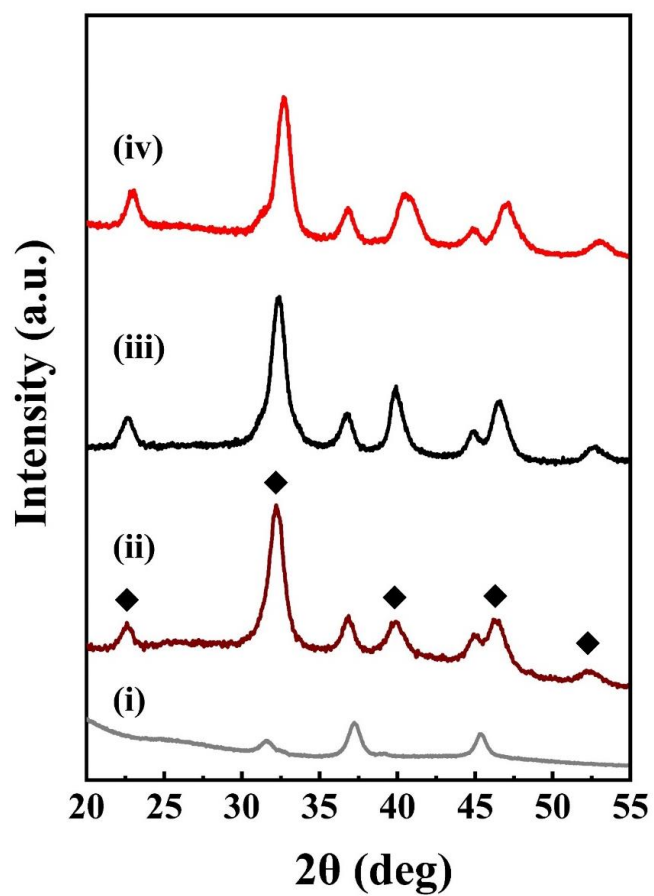


Figure 6.5: XRD patterns over Pd/LFO/MAO: (i) MgAl_2O_4 ; (ii) oxidized LFO/MAO after 5 redox cycles at 1073 K; (iii) oxidized Pd/LFO/MAO after 5 redox cycles at 1073 K; (iv) reduced Pd/LFO/MAO after 5 redox cycles at 1073 K.

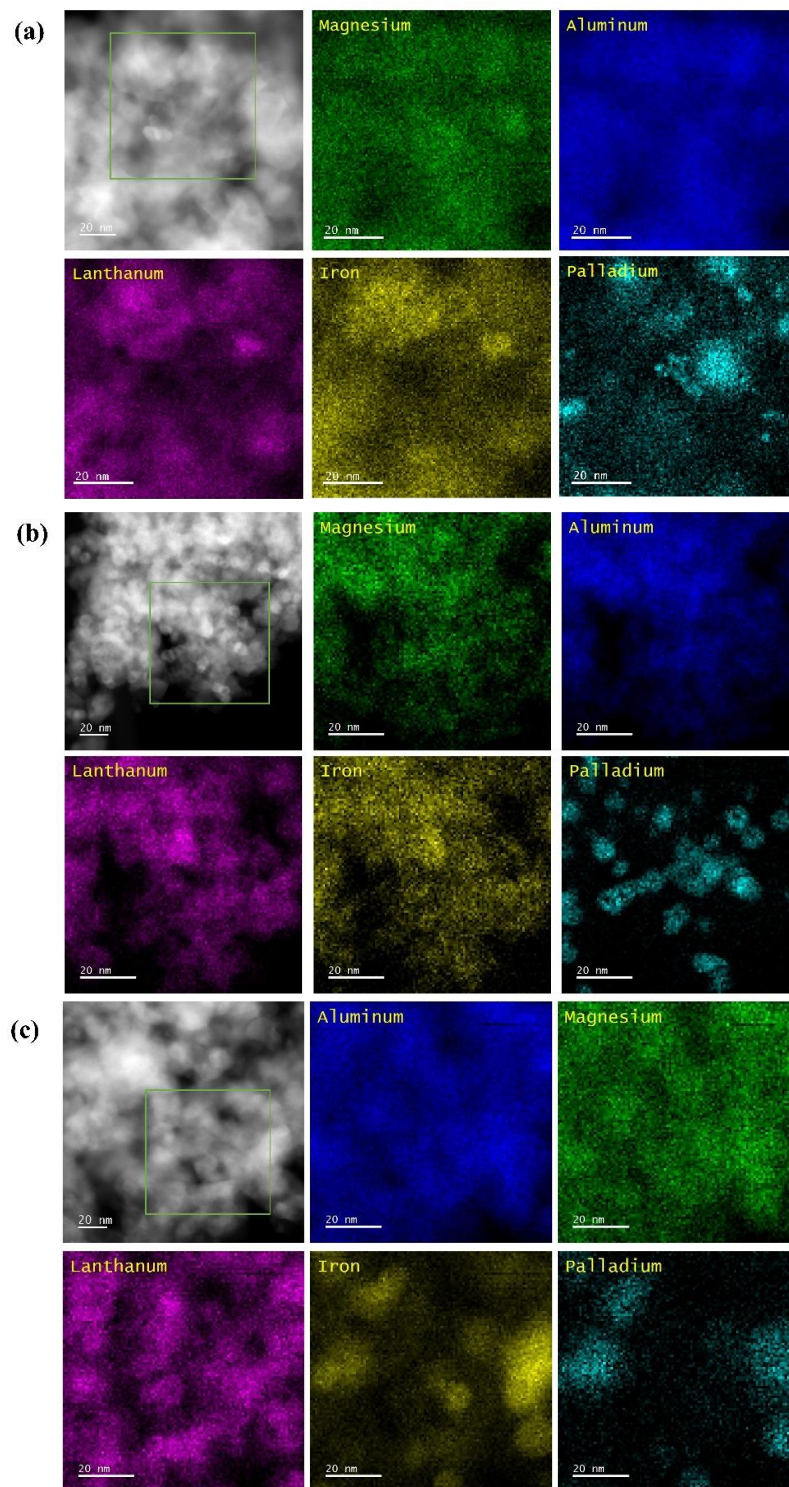


Figure 6.6: Representative STEM/EDS results for Pd/LFO/MAO after five 1073 K redox cycles with the final treatment being **(a)** 1073-K oxidation; **(b)** 773-K reduction; **(c)** 1073-K reduction. EDS maps taken from the region of green box.

Differential, steady-state CO-oxidation rates on the Pd/LFO/MAO sample were distinctly different from those on Rh/LFO/MAO and from what was reported in previous work ⁸⁶, as shown in **Figure 6.7 (a)**. Again, the catalyst showed low activity after oxidation at 1073 K. However, reduction at either 573 K or 773 K increased the rates by more than a factor of 10, while reduction at 1073 K brought the rates back down to the level of the oxidized sample. CO-oxidation, light-off profiles, shown in **Figure 6.8**, showed the same activation and deactivation as the steady-state differential rates. It is noteworthy that, after redox cycling, rates on the Pd/LFO/MAO sample were much higher than those measured on Pd/MAO. **Figure 6.7 (b)** indicates that rates on the redox-cycled Pd/MAO were not greatly affected by reduction temperature but were never higher than that of the Pd/LFO/MAO oxidized at 1073 K. Although the higher rates on Pd/LFO/MAO are likely due in part to higher Pd dispersions, room-temperature CO-adsorption amounts, reported for the Pd/LFO/MAO and Pd/MAO samples as a function of treatment conditions in **Table 6.2**, were always low for the Pd/LFO/MAO sample.

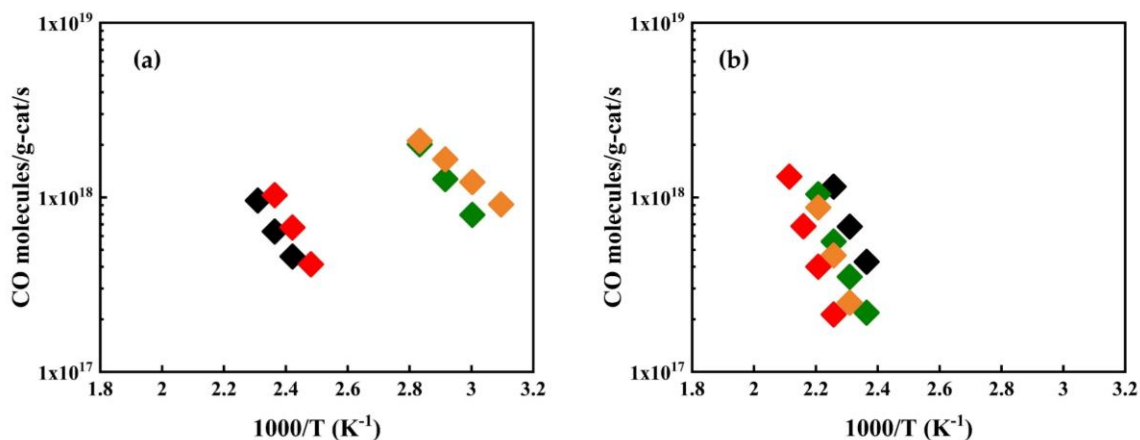


Figure 6.7: Steady-state, differential reaction rates for CO oxidation with 25 Torr of CO and 12.5 Torr O₂ for (a) Pd/LFO/MAO and (b) Pd/MAO as a function of reduction temperature. The samples had undergone 5 redox cycles with the final state of oxidation (black). Reduction pretreatment temperature: 573-K reduction (green), 773-K reduction (orange) and 1073-K reduction (red).

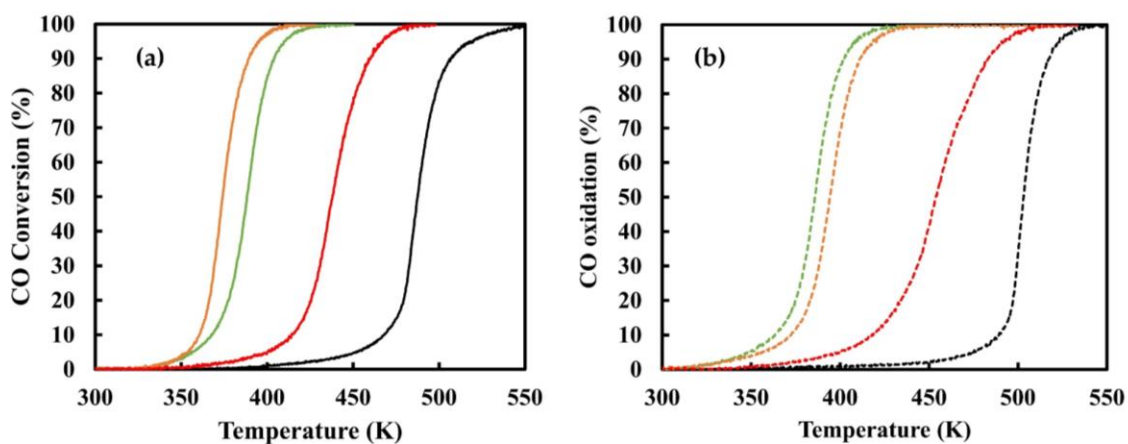


Figure 6.8: Light-off profiles for CO oxidation with 25 Torr of CO and 12.5 Torr O₂ for Pd/LFO/MAO after (a) 1st redox cycle; (b) 5th redox cycle. Reduction pretreatment temperature: 573-K reduction (green), 773-K reduction (orange) and 1073-K reduction (red). The temperature ramping rate was 10 K/min.

Flow-titration measurements were performed on Pd/LFO/MAO and Pd/MAO after reduction at 573, 773, and 1073 K and are reported in **Table 6.3**. Unlike the case for Rh, the oxygen uptakes on both Pd samples indicate that Pd was reduced after reduction

at 573 K. The amount of oxygen required to completely oxidize Pd/MAO was close to that expected to take Pd to PdO. Similar to what was observed on Rh/LFO/MAO after reduction at 1073 K, significantly more oxygen was required to oxidize Pd/LFO/MAO than could be explained by the sum of LFO/MAO and Pd. Some of this added oxygen may be due to Pd-Fe alloy formation.

The equilibrium oxidation isotherms for Pd/MAO and Pd/LFO/MAO at 1073 K are shown in **Figure 6.9**. The isotherm for Pd/MAO in **Figure 6.9 (a)** showed a transition Pd to PdO at a PO_2 of 10^{-1} atm, which is close to the equilibrium value for bulk Pd, $\sim 10^{-0.7-1.3}$ atm, calculated from tabulated values for ΔG ¹³²⁻¹³³. The results in **Figure 6.9 (b)** for Pd/LFO/MAO were more complex. First, in agreement with the flow-titration data, the amount of oxygen that could be added or removed from the sample was much greater than that which can be explained by the Pd oxidation alone. Second, while equilibrium data should be independent of direction, we observed consistently higher PO_2 when approaching a given oxygen stoichiometry from the reduced state on Pd/LFO/MAO. Given that there is evidence for alloy formation and decomposition of the perovskite phase after deep reduction, it is possible that the final states are different when starting from the oxidized or reduced state. The equilibrium PO_2 in the higher PO_2 region, where Pd is expected to be oxidized, was below 10^{-5} atm, much lower than that expected for bulk Pd. In the region where the additional oxygen must be coming from the perovskite phase, the PO_2 ranged from 10^{-8} to 10^{-14} atm, similar to the values for Rh/LFO/MAO for reduction

of the LaFeO_3 phase. The amount of oxygen that could be reversibly added in this region was nearly two O per Pd.

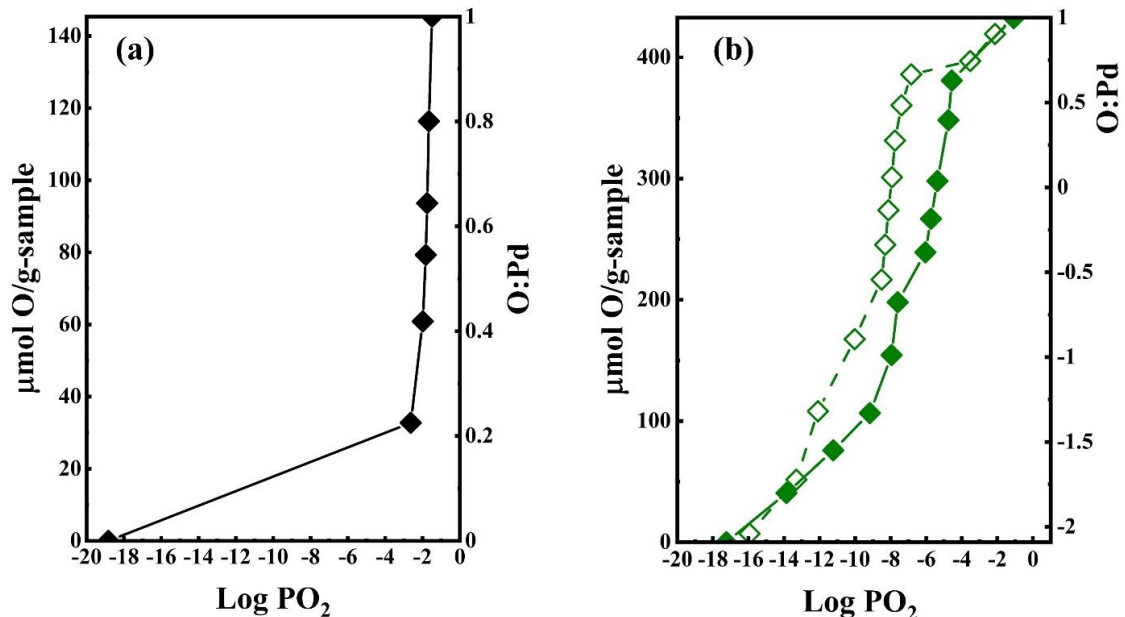


Figure 6.9: Oxidation isotherm obtained using coulometric titration at 1073 K for (a) Pd/MAO and (b) Pd/LFO/MAO. The sample had undergone 5 redox cycles before the measurement. Solid symbols represent the measurement that starts with the reduced sample, and hollow symbols represent the measurement that starts with the oxidized sample.

6.3.3 Pt/LFO/MAO

A detailed study of Pt on 0.5-nm LFO/MAO supports was presented previously¹²². Here, we repeated some of the key experiments on the 1.0-nm films and performed a more detailed study of the redox properties for comparison to Rh/LFO/MAO and Pd/LFO/MAO. The samples were again redox cycled at 1073 K five times prior to the measurements.

The catalytic properties for CO oxidation on Pt/LFO/MAO samples prepared here were essentially identical to what was reported in the earlier work. As shown in **Figure 6.10**, rates on the 1073-K oxidized catalyst were low and were largely unchanged after reduction at either 573 or 773 K. Reduction at 1073 K increased rates by an order of magnitude. The XRD patterns for Pt supported on 1-nm LaFeO₃ films were also similar to those reported in the earlier work, as shown in **Figure 6.11**. In addition to the peaks associated with the spinel and perovskite phases, the diffraction pattern of the oxidized sample showed intense Pt features for the oxidized sample. The intensity of the Pt features decreased greatly after reduction. Rietveld analysis of both the oxidized and reduced samples, shown in **Figure 6.12** and **Table 6.4**, was consistent with the measured Pt loading of 3.3-wt% and suggested that the changes in the Pt peaks were due to a change in crystallite size from 20 nm to 9 nm. The peak positions are inconsistent with formation of a Pt-Fe alloy; and, unlike results for Pd/LFO/MAO, STEM/EDS maps of La and Fe did not show evidence for segregation of Fe after reduction ¹²². Unlike results from earlier work with 0.5-nm LaFeO₃ films, formation of LaAlO₃ appears to be negligible with the 1-nm LaFeO₃ films.

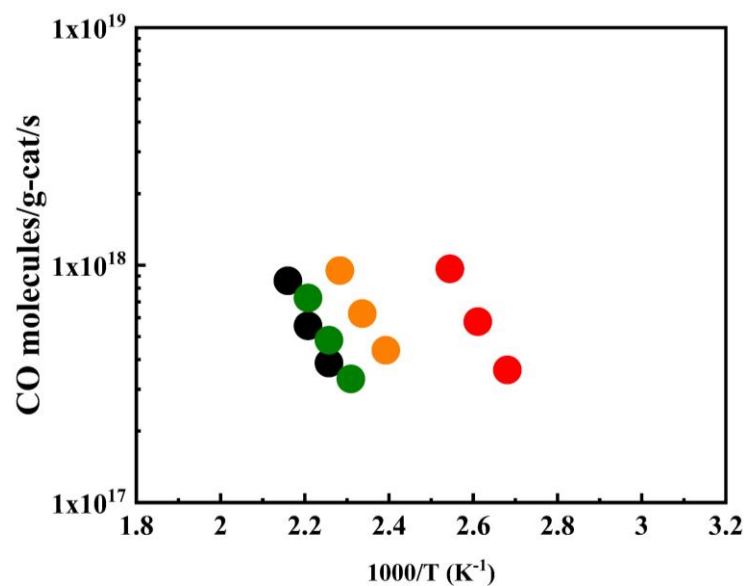


Figure 6.10: Steady-state, differential reaction rates for CO oxidation with 25 Torr of CO and 12.5 Torr O₂ for Pt/LFO/MAO as a function of reduction temperature. The samples had undergone 5 redox cycles with the final state of oxidation (black). Reduction pretreatment temperature: 573-K reduction (green), 773-K reduction (orange) and 1073-K reduction (red).

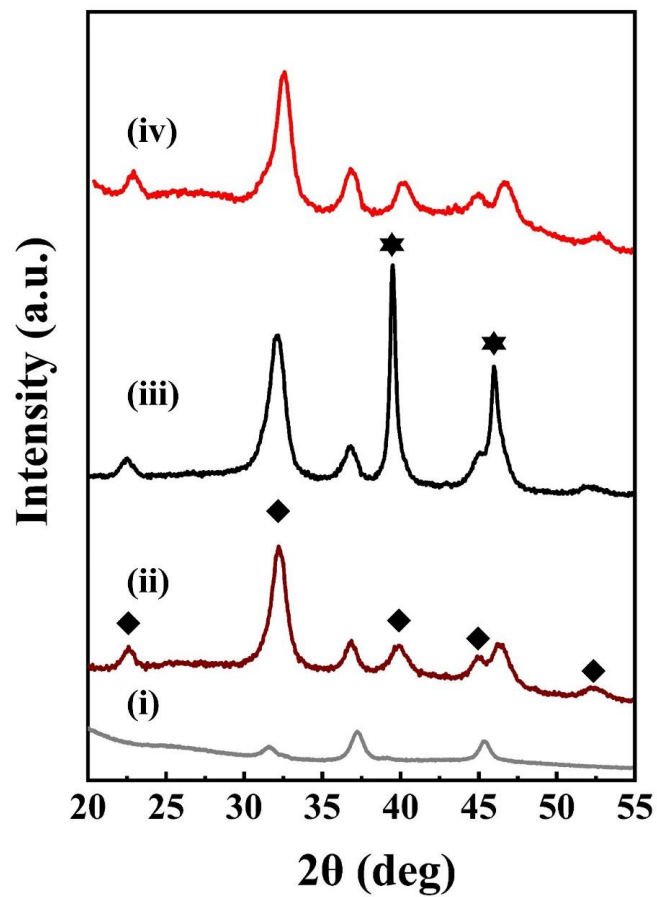


Figure 6.11: XRD patterns over Pt/LFO/MAO: (i) MgAl_2O_4 ; (ii) oxidized LFO/MAO after 5 redox cycles at 1073 K; (iii) oxidized Pt/LFO/MAO after 5 redox cycles at 1073 K; (iv) reduced Pt/LFO/MAO after 5 redox cycles at 1073 K. Perovskite features are marked with diamonds, and Pt features are marked using six-point stars.

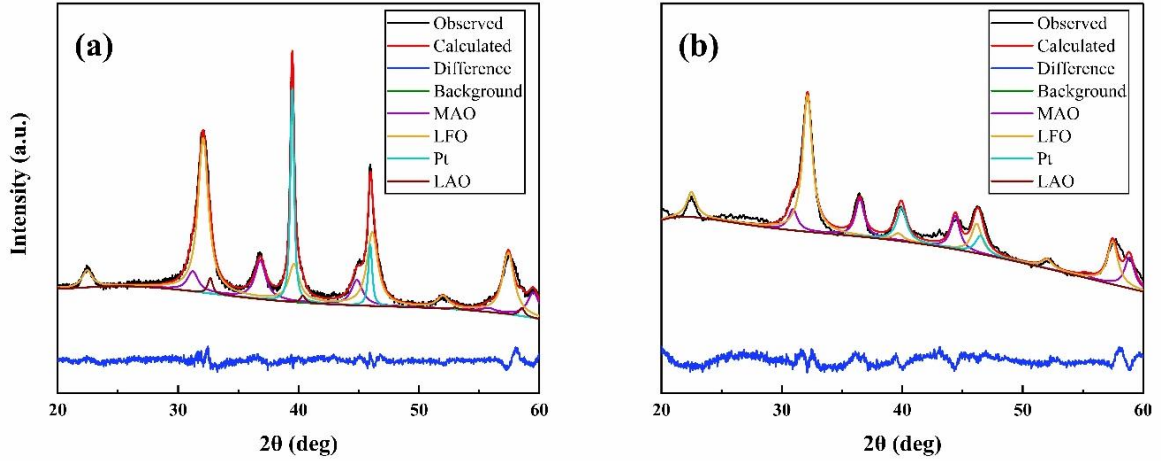


Figure 6.12: Rietveld analysis of (a) oxidized Pt/LFO/MAO and (b) reduced Pt/LFO/MAO after 5 redox cycles.

Table 6.4: Results from Rietveld analysis of the XRD patterns of the oxidized and reduced Pt/LFO/MAO, with the results of Pt/0.5-nm LFO/MAO reported in **Chapter 5.3.1**.

	Pt/LFO/MAO (relative wt.%)		Pt/0.5-nm LFO/MAO (relative wt.%)	
	Oxidized	Reduced	Oxidized	Reduced
MgAl ₂ O ₄	55.2±0.6	63.1±0.6	64.2	66.4
LaFeO ₃	39.4±0.6	33.7±0.7	16	6.2
LaAlO ₃	0.9±0.1	0.1	15.4	21.8
Pt	4.5±0.1	3.1±0.2	4.4	4.1
Pt particle size (nm)	20	9	22	10
% LaFeO ₃ /(LaFeO ₃ + LaAlO ₃)	98	100	51	22

The XRD results are difficult to understand for multiple reasons. First STEM measurements showed that the surface of the 0.5-nm LaFeO₃ films was covered with 1- to 2-nm Pt particles, and provided no evidence for large Pt particles after reduction at 1073 K, shown in the **Figure 6.13** and **Figure 6.14**, and **Chapter 5.3.1**. Second, high-temperature

reduction does not usually redisperse Pt particles. Because STEM images of oxidized Pt on 0.5-nm LFO/MAO provided evidence for epitaxial alignment of Pt on larger LaFeO_3 crystallites, it was suggested that the apparently large Pt crystallite size from XRD resulted from constructive interference from small Pt particles in an ordered array on larger LaFeO_3 crystals.

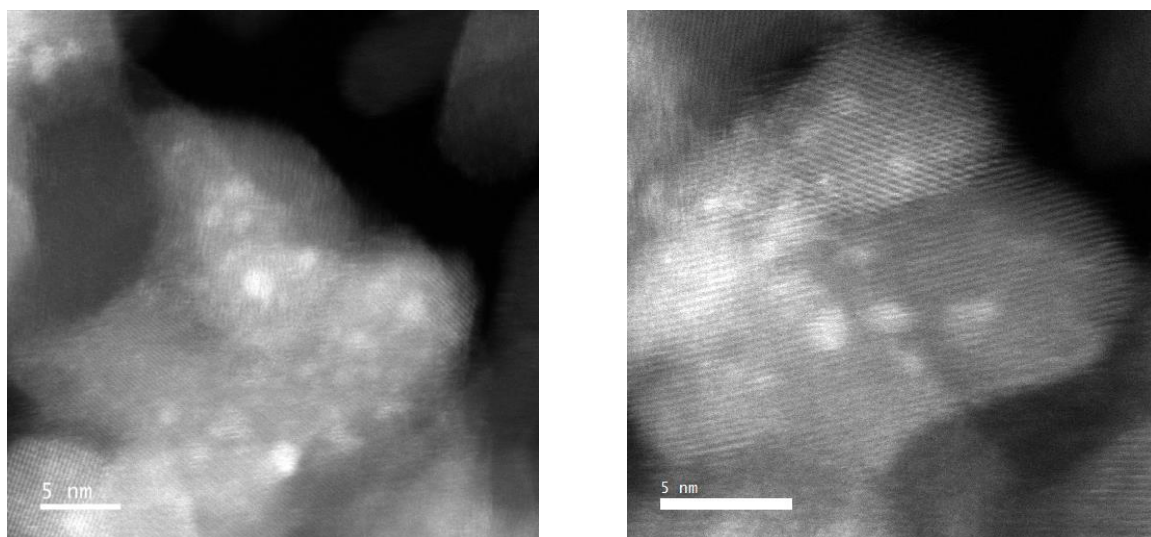


Figure 6.13: High-angle annular dark-field STEM images of the oxidized Pt/0.5-nm LFO/MAO after 5 redox cycles at 1073 K.

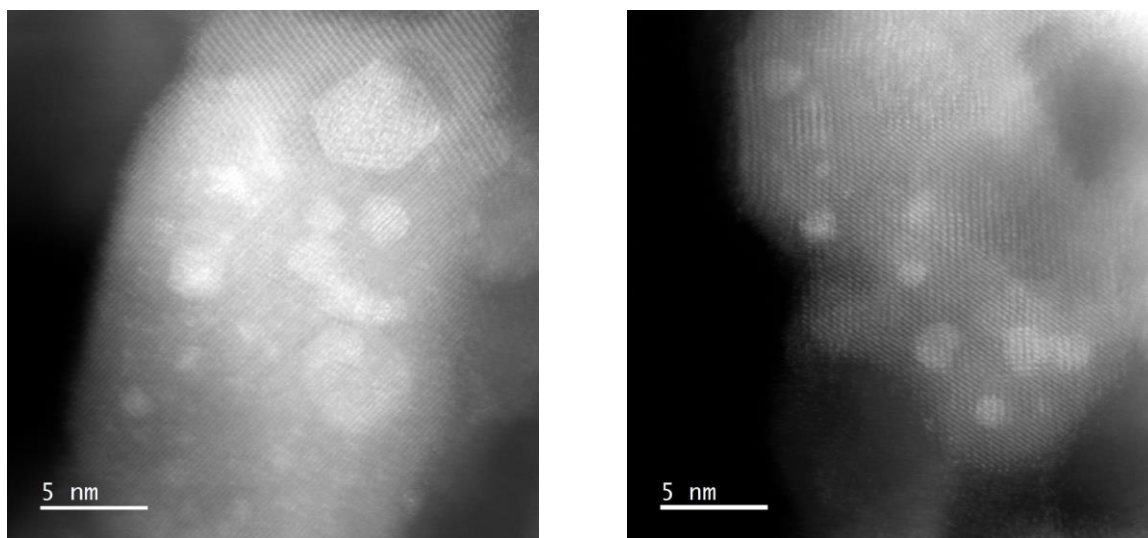


Figure 6.14: High-angle annular dark-field STEM images of the reduced Pt/0.5-nm LFO/MAO after 5 redox cycles at 1073 K.

Flow-titration and coulometric-titration measurements were performed on the Pt/LFO/MAO and Pt/MAO samples to help determine the reasons for the changes in the catalyst. As shown in **Table 6.3**, oxygen uptakes on Pt/MAO were negligible at 1073 K, as expected. The bulk is expected to be unstable at 1073 K. Oxygen uptakes on the reduced Pt/LFO/MAO were significant, however. When the catalyst was reduced at 1073 K, the oxygen uptake at 1073 K was 440 $\mu\text{mol O/g}$. After subtracting off the 170 $\mu\text{mol O/g}$ observed on the bare LFO/MAO support, this amount of oxygen corresponds to 1.8 oxygens per Pt. This result does not appear to depend on the LaFeO_3 film thickness. When the experiment was repeated on a sample with a 0.5-nm LaFeO_3 films, the additional amount of oxygen taken up by the reduced, Pt/0.5-nm LFO/MAO over that taken up by 0.5-nm LFO/MAO again corresponded to 1.8 oxygens per Pt.

Oxygen isotherms for Pt/LFO/MAO at 1073 K, performed starting with the reduced samples, are shown as **Figure 6.15**. The total oxygen uptake again agreed well with that measured by flow titration. The isotherm shows reduction in two regions, with half of the oxygen equilibrating between 10^{-17} to 10^{-14} atm and half between 10^{-8} and 10^{-6} atm. While the lower pressure region is roughly consistent with the PO_2 region where oxygen vacancies are formed in LaFeO_3 ¹³¹, the higher-pressure region is still too low for stable oxidation of Pt. One conclusion that can be reached from these results is that there is a significant restructuring of the LaFeO_3 phase in the vicinity of the Pt upon high-temperature reduction.

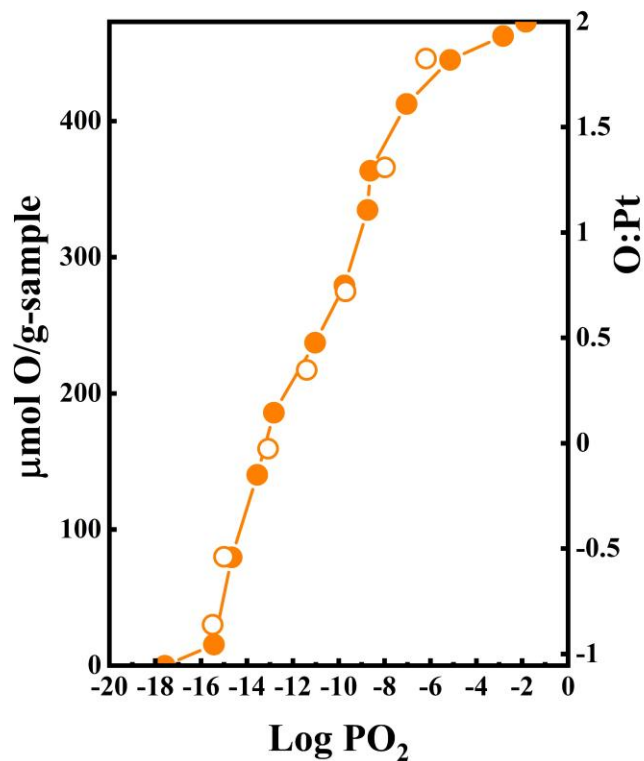


Figure 6.15: Oxidation isotherm obtained using coulometric titration at 1073 K for Pt/LFO/MAO. The sample had undergone 5 redox cycles before the measurement. The initial equilibrium is set by flowing 10% H_2 and 5% H_2O for 1h for the reduced sample. Solid symbols represent the measurement that starts with the reduced sample, and hollow symbols represent the measurement that starts with the oxidized sample.

6.4 Discussion

Most work on perovskite-supported metals has focused on the reversible ingress/egress of metal cations into the lattice of the perovskite. Whether or not occurs with thin-film catalysts remains unclear; however, we suggest that the bonding interactions that allow metal cations to become part of a perovskite lattice can also lead to support effects which are observable in the thin-film systems. Unlike strong metal-support effects observed with titania ¹³⁴, support effects associated with perovskites are strongly dependent on the composition of both the metal and the perovskite. This is observed by comparing Pt and Pd catalysts supported on CaTiO_3 ⁴⁹, where only Pt is strongly affected. It is also observed in the comparison of Rh on CaTiO_3 , SrTiO_3 , and BaTiO_3 films ¹²⁸, where the effects of the A-site cation were found to dramatically affect catalytic properties. In the present work, the metal-support-interaction specificity is observed by the differences for how Rh, Pt, and Pd interact with LFO.

Quantifying the interactions strictly on a numerical basis show that the interactions with LFO are strongest for Rh, followed by Pt and Pd. This is what comes out of the theoretical calculation. This is also a conclusion that could be reached from experiments: Rh/LFO/MAO is inactive for CO oxidation, even after high-temperature reduction; Pt/LFO/MAO becomes active only after reduction at high temperatures; Pd/LFO/MAO sinters into larger particles after 1073-K reduction. However, a closer examination shows that the differences between the catalysts are more subtle. Only Pd/LFO/MAO showed evidence for alloy formation. The unusual XRD results for

Pt/LFO/MAO, explained previously as being due to reversibly epitaxy of small particles¹²², was observed only with Pt. Rh/LFO/MAO was the only catalyst that could not be activated. All of this points towards the formation of composition-specific, chemical bonds at the metal-perovskite interface.

There are similarities between the metals. With each of the metals, high-temperature reduction removed between 1.5 and 2 lattice oxygens per metal atom from the LFO. If the metals remained in the form of single atoms, removal of this much oxygen would allow contact between the metal and cations from the perovskite lattice. Indeed, the previous study of Pt/LFO/MAO reported coordination numbers for Pt-Fe from EXAFS results for the reduced form and not the oxidized form¹²². Interestingly, it is the oxidized, not the reduced, catalyst that shows the strongest differences from conventional supported Pt. Even though the Pt remains in a metallic state, as shown by both the XRD and coulometric-titration results, there must be strong bonding interactions with the LFO for the catalytic properties of Pt/LFO/MAO to be strongly affected. The shift in the equilibrium, oxidation isotherms also suggest bonding interactions between LFO and both Pd and Rh.

There is still clearly much that we do not understand about metals supported on perovskite thin films. Because they offer the possibilities for achieving stable catalysts with unique catalytic properties, understanding the interactions can provide an avenue to better design the catalyst with the desired metal dispersion, catalytic activity, and thermodynamic properties.

6.5 Conclusion

Rh catalysts can be stabilized as 1-nm particles on 1-nm LFO films after 5 redox cycles at 1073 K. It was shown that Pt, Rh, and Pd had different metal-support interactions with LFO films; Rh had the strongest interactions with LFO films, followed by Pt and Pd. The interaction strength directly controlled the metal dispersion on LFO films. The three supported catalysts exhibited the self-regenerative activity for CO oxidation reaction upon oxidation and reduction. The interactions further led to the changes in thermodynamic properties of the supported metals.

CHAPTER 7. CHANGES IN Ni-NiO EQUILIBRIUM DUE TO LaFeO₃ AND THE EFFECT ON DRY REFORMING OF CH₄⁵

Summary

In this chapter, a thermodynamic study of Ni oxidation on Ni/LaFeO₃/MgAl₂O₄ is presented. The results demonstrate that metal-support interactions dramatically affect the equilibrium constant for the reaction and impact the catalytic activities of Ni. The interactions between Ni and LaFeO₃ were studied on catalysts prepared by ALD of 0.5-nm films of LaFeO₃ on MgAl₂O₄. STEM showed that the films covered the support uniformly, even after 5 redox cycles at 1073 K, and XRD showed that the films had the perovskite structure. Equilibrium between Ni and NiO was studied using coulometric-titration and flow-titration measurements on 5-wt% Ni catalysts, with and without LaFeO₃. While equilibrium constants for Ni/MgAl₂O₄ were similar to that expected for bulk Ni, equilibrium PO₂ were shifted to significantly lower values in the presence of LaFeO₃. In studies of Methane Dry Reforming, the shift in equilibrium resulted in catalyst deactivation due to Ni oxidation at low CO:CO₂ ratios, even though Ni/LaFeO₃/MgAl₂O₄ otherwise showed a high reaction rate and excellent tolerance against coking.

⁵ This chapter was reproduced from J. Catal. 2020, 381, 561-569.

7.1 Introduction

An interesting question arises regarding the thermodynamics of metal oxidation and reduction when the metal is supported on a strongly interacting support. With Ni, for example, the thermodynamics of oxidation are normally described by the reaction, $\text{Ni} + \frac{1}{2}\text{O}_2 = \text{NiO}$, for which the equilibrium constant, K_{NiO} , is equal to $\text{PO}_2^{-\frac{1}{2}}$. K_{NiO} is determined from ΔG of the oxidation reaction. If the Ni^{2+} ions exist in a perovskite lattice, rather than as bulk NiO, or even if the NiO phase interacts strongly with the support, the equilibrium constant for this reaction could be affected ¹³⁵. This has very practical implications. In practice, the PO_2 is established by equilibrium with either H_2 and H_2O or CO and CO_2 ; and, at high $\text{H}_2\text{O}:\text{H}_2$ ratios and lower temperatures, the metal can be oxidized. This has been discussed as a potential problem for Co-based Fischer-Tropsch catalysts ¹³⁶. It is also important with Ni-based anodes in Solid Oxide Fuel Cells, since oxidation of Ni can occur at high fuel utilizations and lower temperatures ¹³⁷.

Carbon whisker formation is a major problem with Ni catalysts used in methane-reforming reactions, and much effort has gone into developing ways to limit this carbon. For example, it is known that precious metals, e.g. Pt, Rh and Pd, exhibit significantly better tolerance against carbon deposition ¹³⁸⁻¹³⁹; however, due to the high cost, most research has focused on modifying Ni catalysts. It has been reported that basic oxides, such as CaO or La-containing materials ¹⁴⁰⁻¹⁴², also improve stability against coking. However, perovskite-based supports appear to modify Ni in ways that are different from

that of the individual oxides due to the fact that Ni can, under some conditions, reversibly enter the perovskite lattice ²⁸.

Here, we present results from a thermodynamic and catalytic investigation of Ni on thin LaFeO₃ films. The presence of LaFeO₃ is found to shift the equilibrium constant to significantly lower PO₂, which in turn affects the conditions under which Ni can be used as a steam-reforming catalyst.

7.2 Experimental Methods

7.2.1 Sample Preparation

The MgAl₂O₄ support used in this study was prepared in our laboratory using the method described in **Chapter 2.1**. The 0.5-nm LaFeO₃ films were deposited onto the MgAl₂O₄ support by ALD and the procedure was same as the one described in **Chapter 5.2.1**. To ensure that there was good initial contact with the supports, Ni was added by ALD. The precursor was Ni(TMHD)₂ (Strem Chemicals, Inc.), and the procedures were essentially the same as those used to deposit La₂O₃. The number of ALD cycles was varied in order to achieve a final Ni loading of approximately 1.0-wt% or 5.0-wt%, denoted as 1-Ni/LFO/MAO and Ni/LFO/MAO. After deposition, the samples were alternately oxidized for 30 min in 10% O₂-He mixtures and reduced in 10% H₂-He mixtures for 30 min five times at 1073 K before acquiring data in order to crystallize the LaFeO₃ films.

7.2.2 Characterization Methods

XRD was performed using a Rigaku MiniFlex diffractometer equipped with a Cu K α source ($\lambda = 0.15406$ nm). Specific surface areas were determined from BET isotherms with N₂ at 78 K using a home-built equipment. STEM and EDS were performed with a JEOL JEM-F200 STEM, operated at 200 kV. The loading of Ni on each sample was measured using ICP-OES, equipped with a Mod Lichte nebulizer. CO and H₂ chemisorption measurements were attempted; however, as reported in the previous chapters, we were not able to see significant adsorption uptakes.

Equilibrium measurements were performed using either flow-titration or coulometric titration¹⁴³⁻¹⁴⁴, depending on the range of PO₂ at which oxidation of the catalyst took place. The setup and operational procedure of flow titration and coulometric titration were described in detail in **Chapter 2.4**.

Steady-state, Methane-Dry-Reforming (MDR) rates were performed over the Ni catalysts using 0.1-g samples in the setup described in **Chapter 2.3.1**. Estimates of the Peclet number in the system suggest that flow in the tubular reactors is sufficiently well mixed so that CSTR conditions may be assumed¹⁴⁵. Initially, the reactions on both Ni/MgAl₂O₄ (Ni/MAO) and Ni/LFO/MAO were measured as a function of temperature using 5% each of CH₄ and CO₂ in He, with a total gas flow rate of 100 mL/min. The MDR reaction on Ni/LFO/MAO was also studied as a function of the CH₄:CO₂ ratio, with the total flow rate again fixed at 100 mL/min. Before acquiring rate data, all Ni catalysts were reduced in a 10% H₂-He mixture.

Coking tests were performed by flowing 10% CH₄-He mixtures, with a total flow rate of 100 mL/min, over 0.1-g catalyst samples for 12 h at 1073 K. The carbon contents of the catalysts were then obtained from the amount of CO₂ formed during oxidation at 1073 K. Oxidation was carried out in 20% O₂-He mixtures, at a flow rate of 50 ml/min, using the quadrupole mass spectrometer to measure CO₂ production.

7.3 Results

7.3.1 Sample Characterization

A list of the samples used in this study is shown in **Table 7.1**, together with their BET surface areas and catalyst loadings. The lower surface areas of the LaFeO₃-containing samples are due mainly to the increased mass of the samples, with a small contribution from a decrease in pore size ⁸⁶. The LaFeO₃ loading was 30-wt% (± 1.5 -wt%) determined by weight-gain measurements, while Ni loadings for each sample were measured by ICP-OES with an uncertainty of ± 0.1 -wt%.

Table 7.1: Properties of samples used in this chapter. The oxygen uptakes (and extent of Ni reduction) were measured at 1073 K on samples after the following pretreatments: reduction in dry H₂ at (1) 1073 K, reduction in dry H₂ at 1073 K followed by oxidation in dry air at (2) 973 K, (3) 873 K, and (4) 773 K.

	BET S.A. (± 3 m ² /g)	Ni loading ($\pm 0.1\%$)	$\mu\text{mol O/g uptake (Ni reduction extent)}$ ($\pm 20 \mu\text{mol}$)			
			(1)	(2)	(3)	(4)
Ni/MAO	115	4.8	720 (88%)	0 (0%)	0 (0%)	50 (6%)
Ni/LFO/MAO	55	4.9	870 (100%)	90 (10%)	500 (57%)	760 (87%)
1-Ni/LFO/MAO	58	0.9	200 (100%)			
LFO/MAO	61	-	60 (-)			

XRD patterns for the oxidized and reduced Ni/LFO/MAO and Ni/MAO samples are shown in **Figure 7.1**. As discussed earlier, the diffraction patterns here were obtained on samples that had undergone five oxidation and reduction cycles at 1073 K in order to improve crystallization of the films. Results for Ni/LFO/MAO are reported in **Figure 7.1 (a)**, with the pattern for MgAl₂O₄ shown for comparison. Besides the peaks associated with MgAl₂O₄, the dominant diffraction peaks on the Ni/LFO/MAO sample after the five redox cycles were those associated with the perovskite phase. These features did not change significantly with oxidation or reduction, and an estimate of crystallite size based on the width of the peaks, using Scherrer's Equation, gave values between 9 and 12 nm. More significantly, the reduced sample showed small peaks at 44° and 51° 2 θ for metallic Ni, with a particle size of 10 nm. Compared to normal Ni, the peak positions for metallic Ni on Ni/LFO/MAO were shifted 0.4° to lower angles. This lattice expansion, from 352.4 pm

to 355.3 pm, may be caused by weakening of Ni-Ni bonds due to strong interactions with LaFeO_3 . The peaks due to Ni disappeared after oxidation but there were no observable NiO features. XRD patterns for Ni/MAO, **Figure 7.1 (b)**, show much more intense and narrower Ni features on the reduced sample, due to the presence of larger Ni particles compared to those on LaFeO_3 and only MgAl_2O_4 on the oxidized sample.

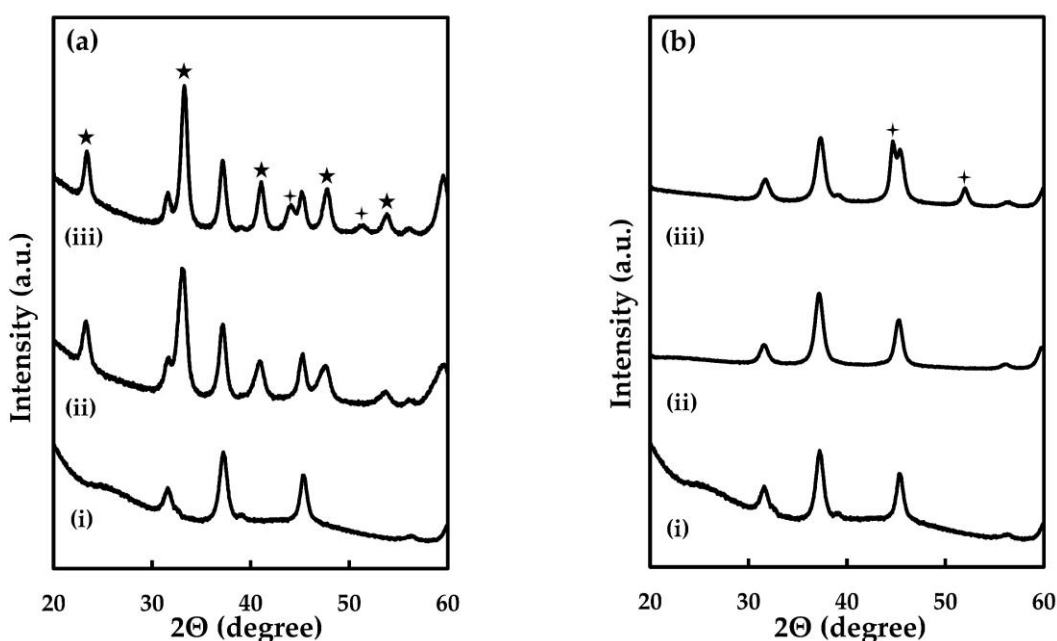


Figure 7.1: XRD patterns of (a) Ni/LFO/MAO and (b) Ni/MAO: (i) unmodified MgAl_2O_4 ; (ii) oxidized Ni-containing sample after 5 redox cycles at 1073 K; (iii) reduced Ni-containing sample after 5 redox cycles at 1073 K. Perovskite features are marked with stars, metallic Ni with 4-point stars.

STEM and EDS results for the oxidized and reduced Ni/LFO/MAO sample are shown in **Figure 7.2** and **Figure 7.3**. The STEM image of the oxidized sample, **Figure 7.2**, does not show any well-defined particles and the EDS elemental maps indicate that La, Fe, and Ni are present as a relatively uniform coating on the surface, although there is a

region near the bottom of the image that may be Ni-rich. Despite the harsh redox cycling, there is no evidence that either the Ni or the LaFeO_3 had agglomerated into large particles. For the reduced sample, there is some indication of Ni and LaFeO_3 agglomeration, shown in **Figure 7.3**, although this may also be due to roughness in the sample. There is clearly overlap in the locations of Ni, La, and Fe. By contrast, the formation of distinct Ni particles is more obvious on reduced Ni/MAO after the same treatment, as shown in **Figure 7.4**.

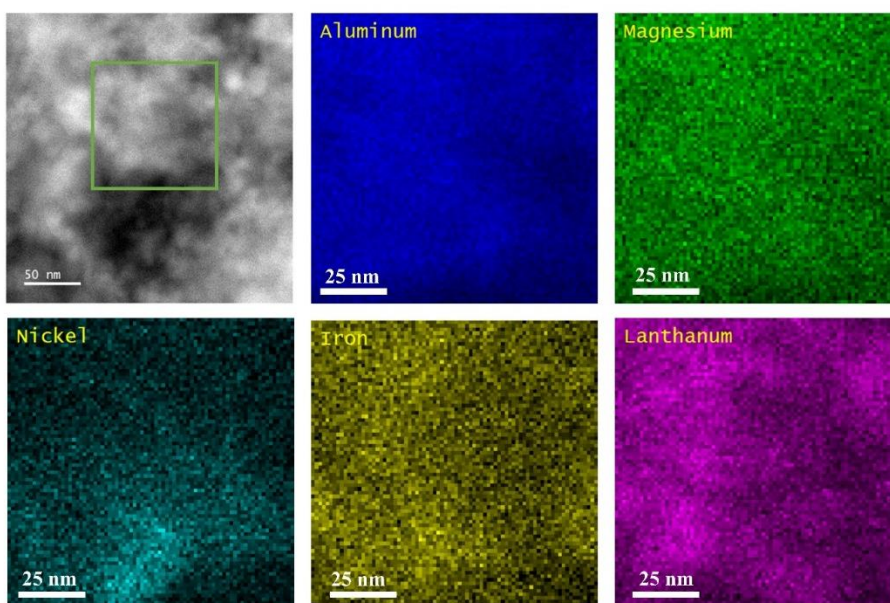


Figure 7.2: High-angle annular dark-field STEM image and EDS maps of Mg, Al, La, Fe and Ni on oxidized Ni/LFO/MAO after 5 redox cycles, taken from the region indicated by the green box.

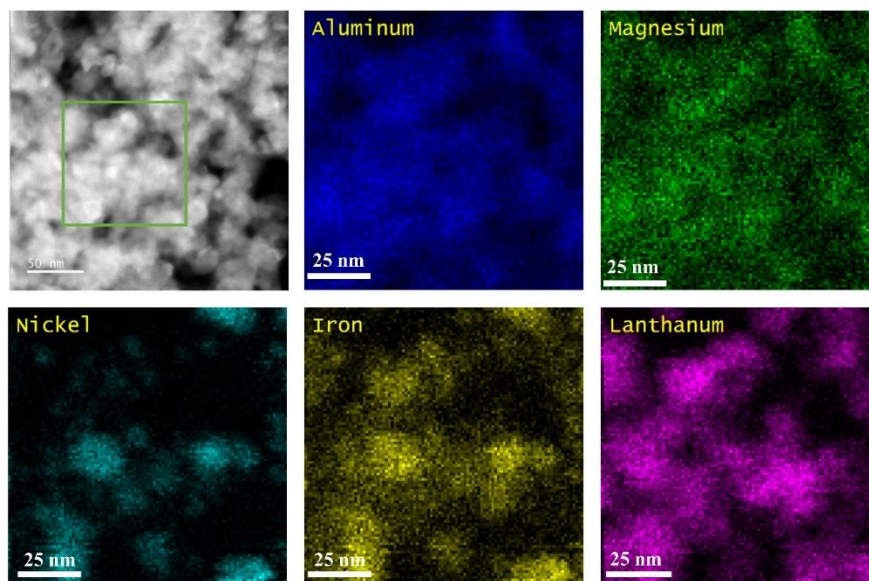


Figure 7.3: High-angle annular dark-field STEM image and EDS maps of Mg, Al, La, Fe and Ni on reduced Ni/LFO/MAO after 5 redox cycles, taken from the region indicated by the green box.

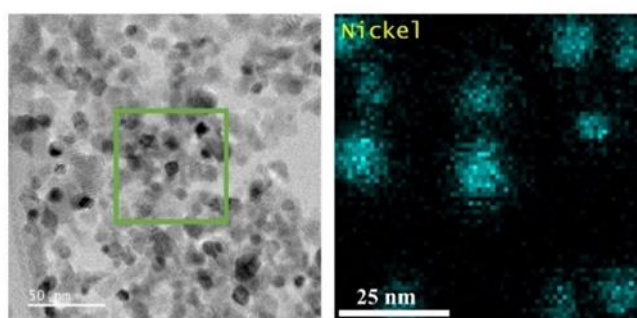


Figure 7.4: High-angle annular dark-field STEM image and EDS map of Ni on reduced Ni/MAO after 5 redox cycles, taken from the region indicated by the green box.

7.3.2 Thermodynamic Measurements

The total amount of oxygen that could be added or removed from the Ni-containing samples after reduction or oxidation at 1073 K was measured by flow titration

and the values are listed in **Table 7.1** (Column (1)). For these experiments, the samples were reduced in dry H_2 at 1073 K, after which the amount of O_2 required to completely oxidize the samples at 1073 K was measured. As expected, there was no reduction of $MgAl_2O_4$; but an uptake of $\sim 60 \mu\text{mol O/g}$ on the reduced LFO/MAO was observed. This indicates that the reduced perovskite phase had a stoichiometry of $LaFeO_{2.95}$. Thermodynamic measurements of Sr-doped $LaFeO_3$ would suggest a similar reduction of Fe under these conditions ¹⁴⁶. By contrast, the oxygen uptakes on the reduced Ni/MAO, Ni/LFO/MAO, and 1-Ni/LFO/MAO, samples were 720, 870, and 200 $\mu\text{mol O/g}$, respectively. For samples with 0.9-, 4.8-, and 4.9-wt% Ni, the reaction of Ni to NiO would require 150, 820 and 830 $\mu\text{mol O/g}$, respectively. Therefore, the oxygen uptakes on the Ni/LFO/MAO and 1-Ni/LFO/MAO samples are in reasonable agreement with those expected for oxidation of both the Ni and $LaFeO_3$ phases. The fact that oxygen uptakes increased proportionally with Ni content also excludes the possibility that Ni is catalyzing reduction of the perovskite. The somewhat lower oxygen uptake on Ni/MAO may indicate that some of the Ni had reacted with the $MgAl_2O_4$ and was unable to reduce back to the metallic state at these conditions.

In the previous investigation of Pt, Pd and Rh supported on $LaFeO_3/MgAl_2O_4$, it was found that reduction or oxidation at temperatures below 1073 K was ineffective for activating or deactivating the catalyst. To explore the effect of pretreatment temperature on Ni/LFO/MAO and Ni/MAO, we measured the oxidation state of pre-reduced samples after oxidation at intermediate temperatures. The catalysts were first reduced at 1073 K,

after which they were oxidized in dry air for 30 min at either 973, 873, or 773 K. The sample temperature was then raised to 1073 K and the oxidation state measured by flow titration. As shown by the data in **Table 7.1** (Columns (2) to (4)), the Ni/MAO catalyst could be fully oxidized at 773 K. By comparison, most of the Ni in the Ni/LFO/MAO remained in the reduced state after oxidation at 773 K. Oxidation was incomplete even after heating in flowing air at 873 K. The increased difficulty of oxidizing the LaFeO₃-containing sample suggests that oxidation of the Ni involves some interaction with the perovskite.

To explore the chemical potential at which oxidation occurs, this work specifically investigated the thermodynamics of oxidation in these catalysts using equilibrium measurements. Data for the redox reaction on the Ni/MAO catalyst at 1073 K are shown in **Figure 7.5**. Because the Ni remained completely reduced for all H₂:H₂O ratios that we could access in the flow-titration apparatus, these measurements were performed by coulometric titration, starting from the reduced sample. After flowing a mixture of 5% H₂O, 10% H₂, and 85% He over the sample for 30 min and then allowing the system to come to equilibrium, the measured PO₂ was 10⁻¹⁶ atm. The PO₂ increased only slightly, from 10⁻¹⁶ atm to 10⁻¹⁵ atm, upon the addition of the first 700 μmol O/g to the sample but then increased rapidly after the Ni was completely converted to NiO. The fact that the PO₂ remained constant during the oxidation process is consistent with equilibrium being established between Ni and NiO. The amount of oxygen required to completely oxidize the metallic Ni in coulometric titration agreed well with the value obtained in the flow-titration measurements in **Table 7.1**. Tabulated data for oxidation of bulk Ni would

predict that the PO_2 should be 10^{-14} atm at 1073 K when both Ni and NiO are present in equilibrium. This is indicated by the dotted line in the plot. The difference between the measured PO_2 for the Ni/MAO catalyst and tabulated data is relatively small but may be real. There are reports that the oxidation potential for a metal can shift to lower PO_2 with particle size due to the effects of surface energy¹³⁶ or interactions with the support¹⁴⁷. The change in the equilibrium PO_2 with the extent of Ni oxidation could indicate that there is a distribution of environments for the Ni.

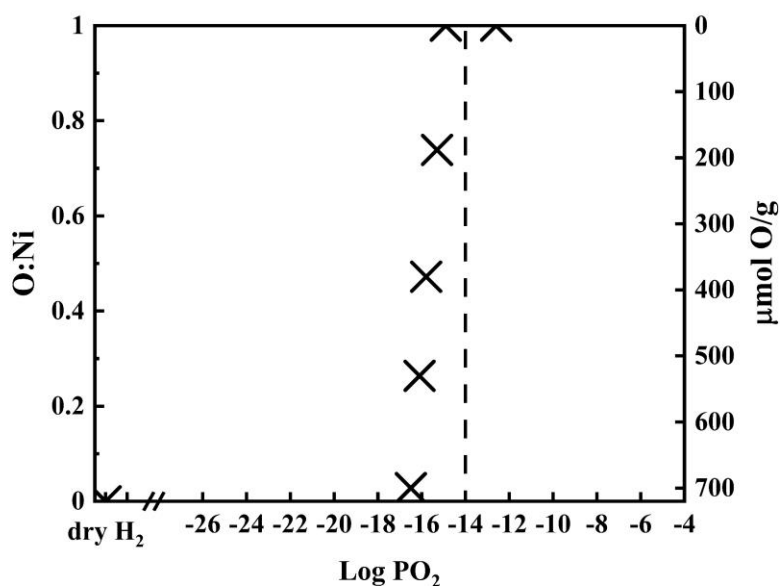


Figure 7.5: Oxidation isotherm obtained using coulometric titration for Ni/MAO at 1073 K (cross). The dotted line is the equilibrium value for bulk Ni.

The data for LFO/MAO were obtained using coulometric titration at 1073 K, shown in the original publication¹³¹. The amount of oxygen removed in coulometric titration agreed reasonably well with the reduction reported in **Table 7.1**. Results from

equilibrium measurements for the Ni/LFO/MAO samples are shown in **Figure 7.6** and **Table 7.2**. Compared to Ni/MAO, Ni/LFO/MAO was significantly easier to oxidize and the data for this sample were measured using flow titration at 973 and 1073 K. To facilitate equilibration, the Ni/LFO/MAO sample was first reduced in dry H₂ before exposing it to a flowing mixture of H₂ and H₂O corresponding to the desired PO₂. Pre-reduction for each data point ensured that Ni oxidation occurred by reaction with H₂O, in the presence of H₂, and was not due to sluggish kinetics for NiO reduction. Compared to bulk Ni, the equilibrium isotherm for Ni oxidation on Ni/LFO/MAO at 1073 K shifted to lower values of PO₂ by about 5 orders of magnitude. Furthermore, from the equilibrium constants at 973 and 1073 K and the thermodynamic identity in Equation 6, the oxidation enthalpy for Ni/LFO/MAO was found to vary between 285 and 325±20 kJ/mol O₂, depending on the extent of reduction. This compares to the tabulated value of 280 kJ/mol O₂ for oxidation of bulk Ni at 1073 K.

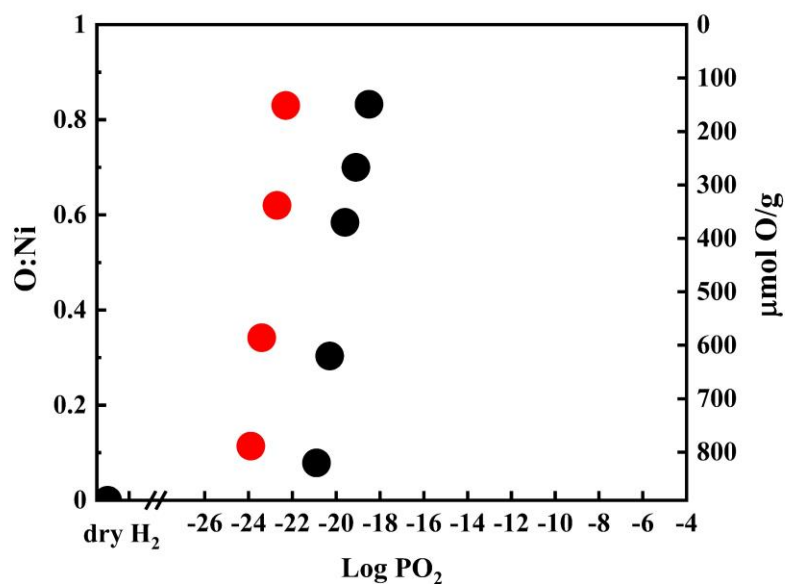


Figure 7.6: Oxidation isotherms obtained using flow titration for Ni/LFO/MAO at 973 K (red) and at 1073 K (black) at 1073 K.

By itself, the change in ΔH is not sufficient to explain the five order-of-magnitude shift in K_{NiO} . The magnitude of $-\Delta S$ must also decrease, from 180 J/mol·K to 140 J/mol·K. A similar decrease in $-\Delta S$ was reported for oxidation of the mixed oxide, $Ce_yZr_{1-y}O_2$, compared to pure CeO_2 ¹⁴⁴. The authors of that study argued that the decreased entropy change was due to a decrease in the number of identical lattice positions that could accommodate the oxygen atoms of the mixed oxide. Similar arguments may explain the changes for Ni on the LFO/MAO support. If Ni was constrained at the surface, such as what would occur in a two-dimensional film, the possible locations for oxygen atoms would decrease.

Table 7.2: Flow-titration measurements of oxygen uptakes following equilibration of the fully reduced Ni/LFO/MAO sample in flowing H₂O-H₂ environments.

H ₂ O content in H ₂ (%)	Log PO ₂ (atm)	μmol O/g uptake (Ni reduction extent %) (± 20 μmol O/g)	
1073 K			
0	-∞	870 800 620 370 270 150	100%
5	-20.9		92%
10	-20.3		71%
20	-19.6		43%
30	-19.1		31%
45	-18.5		17%
973 K			
0	-∞	790 700 520 340 140	91%
3	-23.9		80%
5	-23.4		60%
10	-22.7		39%
15	-22.3		16%

7.3.3 Coke Tolerance

A previous study of Ni on CaTiO₃/MgAl₂O₄ demonstrated that the perovskite-supported catalyst exhibited extreme tolerance towards coking¹⁰⁵. Samples heated in dry, flowing CH₄ at 1073 K for 12 h showed minimal carbon formation, while a reactor containing a more conventional Ni/MAO catalyst showed large amounts of filamentous carbon. To determine whether the Ni/LFO/MAO catalyst might also exhibit resistance to coking, this sample was also exposed to dry flowing methane at 1073 K for 12 h, after which the carbon content of the sample was determined by measuring the CO₂ removed

in flowing air at 1073 K in the same reactor used for flow titration. Similar to the result for Ni/CaTiO₃/MgAl₂O₄, the amount of carbon deposited on the Ni/LFO/MAO sample was small compared to that which formed on the Ni/MAO catalyst, 2.2±0.3 mmol C/g (less than 3-wt%) versus 26±2 mmol C/g (30-wt%). Indeed, the amount of carbon that forms on the Ni/LFO/MAO is so small that it may not even be associated with coking of the Ni component.

7.3.4 Methane Dry Reforming

To determine how the support and redox properties might affect catalytic activities, the Methane-Dry-Reforming (MDR) reaction was investigated on the reduced Ni/LFO/MAO and Ni/MAO samples. To ensure that the catalysts were in a stable state, the catalysts were pretreated using 5 redox cycles with 10% O₂ and 10% H₂ at 1073 K. Both catalysts were in a reduced state prior to carrying out the reaction, and the initial reaction conditions were chosen to be 5% CH₄ and 5% CO₂ in He. The steady-state conversions were measured after the system had stabilized for 2 h at each temperature point. While the Ni/MAO behaved as a conventional Ni catalyst for this reaction, we found that it was not possible to operate the Ni/LFO/MAO in a stable manner under differential reaction conditions. However, high rates could be achieved under integral reaction conditions. In **Figure 7.7**, the methane conversion is plotted as a function of temperature for both catalysts, using a fixed Gas Hourly Space Velocity (GHSV) of 60000 mL·g⁻¹·h⁻¹ (100 mL/min total flow rate, 100 mg catalyst). On Ni/LFO/MAO, rates were so high that conversions essentially reached equilibrium for the MDR reaction. The equilibrium conversions,

which include consumption of CO₂ due to the Reverse WGS reaction, were calculated and are shown in the plot. The reaction was also measured on the LaFeO₃/MgAl₂O₄, and there was no activity observed.

To compare these rates to literature values, turnover frequencies (TOF) were calculated from estimates of the Ni dispersion obtained from XRD measurements of the Ni particle size. Based on the Scherrer equation, the average Ni crystallite size for Ni/LFO/MAO was 10 nm, implying a corresponding dispersion of 12%¹⁴⁸. The calculated TOF for Ni/LFO/MAO at 923 K was then 79.8 s⁻¹, which was notably higher than the values reported on Ni supported on SiO₂ in the literature¹⁴⁹. The estimated TOF at these conditions for Ni/MAO, 30 s⁻¹, was similar to that reported for conventional Ni catalysts. The Ni/LFO/MAO catalyst was also stable. As shown in **Figure 7.8**, rates measured at 893 K were largely unchanged over a period of 10 h.

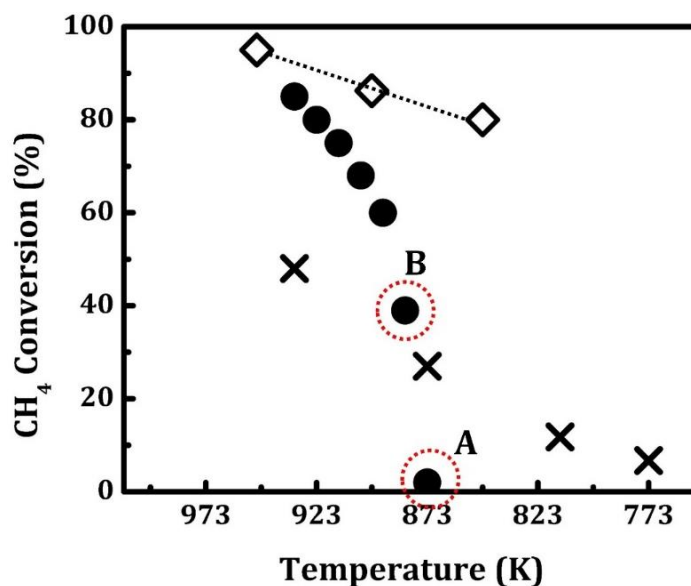


Figure 7.7: CH₄ conversions for the MDR reaction measured over 0.1-g samples of Ni/LFO/MAO (circle) and 5-Ni/MAO (cross). The feed concentration was 5% each for CH₄ and CO₂ in He and the total flow rate was kept constant at 100 mL/min. Equilibrium conversions for the MDR reaction (diamonds) are also shown.

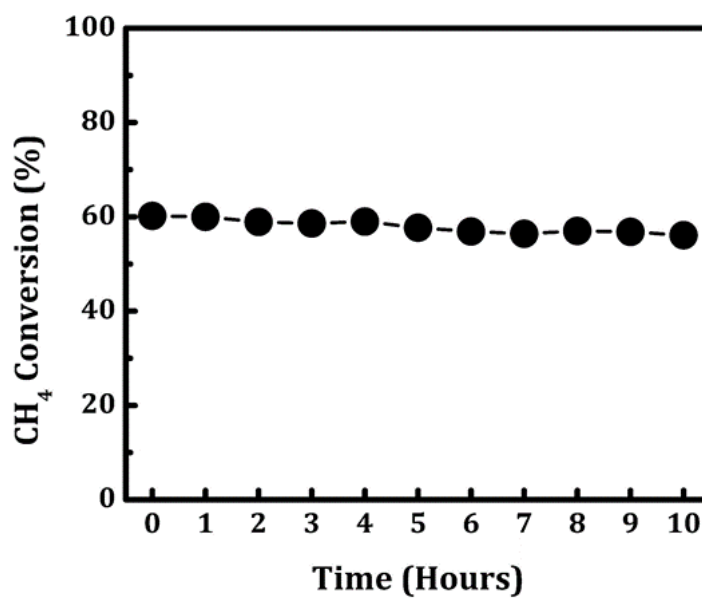


Figure 7.8: CH₄ conversions for the MDR reaction measured over 0.1-g samples of Ni/LFO/MAO at 893 K for 10 hours. The feed concentration was 5% each for CH₄ and CO₂ in He and the total flow rate was kept constant at 100 mL/min.

The data in **Figure 7.7** show a nearly stepwise transition from active to inactive states at approximately 873 K. It is important to note that this large change in activity was completely reversible upon changing the reaction temperature between 873 K and 923 K. The conversions reported in the plot were stable over the period of at least several hours and did not depend on whether the experimental condition was approached from the high- or low-temperature side, so that the large change in conversion between points marked A and B was not due to an irreversible process, such as coking or sintering of Ni particles. As discussed in the Experimental Methods section, it is important to recognize that correlations of the flow conditions in our tubular reactor indicate that mixing will be sufficiently large to allow the reactor to be treated as a Continuous Stirred Tank Reactor (CSTR) ¹⁴⁵. This implies that all parts of the catalyst bed will be exposed to the product composition.

The following observations demonstrate that the dramatic drop in conversions on the Ni/LFO/MAO sample at ~873 K is due to surface oxidation of the Ni. First, the equilibrium constant for Ni oxidation on this catalyst can be extrapolated from the measurements in **Figure 7.6** and Equation 6. Values for K_{NiO}^{-2} in the temperature range at which the rates showed a precipitous drop are reported in , using K_{NiO}^{-2} of $10^{-18.5}$ atm at 1073 K and $-\Delta H$ of 320 kJ/mol O₂. **Table 7.3** also shows the PO₂ established by the reaction conditions, calculated from the CO₂:CO ratio in the products, shown in **Figure 7.9**, assuming equilibrium for $\text{CO} + \frac{1}{2}\text{O}_2 = \text{CO}_2$. **Table 7.3** demonstrates that the conditions established by the reaction at points A and B in the plot are very close to the equilibrium

conditions at which NiO should form. At higher temperatures, the PO_2 established by the reaction are significantly lower than K_{NiO}^{-2} , which implies that the Ni should remain metallic. Second, additional evidence for deactivation being due to Ni oxidation came from the fact that, in the region of points A and B, small changes in the GHSV caused large changes in the conversions. For example, starting from point B, small increases in the total feed flow rate led to a precipitous drop in the conversion due to a decrease in the $\text{CO}_2:\text{CO}$ ratio and subsequent deactivation due to oxidation of the Ni.

Table 7.3: The extrapolated K_{NiO}^{-2} for Ni oxidation on the Ni/LFO/MAO samples together with the calculated PO_2 from the MDR reaction.

Temperature (K)	Extrapolated K_{NiO}^{-2} from thermodynamic data	Calculated Log PO_2 for the reaction conditions.
923	-24.0	-24.8
903	-24.8	-25.4
893	-25.3	-25.4
883	-25.7	-25.1
873	-26.2	-22.4

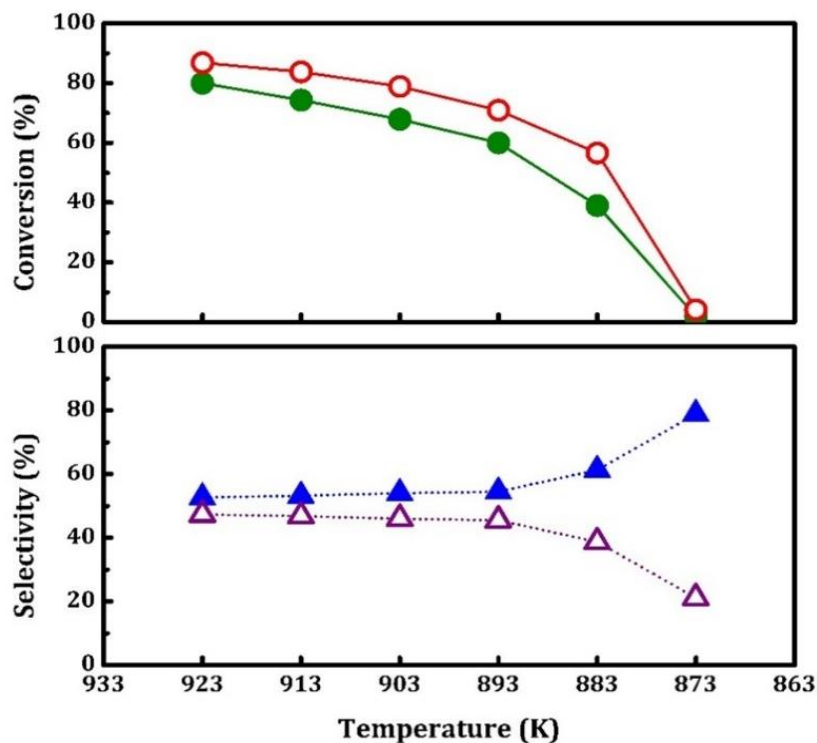


Figure 7.9: Steady-state conversions of CH₄ (green) and CO₂ (red) for MDR over 0.1-g sample of Ni/LFO/MAO, and the corresponding product distributions, CO (blue triangle) and H₂ (red triangle). The feed concentration was 5% each for CH₄ and CO₂ in He and the total flow rate was kept constant at 100 mL/min.

To provide additional evidence that the drop in activity at lower temperatures in **Figure 7.7** is due to Ni oxidation, the MDR reaction was performed at 873 K (the temperature of point “A” in **Figure 7.7**) while varying the CH₄:CO₂ ratio in the feed. For these experiments, the CH₄ partial pressure was fixed at 5% and the CO₂ partial pressure was decreased while maintaining a constant GHSV. As shown in **Figure 7.10**, the catalyst was essentially inactive when the ratio of CH₄:CO₂ was 1, but the conversions of both reactants rapidly increased when the ratio was raised above approximately 1.67. At this point, the CO₂ conversion increased to 80%, leading to a CO:CO₂ ratio of 5 and a PO₂ of

$10^{-26.6}$ atm, a value just below the calculated equilibrium constant, $K_{\text{NiO}}^{-2} = 10^{-26.2}$ atm, implying the Ni should exist in the metallic state. Because the conversion of CO_2 remained high with further increases in the $\text{CH}_4\text{:CO}_2$ ratio, the Ni catalyst remained metallic and catalytically active. Results from the complementary experiment are shown in **Figure 7.11**. In this case, the temperature was fixed at 883 K (the temperature of point “B” in **Figure 7.7**) and the CO_2 partial pressure was increased while fixing the CH_4 partial pressure. For a $\text{CH}_4\text{:CO}_2$ ratio of 1, the conversions of both CH_4 and CO_2 are reasonably high. However, when the CO_2 partial pressure increased, the conversions, along with the $\text{CO}\text{:CO}_2$ ratio, decreased, falling to near zero at a ratio of 3. This is again consistent with Ni becoming oxidized with increasing $\text{CO}_2\text{:CH}_4$ ratio. If deactivation were due to coking, increasing the CO_2 concentration should stabilize the catalyst, rather than cause deactivation.

It is important to notice that reaction rates in **Figure 7.7**, **Figure 7.10**, and **Figure 7.11** changed too rapidly for bulk oxidation or reduction of Ni. Steady-state conversions were established in just a few minutes, and the reactant flow rates were insufficient to add or remove the oxygen required to completely oxidize the Ni. Also, as shown in **Table 7.1**, complete oxidation of the Ni on the Ni/LFO/MAO sample only occurred at higher temperatures in the flow-titration experiments. Therefore, the oxidation that is observed in the reaction experiments appears to be associated with surface Ni only. The fact that the equilibrium properties for surface Ni can be predicted from the bulk measurements is of additional interest.

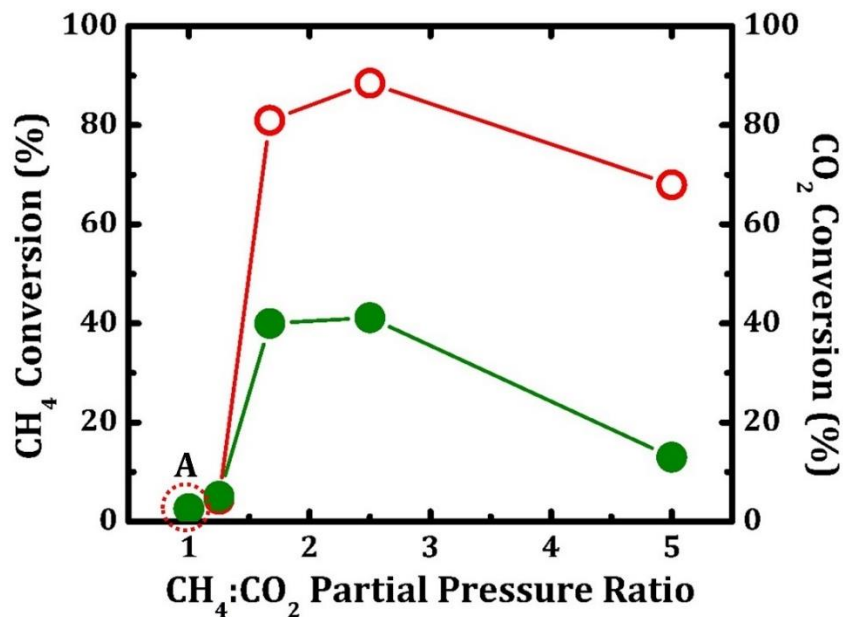


Figure 7.10: Steady-state conversions of CH₄ (green) and CO₂ (red) for MDR over 0.1-g sample of Ni/LFO/MAO at 873 K. The total and CH₄ flow rates were fixed at 100 mL/min and 5 mL/min, respectively, while CO₂ flow rate was varied to adjust the CH₄:CO₂ ratio.

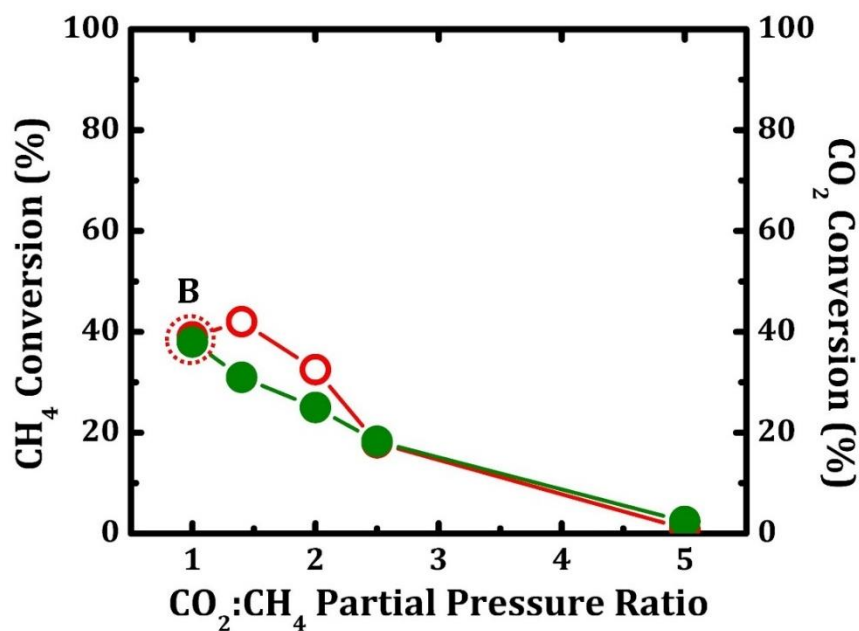


Figure 7.11: Steady-state conversions of CH₄ (green) and CO₂ (red) for MDR over 0.1-g sample of Ni/LFO/MAO at 883 K. The total and CH₄ flow rates were fixed at 100 mL/min and 5 mL/min, respectively, while CO₂ flow rate was varied to adjust the CO₂:CH₄ ratio.

7.4 Discussion

Most prior catalytic work on perovskite-supported metals has focused on the fact that metal dispersions can be maintained due to reversible ex-solution of the metal atoms into the perovskite lattice. Far less attention has been given to the fact that strong interactions between the perovskite and the metal particles could alter other catalytic properties. While a number of groups have shown that perovskite-supported Ni can exhibit extreme tolerance against coke formation in the presence of dry methane ^{28, 105, 150}, it has only recently been demonstrated that ex-solved metals can exhibit dramatically different properties for other reactions. Specifically, it was shown that Pt supported on CaTiO₃ thin films exhibited a higher activity for CO oxidation than Pt on non-interacting supports but was dramatically less active for hydrogenation of toluene ⁴⁹. The present study extends the observations of support effects on the thermodynamic properties of the metal. A major reason that the properties of perovskite-supported materials have not previously been investigated more thoroughly is that the perovskite surface areas tend to be low and an unknown fraction of the metal remains in the bulk of the perovskite, inaccessible to reactants ^{28, 34, 43-44}. This has made comparisons between perovskite-supported metals with more conventional supported metals difficult.

In the present case, it is interesting to ask how contact with LaFeO₃ could so dramatically change the properties of Ni. In the absence of support migration to form overlayers on the metal catalyst (a phenomenon often referred to as Strong Metal Support Interactions (SMSI)) ^{134, 151}, the effects of the support on the metal are not expected to extend

more than a few atomic distances from the metal-support interface ¹⁵². This would imply that the affected Ni in our study must essentially be in direct contact with the perovskite since most of the Ni in three-dimensional particles would be well separated from the support. This raises additional questions. If the Ni on Ni/LFO/MAO is mostly present near the interface, why is it so difficult to oxidize the Ni at temperatures below 973 K? The difficulty in oxidizing the Ni suggests that there is a significant barrier to this oxidation, possibly associated with metal migration into the perovskite lattice. It is even more surprising that we observe rapid, reversible deactivation of catalyst activity, apparently due to Ni surface oxidation, at lower temperatures, ~873 K, upon only minor changes in the CO:CO₂ ratio. Finally, while it was very difficult to measure rates on the Ni/LFO/MAO sample, it is clear that the catalyst was very active in its metallic state, showing conversions significantly higher than the conventional Ni/MAO.

It is noteworthy that the Ni/LFO/MAO catalyst of the present study exhibited properties that were quite different from what was observed previously for Ni/CaTiO₃/MgAl₂O₄ ¹⁰⁵. Deactivation issues at differential reaction conditions were not observed in the CaTiO₃-supported materials and rates on activated catalyst were more similar to that of conventional supported Ni. This would imply that some perovskites influence metal catalyst properties more than other perovskites. This should not be surprising. Early ex-solution work showed that not all catalytic metals could enter all perovskite lattices ¹⁷. Similarly, based on experimental results and DFT simulations, Yanagisawa *et al.* reported that Pd showed very different chemical potentials for particle

segregation when placed in either LaFeO_3 or CaTiO_3 ¹³⁰. At the time, results from those authors indicated much smaller differences for Pt in LaFeO_3 and CaTiO_3 . This demonstrates that, even when a metal can ex-solve from two different perovskites, the thermodynamic properties and reducibility of the metal could still be quite different.

While the strong support effects observed in this study and the apparent differences between catalysts made with various perovskite supports certainly add a level of complexity to these catalysts, it also represents an opportunity that has not been fully explored. The potential to develop highly active catalysts with high stability against sintering and coking is certainly something that deserves additional study.

7.5 Conclusions

Thin LaFeO_3 films, deposited onto MgAl_2O_4 by ALD, are stable to redox cycling at 1073 K and can be used as catalyst supports for Ni. The presence of the perovskite films shifts the thermodynamic equilibrium for Ni oxidation to significantly lower PO_2 . Ni supported on $\text{LaFeO}_3/\text{MgAl}_2\text{O}_4$ shows high activity for the MDR reaction and good tolerance against coking but deactivates due to Ni oxidation at low conversions.

CHAPTER 8. CONCLUSIONS

Sintering is one of the most severe deactivation mechanisms of metal catalysts used in high-temperature applications, e.g., automotive catalytic converters. It was reported that perovskite materials could stabilize the metal particles according to the mechanism of ex-solution; however, the large crystallite sizes and low surface areas of the bulk perovskite materials have limited the practical application of this concept.

ALD allows the preparation of high-surface-area thin films of functional supports. Chapter 3 demonstrates that the 0.5-nm films of metal oxides on γ - Al_2O_3 had better uniformity and thermal stability than the supports prepared by the conventional impregnation methods. The films of various metal oxides were used as the supports for Pd catalysts, and the support composition effects for CO and CH_4 oxidation over Pd catalysts were investigated systematically. This study showed that ALD could be used to fabricate high-surface-surface supports for heterogeneous catalysts and that good contact between the support and the metal particles could lead to strong metal-support interaction.

In Chapter 4, a Pt catalyst supported on 0.5-nm LaCoO_3 films was studied. XRD showed that the films exhibited the perovskite structure after redox cycling at 1073 K and STEM/EDS data demonstrated that the films covered the substrate uniformly. Similar to the metals doped in bulk perovskite supports, ALD catalysts prepared with 3-wt% Pt showed that the Pt remained well dispersed on the perovskite film, even after repeated oxidations and reductions at 1073 K. Pt catalyst supported on LaCoO_3 films showed self-

regenerative activity for CO oxidation and WGS reaction with no deactivation upon redox cycling. Unfortunately, STEM data suggested that the LaCoO_3 was not stable to high-temperature reduction, with reversible segregation of Co being observed in EDS.

LaFeO_3 , with better thermal stability, was chosen as the support for Pt catalysts in further investigations. In Chapter 5, evidence for the preferential alignment of Pt particles on LaFeO_3 films is reported. Pt particles were epitaxially aligned with respect to the underlying LaFeO_3 following oxidation at 1073 K, and there was a reorientation of the Pt after reduction at that temperature. Interactions with the support in this case stabilized the Pt in the form of 1 to 2-nm particles, even after repeated oxidation and reduction treatments at 1073 K. The catalyst, again, showed self-regenerative properties. It was found to switch between “active” and “inactive” states for CO oxidation after high-temperature reduction or oxidation and showed hysteretic behavior, i.e., only high-temperature oxidation and reduction could activate and deactivate the catalyst. The properties of Pt were affected by the metal-perovskite interaction, as demonstrated by the fact that CO adsorption is suppressed, and both the reaction order and activation energy for CO oxidation are affected.

In Chapter 6, a comparison of Rh, Pd, and Pt supported on LaFeO_3 films was reported to demonstrate the differences in metal- LaFeO_3 interaction strength. DFT computational calculations showed that Rh has the strongest binding energy to the LaFeO_3 surface, followed by Pt and Pd. Experimental observations were consistent with the calculations, showing that, after 5 redox cycles at 1073 K, the Rh particles could be

stabilized as 1-nm particles, and Pt particles under 5 nm, while Pd showed significant agglomeration. The differences in metal-support interactions also affected the catalytic activity of the metal. For Pd on LaFeO₃, due to the weakest binding energy, the catalyst could be activated after reduction at 573 K or 773 K; but for Rh, even 1073-K reduction could not fully activate it for CO oxidation reaction. By measuring the oxygen uptakes for each sample after reduction, I found that the amount of reduction for metals supported on LaFeO₃ films was much higher than what occurred with pure LaFeO₃ films or with the metals on non-reducible supports, implying that metals can induce the reduction of the LaFeO₃ phase. The equilibrium oxygen isotherms measured using coulometric titration further supported the hypothesis that LaFeO₃ phase was involved in the surface reconstruction of the sample during redox cycling. The equilibrium oxidation PO₂ of Rh and Pd metals were shifted towards lower values in the presence of the LaFeO₃ films.

As shown in Chapter 6, metal-perovskite interactions can affect the thermodynamic properties of supported metal catalysts. Very promising results were also obtained in a thermodynamic and catalytic investigation of 5-wt.% Ni on thin LaFeO₃ films, demonstrated in Chapter 7. LaFeO₃ was found to be stable to redox cycling and showed strong interactions with Ni. The strong Ni-LaFeO₃ interactions further led to excellent tolerance against coking. The presence of LaFeO₃ was found to shift the equilibrium constant, K_{NiO} , of the reaction $\text{Ni} + \frac{1}{2}\text{O}_2 = \text{NiO}$, to significantly lower PO₂, which in turn affected the conditions under which Ni could be used as a steam-reforming

catalyst. The shift in equilibrium caused deactivation due to Ni oxidation at low CO:CO₂ ratios, and reactivation at high CO:CO₂ ratios.

Overall, the work in this thesis showed that how the metal-support interactions would affect the physical, catalytic, and thermodynamic properties of metals supported on perovskite thin films prepared by ALD.

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