Investigation of the Thermodynamic Properties of Surface Ceria and Ceria–Zirconia Solid Solution Films Prepared by Atomic Layer Deposition on $\text{Al}_2\text{O}_3$

Tzia Ming Onn, Xinyu Mao, Chao Lin, Cong Wang and Raymond J. Gorte *

Department of Chemical and Biomolecular Engineering, University of Pennsylvania, 34th Street, Philadelphia, PA 19104, USA; tonn@seas.upenn.edu (T.M.O.); xinyumao@seas.upenn.edu (X.M.); linchao@seas.upenn.edu (C.L.); wangcong@seas.upenn.edu (C.W.)

* Correspondence: gorte@seas.upenn.edu

Received: 29 August 2017; Accepted: 11 October 2017; Published: 15 October 2017

Abstract: The properties of 20 wt % CeO$_2$ and 21 wt % Ce$_{0.5}$Zr$_{0.5}$O$_2$ films, deposited onto a $\gamma$-Al$_2$O$_3$ by Atomic Layer Deposition (ALD), were compared to bulk Ce$_{0.5}$Zr$_{0.5}$O$_2$ and $\gamma$-Al$_2$O$_3$-supported samples on which 20 wt % CeO$_2$ or 21 wt % CeO$_2$–ZrO$_2$ were deposited by impregnation. Following calcination to 1073 K, the ALD-prepared catalysts showed much lower XRD peak intensities, implying that these samples existed as thin films, rather than larger crystallites. Following the addition of 1 wt % Pd to each of the supports, the ALD-prepared samples exhibited much higher rates for CO oxidation due to better interfacial contact between the Pd and ceria-containing phases. The redox properties of the ALD samples and bulk Ce$_{0.5}$Zr$_{0.5}$O$_2$ were measured by determining the oxidation state of the ceria as a function of the H$_2$:H$_2$O ratio using flow titration and coulometric titration. The 20 wt % CeO$_2$ ALD film exhibited similar thermodynamics to that measured previously for a sample prepared by impregnation. However, the sample with 21 wt % Ce$_{0.5}$Zr$_{0.5}$O$_2$ on $\gamma$-Al$_2$O$_3$ reduced at a much higher $P_{O_2}$ and showed evidence for transition between the Ce$_{0.5}$Zr$_{0.5}$O$_2$ and Ce$_{0.5}$Zr$_{0.5}$O$_{1.75}$ phases.

Keywords: Atomic Layer Deposition; ceria; ceria–zirconia; thermodynamics; improved stability

1. Introduction

Ceria is a component in a number of commercial catalysts, as demonstrated in a recent, comprehensive review [1]. Two important examples include the use of ceria-based materials as oxidation catalysts in Diesel particulate filters [2] and the use of ceria–zirconia solid-solutions as Oxygen-Storage Capacitors (OSC) in automotive three-way catalysts [3–7]. The critical property of ceria that makes it useful in these and other catalytic applications is the relative ease with which it changes oxidation states between Ce$^{3+}$ and Ce$^{4+}$. This, together with the fact that reduced ceria can be oxidized by steam or CO$_2$ [8] and then transfer oxygen to transition metals with which it is in contact make it a promoter of hydrocarbon oxidation [9,10], water-gas-shift (WGS) reaction [11–14], steam reforming [15–18], and more.

It is known that pure ceria becomes essentially unreducible after harsh redox cycling [19]. Although this loss in reducibility is accompanied by a loss in surface area, it is not simply a kinetic phenomenon, since the ceria–zirconia solid solutions that are used in three-way catalysts also have low surface areas but still maintain their OSC properties [20]. While the loss in surface area does not prevent the application of ceria–zirconia solid solutions for OSC, high surface areas are required in other cases. For example, for CO-oxidation and WGS reactions over Pd/ceria, the sites at the Pd–ceria boundary have been shown to exhibit much higher rates [21]. In these examples, the surface area of the ceria should be as high as possible.
An obvious approach for maintaining a high surface area for the ceria phase is to deposit it onto a high-surface-area support that has good thermal stability, such as γ-Al₂O₃. The ceria phase is usually added by infiltration with metal salts, followed by calcination; however, the use of a support for the ceria phase is often only partially effective because the ceria does not typically cover the entire surface. For example, rates on a catalyst in which Pd is deposited onto a ceria/γ-Al₂O₃ support prepared by infiltration of ceria are often much lower than rates on ceria-supported Pd because much of the Pd is not in contact with ceria in the former case [22]. Finally, it can be difficult to produce a supported, ceria–zirconia solid solution because this requires good mixing of the Ce and Zr cations during the precipitation stage in catalyst preparation.

Work from our laboratory has recently demonstrated that one can use Atomic Layer Deposition (ALD) to prepare thin ceria [22] and ceria–zirconia [23] films that uniformly cover a γ-Al₂O₃ support. The principle behind ALD is that an organometallic precursor is allowed to react with the substrate surface, after which the adsorbed precursor is oxidized in a separate step. Because reaction of the precursor with the substrate is limited to a monolayer at most, ALD allows the formation of uniform, atomic-scale, oxide films. There are comprehensive reviews of ALD topics that are available [24,25]. Mixed oxides are easily formed by alternating between different precursors. Because oxides have low surface energies compared to metals, the uniform films formed by ALD tend to be thermally stable. In the cases of ceria and ceria–zirconia films on γ-Al₂O₃, the γ-Al₂O₃ remains “covered”, even after calcination to 1173 K.

As mentioned previously, the reducibility of ceria depends on the surface area and/or crystallite size [19,26] and ceria–zirconia solid solutions are more reducible than pure ceria [20,27]. Because the films prepared by ALD can be sub-nanometer in thickness, it is anticipated that the reducibility of these materials may be very different from even ordinary polycrystalline ceria. Quantification of reducibility can be difficult and kinetic measures, such as Temperature Programmed Reduction peak temperatures, can be dramatically affected by the presence of catalysts and other factors. Therefore, we chose to quantify reducibility by measuring the thermodynamic properties of ALD-prepared films using flow titration and coulometric titration [20,27]. In both of these techniques, the sample is equilibrated at high temperatures in a specified \( P_{O_2} \) and the extent of ceria reduction (e.g., \( x \) in \( \text{CeO}_{2−x} \)) is then determined as a function of that \( P_{O_2} \) and temperature. The \( P_{O_2} \) is typically established by equilibrium with \( H_2 \) oxidation (i.e., \( P_{O_2} = K_{\text{equi}}^{-1} \frac{P_{H_2O}}{P_{H_2}} \)) and is therefore fixed by passing a mixture of \( H_2 \) and \( H_2O \) over the sample at a specified \( H_2O:H_2 \) ratio. Because the activity of solids is one, the equilibrium constant for oxidation of \( \text{CeO}_{2−x} \), and therefore the free energy of oxidation at that value of \( x \), is determined directly from the measured \( P_{O_2} \). Furthermore, the temperature dependence of the equilibrium constant can be used to determine the heat of oxidation through the Clausius-Clapeyron Equation.

What we will show is that 0.4-nm, ALD ceria films on γ-Al₂O₃ have thermodynamic redox properties that are different from that of bulk ceria but essentially identical to that reported previously for polycrystalline ceria formed by impregnation into γ-Al₂O₃. This may be due the film coalescing into particles upon redox cycling. By contrast, the 0.5-nm ceria–zirconia films were stable and very different from either bulk ceria or ceria–zirconia solid solution. The films exhibit evidence for an equilibrium transition between the \( \text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2 \) and \( \text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_{1.75} \) phases.

2. Results

2.1. Sample Characterization

The synthesis and characterization of the CeO₂(ALD)/γ-Al₂O₃ and the CZ(ALD)/γ-Al₂O₃ samples have been presented in detail elsewhere [22,23]. Results from Transmission Electron Microscopy (TEM) indicated that the γ-Al₂O₃ was uniformly covered by the ALD films, and there was good agreement between the thicknesses of the films determined from TEM and value of 0.4-nm estimated from the sample weight changes. By contrast, TEM of a CeO₂(IMP)/γ-Al₂O₃ sample with
the same ceria loading as the ALD sample showed the presence of relatively large CeO$_2$ crystallites that covered only a fraction of alumina surface [22].

The differences between the ALD and impregnated samples are readily apparent from the XRD patterns, shown in Figure 1. All of the samples in this figure were calcined in air to 1073 K for 2 h prior to the measurements. To normalize the intensities, 12.5 wt % carbon was added to each sample and the height of the peak XRD peak at 26.7 degrees 2θ was fixed. The XRD pattern for the unmodified γ-Al$_2$O$_3$ is shown in Figure 1a for reference. In agreement with the previous report [22], the patterns for the CeO$_2$(ALD)/γ-Al$_2$O$_3$ (Figure 1b) and CeO$_2$(IMP)/γ-Al$_2$O$_3$ (Figure 1c) samples, both of which had 20 wt % CeO$_2$, are very different. The diffraction pattern of CeO$_2$(ALD)/γ-Al$_2$O$_3$ remained unchanged from that of γ-Al$_2$O$_3$, either because the CeO$_2$ film is amorphous or because the thickness of the CeO$_2$ film is less than the coherence length of the X-rays [22]. By contrast, the CeO$_2$(IMP)/γ-Al$_2$O$_3$ shows relatively intense peaks corresponding to the fluorite structure of CeO$_2$.

![XRD patterns](image)

**Figure 1.** XRD patterns of (a) γ-Al$_2$O$_3$ support after calcination to 1173 K in air, and ALD-modified samples, (b) 20CeO$_2$–Al$_2$O$_3$ and (d) 20Ce$_{0.5}$Zr$_{0.5}$O$_2$–Al$_2$O$_3$ heated to 1073 K. The patterns in (c) and (e) were obtained from CeO$_2$(IMP)/Al$_2$O$_3$ and CZ(IMP)/Al$_2$O$_3$ respectively. The loadings of materials are the same for the ALD-modified supports and the infiltrated supports. Peaks were normalized to a distinct graphite peak around 2θ = 26.7°. Characteristic peaks for ceria–zirconia solid solution are marked by ●, while peaks for CeO$_2$ and ZrO$_2$ are marked by * and □ respectively.

The XRD patterns for the CZ(ALD)/γ-Al$_2$O$_3$ (Figure 1d) and CZ(IMP)/γ-Al$_2$O$_3$ (Figure 1e) samples, both with 21 wt % Ce$_{0.5}$Zr$_{0.5}$O$_2$, are similarly different. There is evidence for a fluorite-related feature at 29.4 degrees 2θ on the ALD sample; but the feature is very broad and weak, again suggesting that the oxide remains in the form of amorphous film. The peak position, roughly half way between the expected angles for CeO$_2$ and ZrO$_2$, is consistent with formation of a solid, ceria–zirconia solution [28]. Because it is difficult to form a single-phase, ceria–zirconia solid solution by impregnation, the impregnated sample shows two features in this region, at approximately 28 and 30 degrees 2θ, which are due to ceria- and zirconia-rich phases, respectively [28]. Again, the intensities of the peaks on CZ(IMP)/γ-Al$_2$O$_3$ are much greater, implying the presence of three-dimensional crystallites.

Because redox cycling, alternating between reducing and oxidizing environments at high temperatures, has been shown to affect ceria crystallite size much more strongly than simple,
high-temperature calcination [19], we also measured XRD patterns for the CeO$_2$(ALD)/γ-Al$_2$O$_3$, CZ(ALD)/γ-Al$_2$O$_3$, and CeO$_2$(IMP)/γ-Al$_2$O$_3$ samples after redox cycling, with results shown in Figure 2. The CeO$_2$(IMP)/γ-Al$_2$O$_3$ sample underwent three cycles of alternating reduction (90% H$_2$ and 10% H$_2$O for 30 min) at 1073 K and oxidation (dry air for 30 min) at 1073 K. The two ALD-prepared samples were used for the thermodynamic measurements that will be discussed later in this paper and were exposed to many oxidation and reduction cycles over a period of several weeks, at temperatures between 873 and 1073 K. Redox cycling significantly narrowed and increased the intensity of the peak at approximately 2θ = 28° for the CeO$_2$(IMP)/γ-Al$_2$O$_3$ sample. Using the width at half height of the (220) diffraction peak, the ceria crystallite size on the CeO$_2$(IMP)/γ-Al$_2$O$_3$ sample increased from 7 to 18 nm. Redox aging also caused changes in the XRD pattern for the CeO$_2$(ALD)/γ-Al$_2$O$_3$ sample. The (220) diffraction peak remained much lower than that of even the fresh CeO$_2$(IMP)/γ-Al$_2$O$_3$ sample. The CZ(ALD)/γ-Al$_2$O$_3$ sample also exhibited a weak peak that can be associated with a Ce$_{0.5}$Zr$_{0.5}$O$_2$ phase; but, again, this feature is weak in intensity and very broad.

Figure 2. XRD patterns of (a) 20Ce$_{0.5}$Zr$_{0.5}$O$_2$–Al$_2$O$_3$, (b) 20CeO$_2$–Al$_2$O$_3$, and (c) CeO$_2$(IMP)/Al$_2$O$_3$ after redox cycling conditions. The CeO$_2$(IMP)/γ-Al$_2$O$_3$ sample underwent three cycles of alternating reduction (90% H$_2$ and 10% H$_2$O for 30 min) and oxidation (dry air for 30 min) at 1073 K. The ALD-prepared samples, (a) and (b), were exposed to similar oxidation and reduction cycles over a period of several weeks, at temperatures between 873 and 1073 K. Peaks were normalized to a distinct graphite peak around 2θ = 26.7°. Characteristic peaks for ceria–zirconia solid solution are marked by ●, while peaks for CeO$_2$ are marked by *.

The sites at the interface between Pd and ceria are known to be considerably more active for CO oxidation than either Pd or ceria sites individually [21,29]. Therefore, another indication of how well CeO$_2$ or Ce$_{0.5}$Zr$_{0.5}$O$_2$ cover the γ-Al$_2$O$_3$ in these composite oxides was gained by adding Pd to the oxide supports and then measuring CO oxidation rates. With the exception of the bulk CeO$_2$, 1 wt % Pd was added to the γ-Al$_2$O$_3$, CeO$_2$(ALD)/γ-Al$_2$O$_3$, CeO$_2$(IMP)/γ-Al$_2$O$_3$, CZ(ALD)/γ-Al$_2$O$_3$, and CZ(IMP)/γ-Al$_2$O$_3$ after each of the supports had been calcined at 1073 K for 2 h. The bulk CeO$_2$
was calcined to only 773 K as it may lose significant surface area after high temperature treatment. After adding the Pd, the catalysts were dried and then calcined to 773 K. BET surface areas and the Pd dispersions, measured after reduction at 673 K, are reported in Table 1; and differential reaction rates are shown in Figure 3. All of the catalysts had similar BET surface areas and Pd dispersions but the catalytic activities varied significantly. To obtain rates under differential conditions, it was therefore necessary to measure them over different temperature ranges. Since the activation energies were similar, it was possible to extrapolate the rates to a common temperature and qualitatively estimate the contact between Pd and the ceria phase in each sample.

![Figure 3.](image)

**Figure 3.** Steady-state, differential reaction rates for CO oxidation reaction with partial pressure of CO and O2 at 25 Torr and 12.5 Torr, respectively. The supports were heated at 1073 K in air for 2 h before 1 wt % of Pd was introduced. After calcination at 773 K in air, the CO oxidation rates were compared for the following catalysts: (○) Pd/Al2O3, (□) Pd/Al2O3, (●) Pd/CeO2(IMP)/Al2O3, (♦) Pd/CZ(IMP)/Al2O3, (■) Pd/20Ce0.5Zr0.5O2/Al2O3, and (◊) Pd/Al2O3. The catalyst, (○) Pd/Al2O3, heated to 773 K in air, was added for comparison. The CeO2 support was heated to 773 K.

**Table 1.** Metal Dispersion and BET Surface Area of Catalysts.

<table>
<thead>
<tr>
<th></th>
<th>Pd Dispersion (%)</th>
<th>BET Surface Area (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd/Al2O3</td>
<td>28</td>
<td>96</td>
</tr>
<tr>
<td>Pd/CeO2(IMP)/Al2O3</td>
<td>23</td>
<td>80</td>
</tr>
<tr>
<td>Pd/CZ(IMP)/Al2O3</td>
<td>26</td>
<td>82</td>
</tr>
<tr>
<td>Pd/20CeO2–Al2O3</td>
<td>33</td>
<td>77</td>
</tr>
<tr>
<td>Pd/20Ce0.5Zr0.5O2/Al2O3</td>
<td>34</td>
<td>71</td>
</tr>
<tr>
<td>Pd/Al2O3</td>
<td>40</td>
<td>45</td>
</tr>
</tbody>
</table>

First, at 373 K, the Pd/Al2O3 sample was nearly 100 times more active than Pd/γ-Al2O3, demonstrating that the Pd–CeO2 interfacial sites are indeed more active for this reaction. Although the differential rates on Pd/Al2O3 and γ-Al2O3 were also a factor of three higher than those on Pd/γ-Al2O3, this is likely due to the higher surface area of the ALD sample. In any case, the results on Pd/CeO2(IMP)/γ-Al2O3 suggest that all of the Pd is in contact with CeO2 ALD film and that CeO2 must cover the entire surface of the support. This is the same conclusion reached earlier from WGS measurements on similar samples [22]. The Pd/CZ(IMP)/γ-Al2O3 catalyst exhibited rates similar to that found on Pd/Al2O3 and the two impregnated samples showed activities closer to that of Pd/γ-Al2O3. These results imply that Pd is not in good contact with the ceria phases on the supports prepared by impregnation. The lower activity of Pd/CZ(IMP)/γ-Al2O3 compared to Pd/CeO2(IMP)/γ-Al2O3 may be due to the fact that the presence of ZrO2 decreases contact area between Pd and CeO2 in the Pd/CZ(IMP)/γ-Al2O3 sample.
2.2. Thermodynamic Measurements

Thermodynamic measurements were performed on the bulk Ce$_{0.5}$Zr$_{0.5}$O$_2$, the CeO$_2$(ALD)/γ-Al$_2$O$_3$, and the CZ(ALD)/γ-Al$_2$O$_3$ samples after each sample has been calcined to 1073 K for 2 h. To determine the maximum extents of reduction in the CeO$_2$(ALD)/γ-Al$_2$O$_3$ and the CZ(ALD)/γ-Al$_2$O$_3$ samples, the samples were initially exposed to dry, flowing H$_2$ at 973 K in the flow-titration system. Assuming that all the oxygen which could be reversibly removed was due to reduction of Ce$^{4+}$ to Ce$^{3+}$, the calculated O:Ce ratio for both samples was 1.55 after reduction. This value did not change with repeated oxidation-reduction cycles and differs from the value expected for complete reduction by 10%. The probable reason for the discrepancy is the uncertainty in the ceria loading (e.g., Sample weights can be difficult to measure due to water adsorption upon exposure to laboratory air). The result demonstrates that the ceria in the ALD films is fully reducible.

The thermodynamic, redox properties of the CeO$_2$(ALD)/γ-Al$_2$O$_3$ sample were measured using both flow-titration (the solid data points) and coulometric-titration (the unfilled points) measurements; and a plot of the cerium oxygen stoichiometry as a function of $P_{O_2}$ is shown in Figure 4. For comparison purposes, the figure also includes data from earlier work on bulk ceria and from an impregnated, 30 wt % ceria on La-treated Al$_2$O$_3$ (shown in the inset) [19]. Flow-titration measurements were performed at 873, 973, and 1073 K but coulometric-titration was performed only at 1073 K on this sample. The data at 1073 K showed that there was good agreement between the two techniques in the $P_{O_2}$ range where the measurements overlapped. The redox thermodynamics for the CeO$_2$(ALD)/γ-Al$_2$O$_3$ sample differ dramatically from that for bulk ceria. As noted in previous publications, bulk ceria is very difficult to reduce [30]. Of equal interest, the thermodynamic data for the CeO$_2$(ALD)/γ-Al$_2$O$_3$ sample are remarkably similar to the previously published data for impregnated ceria on La-doped alumina in regions where the $P_{O_2}$ values overlap. For example, at 973 K and a $P_{O_2}$ of $10^{-20}$ atm, the O:Ce ratio was close to 1.75 on both samples. Similarly, at 873 K and a $P_{O_2}$ of $10^{-25}$ atm, the O:Ce ratio was close to 1.78 on both samples. As shown by the earlier XRD data, the CeO$_2$(ALD)/γ-Al$_2$O$_3$ showed some formation of CeO$_2$ crystallites upon redox cycling, but the crystallites on the ALD-prepared sample were clearly much smaller. The fact that the thermodynamic data did not change would suggest that equilibrium data is not a strong function of crystallite size, at least over the range of crystallite sizes investigated here.

![Figure 4](image_url)

**Figure 4.** Oxidation isotherms for 20CeO$_2$–Al$_2$O$_3$ at selected temperatures (873 K, 973 K, 1073 K). The results for pure ceria were obtained from a previous publication from our group [19], and were determined by flow titration at (+)—873 K, (×)—973 K, and (*)—1073 K. The (■), (▲), and (○) symbols show the isotherms for 20CeO$_2$–Al$_2$O$_3$ determined by flow titration at 873 K, 973 K and 1073 K respectively. The (○) symbol shows the isotherm for 20CeO$_2$–Al$_2$O$_3$ determined by coulometric titration at 1073 K. For comparison, previous results for infiltrated ceria on alumina-based support obtained from coulometric titration at 873 K and 973 K are shown [19].
The oxidation isotherms for bulk Ce0.5Zr0.5O2 and for CZ(ALD)/γ-Al2O3 are shown in Figure 5. Results for the bulk Ce0.5Zr0.5O2 were only measured at 1073 K but the data again agree well with previously published data for a sample with this composition in regions where measurements were previously performed [27]. Similar to results for bulk CeO2 and CeO2(ALD)/γ-Al2O3, the equilibrium oxygen stoichiometry in the bulk Ce0.5Zr0.5O2 sample varied gradually with the $P_{O_2}$. The data for the CZ(ALD)/γ-Al2O3 sample were significantly different. First, flow titration was not useful in measuring the properties for the CZ(ALD)/γ-Al2O3 sample because the sample was completely reduced at all experimentally accessible H2O:H2 ratios between 873 K and 1073 K. It was therefore necessary to measure the equilibrium isotherms at 873 and 1073 K using coulometric titration. Interestingly, the isotherms at both temperatures were nearly vertical lines, which is an indication that there is equilibrium between two well-defined compounds. The transitions for reduction of Ce3+ to the Ce4+ states occur at $P_{O_2}$ of approximately 10−9 atm at 1073 K and 10−15 atm at 873 K. These values are much higher than the equilibrium $P_{O_2}$ for the CeO2(ALD)/γ-Al2O3 sample, showing that the mixed oxide is much easier to reduce.

Figure 5. O/Ce ratio as a function of $P(O_2)$ for 20Ce0.5Zr0.5O2–Al2O3, determined by flow titration, at temperatures (●)—773 K, (▲)—873 K, and (●)—1073 K. The (○) symbol shows the isotherm for 20Ce0.5Zr0.5O2–Al2O3, determined by coulometric titration at 1073 K. Oxidation isotherm result for pure ceria–zirconia (Ce0.5Zr0.5O2) are obtained by flow titration at (*)—1073 K, and the result is consistent with previous literature [26].

Heats of oxidation can be calculated from the temperature dependence of the isotherm using Equation (1):

$$-\Delta H = R \frac{\partial \ln P(O_2)}{\partial T}$$

(1)

The heats, $-\Delta H$, calculated from this equation and the data in Figures 4 and 5 are plotted in Figure 6, together with previously reported numbers for CeO2 supported on La-Al2O3 [19] and for bulk Ce0.5Zr0.5O2 [26]. The heats of oxidation for both the CeO2(ALD)/γ-Al2O3 and CZ(ALD)/γ-Al2O3 samples were between 550 and 600 kJ/mol O2, independent of the extent of reduction. This is much lower than the reported heat of oxidation for bulk CeO2, 760 kJ/mol O2. In the previous study of impregnated CeO2 on La-doped Al2O3, $-\Delta H$ was reported to vary with stoichiometry, increasing from 500 kJ/mol O2 at low extents of reduction and to a value close to that of the bulk oxide at high reduction levels. $-\Delta H$ for Ce0.5Zr0.5O2 were reported to be in the range of 500 kJ/mol O2. The uncertainty in the calculated $-\Delta H$ is relatively high, perhaps ~50 kJ/mol, when the oxide stoichiometry varies with $P_{O_2}$, as it does for the CeO2(ALD)/γ-Al2O3 sample. However, when the isotherm is a vertical line, as with the CZ(ALD)/γ-Al2O3 sample, the uncertainty is much less. Therefore, we suggest that the oxidation enthalpies for all of these catalysts may be similar, at least for low extents of reduction.
was suggested that each lattice oxygen that is adjacent to a pair of Ce

According to this hypothesis, the equilibrium properties of ceria–zirconia films should change with

citric acid.

is no possibility for adjacent vacancies and

−

is probably not matter. It is interesting that the ceria–zirconia film in the CZ(ALD)/

γ

√

underlying support; if expansion-contraction issues are responsible, the underlying support will

dominant, it may be possible to stabilize the CeO₂ films by using something other than

expansion and contraction that must occur in the film upon oxidation and reduction. If wetting issues

does not appear to be a serious issue with these materials. However, there was evidence of CeO₂

formation does not appear to be a serious issue with these materials. However, there was evidence of CeO₂

crystallite growth on the CeO₂(ALD)/γ-Al₂O₃ sample under redox cycling. This may be partly due

to differences in the “wetting” properties of CeO₂ and Ce₂O₃ on γ-Al₂O₃ or it may be due to the

expansion and contraction that must occur in the film upon oxidation and reduction. If wetting issues

dominate, it may be possible to stabilize the CeO₂ films by using something other than γ-Al₂O₃ as

the underlying support; if expansion-contraction issue are responsible, the underlying support will

probably not matter. It is interesting that the ceria–zirconia film in the CZ(ALD)/γ-Al₂O₃ sample

appears to be more stable but the reasons for this are still uncertain.

Since there was no loss in reducibility upon redox cycling on any of the samples, CeAlO₃ formation
does not appear to be a serious issue with these materials. However, there was evidence of CeO₂

crystallite growth on the CeO₂(ALD)/γ-Al₂O₃ sample under redox cycling. This may be partly due

to differences in the “wetting” properties of CeO₂ and Ce₂O₃ on γ-Al₂O₃ or it may be due to the

expansion and contraction that must occur in the film upon oxidation and reduction. If wetting issues

dominate, it may be possible to stabilize the CeO₂ films by using something other than γ-Al₂O₃ as

the underlying support; if expansion-contraction issue are responsible, the underlying support will

probably not matter. It is interesting that the ceria–zirconia film in the CZ(ALD)/γ-Al₂O₃ sample

appears to be more stable but the reasons for this are still uncertain.

The thin Ce₀.₅Zr₀.₅O₂ film on the CZ(ALD)/γ-Al₂O₃ sample appears to exhibit different equilibrium

R₂ from that of bulk Ce₀.₅Zr₀.₅O₂. While this could be due to surface energies, we suggest that it may also due to the confined geometry of the film. In previous work with bulk ceria–zirconia mixed oxides [31], it was argued that the shape of the isotherm results primarily from changes in the entropy of oxidation, rather than changes in the heats of oxidation. This conclusion was based on the fact that \( -\Delta H \) was found to be independent of the extent of reduction. To explain how the oxidation entropy would change with the extent of reduction while the enthalpy was constant, it was suggested that each lattice oxygen that is adjacent to a pair of Ce⁴⁺ ions is energetically equivalent. However, since it should be energetically difficult to remove a lattice oxygen that is next to a vacancy, the number of possible oxygens that can be removed next to each set of adjacent Ce⁴⁺ ions will decrease as the solid becomes progressively reduced. In a film that is less than one unit cell in thickness, there is no possibility for adjacent vacancies and \( -\Delta G \) could be independent of the extent of reduction. According to this hypothesis, the equilibrium properties of ceria–zirconia films should change with thickness, a possibility that would be interesting to test in future work.

Figure 6. \(-\Delta H\) of oxidation as a function of O/Ce ratio for (■)—20Ce₀.₅Zr₀.₅O₂–Al₂O₃ and

(□)—20CeO₂–Al₂O₃. Results for (▲)—bulk CeO₂, (○)—bulk Ce₀.₅Zr₀.₅O₂, and (×)—infiltrated CeO₂ on alumina-based support are obtained from previous work for comparison [19].

3. Discussion

The results in this paper demonstrate that novel ceria and ceria–zirconia supports can be prepared by ALD onto stable supports. In particular, the thin films grown on γ-Al₂O₃ are shown to be stable to high temperature sintering and relatively immune to redox cycling. The ALD-grown materials are structurally very different from materials having the same compositions but prepared by conventional impregnation. Not only do the ALD films form a more uniform coverage over the

alumina-based support are obtained from previous work for comparison [19].
Obviously, there is still much to learn about the properties of thin ceria and ceria–zirconia films prepared by ALD. The materials clearly show interesting properties as catalyst supports. Studying their redox properties may help to elucidate how surfaces and interfaces with other oxides affect thermodynamic equilibria.

4. Experimental Methods

4.1. Sample Preparation and Characterization

Samples were prepared by both ALD and conventional impregnation methods, using γ-Al2O3 (Strem Chemicals, Inc., Newburyport, MA, USA) as a support that had been calcined at 1173 K and had a BET surface area of 130 m²/g. The ALD-prepared samples were synthesized in a home-built apparatus using very similar methods to that described in previous work [32]. Briefly, the ALD cycle consisted of exposing the evacuated γ-Al2O3 substrate to a few Torr of the organometallic precursors, either Ce(TMHD)₄ (Strem Chemicals, Inc.) or Zr(TMHD)₄ (Strem Chemicals, Inc.), at 503 K for ~300 s, followed by evacuation to ~50 millitorr and precursor oxidation. It should be noted that the substrate was exposed to each gaseous precursor for multiple times to ensure surface saturation. One change in the present study from that in previous work was that precursor oxidation was performed at 503 K for 300 s using an O2 plasma generated by adding ~100 Torr of O2 to the substrate chamber, followed by contacting a tesla coil to a Cu wire that was wrapped around the substrate chamber. Oxidation using a plasma has previously been shown to be very effective at removing difficult-to-oxidize species at low temperatures [33]. To ensure that the ligands were completely oxidized, we removed each sample from the system after every 5 cycles and then heated it to 673 K in a muffle furnace for 5 min.

Growth rates for both CeO2 (0.016 nm/cycle) and ZrO2 (0.024 nm/cycle) were determined by measuring the sample mass after every five cycles and were identical to that which was reported in earlier publications from our laboratory [22,23]. The present study focused on just two ALD-prepared samples: a CeO2/γ-Al2O3 made with 20 ALD cycles of ceria (20 wt % CeO2, CeO2(ALD)/γ-Al2O3) and a Ce0.5Zr0.5O2/γ-Al2O3 made with 12 ALD cycles of ceria and 8 ALD cycles of zirconia (21 wt % Ce0.5Zr0.5O2, CZ(ALD)/γ-Al2O3). In both samples, the films were estimated to be 0.4-nm thick, based on the sample weight changes, assuming a uniform film over the entire alumina surface.

Conventional alumina-supported catalysts containing 20 wt % CeO2 (CeO2(IMP)/γ-Al2O3) or 21 wt % of a CeO2–ZrO2 mixture (CZ(IMP)/γ-Al2O3) were prepared by infiltration with aqueous solutions of cerium (III) nitrate hexahydrate (Ce(NO3)₃·6H2O, Sigma Aldrich, St. Louis, MO, USA) or a mixture of zirconium oxynitrate hydrate (ZrO(NO3)₂·xH2O, Sigma Aldrich, degree of hydration of fresh bottle ~6) and Ce(NO3)₃·6H2O. The samples were then dried at 333 K overnight, followed by calcination to 673 K for 6 h to remove the remaining nitrates. Bulk CeO2 was prepared by precipitating an aqueous solution of Ce(NO3)₃·6H2O with excess ammonium hydroxide (NH₄OH, Fisher Scientific, Hampton, NH, USA), then drying the sample overnight at 333 K followed by calcination at 773 K for 6 h [22]. Bulk Ce0.5Zr0.5O2 was prepared by first dissolving stoichiometric amounts of Ce(NO3)₃ and ZrO(NO3)₂ in distilled water. The aqueous mixture was titrated at a rate of 5 mL/min into a solution of ammonium hydroxide, while stirring. The precipitate was allowed to dry overnight at 333 K, followed by calcination to 773 K for 6 h [23].

Samples containing 1 wt % Pd were prepared by incipient wetness using aqueous solutions of tetraminepalladium(II) nitrate (Sigma Aldrich). The materials were dried overnight at 333 K and calcined at 773 K in air for 6 h to remove any organics and nitrates. It is noteworthy that the ceria-containing samples prepared by ALD were relatively hydrophobic, a fact that has been reported previously for flat surfaces modified by CeO2 ALD [34]. However, the aqueous solutions did slowly absorb into the powders and the preparation procedure for adding Pd was the same except for the time required to impregnate.

X-ray Diffraction (XRD) patterns were recorded on a Rigaku Smartlab diffractometer (Toyko, Japan) equipped with a Cu Ka source (λ = 0.15416 nm). Crystalline graphite, physically mixed with the
samples in a ratio of 1:8, was used as a reference for the peak positions in XRD. The Pd dispersions were determined by CO chemisorption at room temperature on the reduced catalysts. In this procedure, the samples were first oxidized in 200 Torr O₂ at 673 K and reduced in 200 Torr H₂ at 673 K before measuring CO uptakes. Dispersions were calculated assuming one CO per surface Pd.

Steady-state rates for CO oxidation were measured under differential conditions in a quartz-tube, flow reactor using 25 Torr CO and 12.5 Torr O₂. The total flow rate of He was maintained at 60 mL/min and the mass of catalyst was 0.10 g. Products were analyzed using a gas chromatograph (SRI8610C) (Torrance, CA, USA) equipped with a Hayeseq Q column and a TCD detector. All rates in this study were normalized to the mass of the catalyst. Differential conversions were maintained in all cases.

4.2. Redox Equilibrium Measurements

Equilibrium oxidation isotherms were obtained by both flow titration and coulometric titration. In flow titration, the oxidation state of the catalyst is measured by determining the amount of oxygen required to completely re-oxidize the sample after it has been equilibrated at a given P₀₂. While the equilibrium stoichiometry for a specified H₂–H₂O ratio was the same whether starting from an oxidized or a reduced sample, we found that equilibrium was achieved more rapidly starting from the reduced form. Therefore, the experiments were performed in the following manner: 0.5 g of sample were placed in a quartz-tube flow reactor, exposed to dry flowing H₂ (30 mL/min) at the temperature of interest for 0.5 h, and then exposed to a flowing H₂–H₂O mixture (30 mL/min) for 1 h. The H₂–H₂O mixture was produced by passing H₂ through a temperature-controlled water bubbler, using the equilibrium vapor pressure to calculate the H₂O partial pressure. After purging the sample with dry He for 0.5 h, flowing air (21% O₂ and 79% N₂, Airgas) was passed over the sample at a rate of 3.1 mL/min and the composition of the effluent gas was determined using a quadrupole mass spectrometer. The amount of oxygen required to re-oxidize the sample was obtained by integrating the difference between the N₂ and O₂ signals. This in turn provides the oxidation state of the ceria that had been in equilibrium with the H₂–H₂O mixture.

Because the H₂–H₂O ratio can only be controlled over a limited range in flow titration, coulometric titration was also used to verify the flow-titration data and to extend the range of P₀₂ equilibrium measurements [19]. In coulometric titration, a 0.5 g sample was inserted into a YSZ (yttria-stabilized zirconia) tube that had Ag electrodes painted on both inside and outside. The YSZ tube was then placed in a horizontal tube furnace and then heated to the temperature of interest, either 873 K or 1073 K, using a heating rate of 1.0 K/min. During the temperature ramp, a mixture of 5% O₂, 10% H₂O, and 85% Ar was allowed to flow over the sample at a flow rate of 110 mL/min in order to ensure that the sample was completely oxidized at the start of the measurements. After 1 h at the temperature of interest, the flow was stopped and the ends of the YSZ tube were sealed with Cajon fittings. Specified amounts of oxygen were then electrochemically pumped from the inside of the YSZ tube by applying a current across the electrodes using a Gamry instruments potentiostat. After allowing the system to come to equilibrium with the electrodes at open circuit, the equilibrium P₀₂ was calculated from the Nernst equation and the open circuit potential. To demonstrate equilibrium, oxidation isotherms were also measured starting with the reduced sample.

5. Conclusions

Atomic Layer Deposition (ALD) of CeO₂ and Ce₀.₅Zr₀.₅O₂ films on γ-Al₂O₃ produces materials in which the alumina surface is coated with either ceria or a ceria–zirconia mixed oxide. The films exhibit good thermal stability upon oxidation and are also reasonably stable to redox cycling. Although the thermodynamic, redox properties of the CeO₂ films prepared by ALD were similar to those of a sample prepared by impregnation, the ALD samples showed better catalytic properties as supports for Pd due to improved contact between the ceria and the Pd. Thermodynamic measurements on the mixed-oxide film indicated that solid solutions were formed and these were much more easily reduced than normal ceria.
Acknowledgments: Tzia Ming Onn and Raymond J. Gorte are grateful to the Department of Energy, Office of Basic Energy Sciences, Chemical Sciences, Geosciences and Biosciences Division, Grant No. DE-FG02-13ER16380 for support of this work.

Author Contributions: Tzia Ming Onn and Raymond J. Gorte conceived and designed the experiments; Xinyu Mao, Chao Lin, and Cong Wang performed the experiments; Tzia Ming Onn and Raymond J. Gorte analyzed the data; Tzia Ming Onn and Raymond J. Gorte wrote the paper.

Conflicts of Interest: The authors declare no conflict of interest.

References


© 2017 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/).