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Characterization of ceria films on α-$Al_2O_3(0001)$ and polycrystalline zirconia using O_2 TPD with labeled $^{18}O_2$

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The nature of weakly bound oxygen on ceria films was studied using temperature-programmed desorption with labeled $^{18}O_2$. For α-$Al_2O_3(0001)$-supported ceria, a desorption feature between 800 and 1300 K is shown to result from partial reduction of ceria. However, this oxygen accounts for only a small fraction of the total oxygen in the ceria film and isotopic labeling studies suggest that this oxygen does not exchange freely with the remaining oxygen in the film. In contrast, results for zirconia-supported ceria demonstrate that much more oxygen desorbs in the low temperature regime below 1300 K, and that there is significant isotope exchange throughout the ceria film and with the zirconia substrate. Finally, exposure of reduced, zirconia-supported ceria to water at 670 K resulted in reoxidation of the ceria film. Oxygen from ceria was then shown to react with CO adsorbed on supported Rh particles, completing the catalytic cycle for the water–gas-shift reaction.

Keywords: ceria, ceria–zirconia, oxygen storage, CO oxidation, water–gas shift, temperature-programmed desorption of O_2, $^{18}O_2$ exchange

1. Introduction

Ceria plays a number of roles in automotive emissions-control catalysis, including providing activity for the water–gas-shift reaction [1–8], maintaining the dispersion of the catalytic metals [9], and stabilizing the surface area of the support [4]. However, the most important function of ceria in these catalysts is to provide oxygen-storage capacity [5,10–12]. This function is related to the fact that cerium has multiple, stable oxidation states that allow it to undergo oxidation and reduction reactions. There is ample evidence suggesting that contact between the ceria and other oxide additives such as zirconia further enhances both the oxygen-storage capacity of the catalyst as well as the thermal stability of the support [13–19]. Despite these findings, many questions remain concerning the nature of the oxygen-transport properties within ceria and the manner in which contact with zirconia enhances these properties.

To address the issue of how labile oxygen is held in these materials, studies of oxygen desorption from model catalysts have been performed [20]. Our previous model-catalyst studies have shown that there exists a weakly bound oxygen species on thin ceria films supported on α-$Al_2O_3(0001)$ which is not present on $CeO_2(111)$ single-crystal surfaces [20]. This low-temperature O_2 desorption state has also been shown to correlate with the CO oxidation activity of precious metals supported on ceria under fuel-rich operating conditions. For example, during temperature-programmed desorption of CO-dosed Rh/ceria model catalysts, a significant fraction of the CO is oxidized to CO_2 only if the catalyst has been pretreated at low temperature. In contrast, if the catalyst has been heated sufficiently to desorb the weakly bound oxygen prior to CO adsorption, CO_2 is not observed during TPD [20]. These results demonstrate that the weakly bound oxygen can react with CO adsorbed on supported metals to produce CO_2.

The focus of the work described here was to further characterize the nature of the low-temperature O_2 desorption state observed in TPD. We show that this state corresponds to removal of a subset of oxygen in the ceria film, rather than desorption of molecularly adsorbed O_2. The fraction of oxygen in the ceria film that desorbs at low temperature was found to be enhanced by the presence of zirconia. Isotopic labeling studies demonstrated that oxygen transport also occurs between ceria and zirconia when the two oxides are in intimate contact. Finally, it was shown that water can be used to reoxidize reduced ceria. This observation may be important for understanding the water–gas-shift activity of ceria-supported metals.

2. Experimental

The experimental setup used in this study was identical to that described previously [21]. An ion-pumped vacuum chamber, which had a base pressure of 3×10^{-10} Torr, was used for the TPD experiments. This chamber was equipped with a cylindrical mirror analyzer for Auger electron spectroscopy and a quadrupole mass spectrometer. To improve sensitivity for the detection of desorbing species during TPD experiments, the quadrupole mass analyzer was placed in a stainless-steel cone with a small aperture, in front of which the sample could be placed. Samples were exposed to the adsorbates through beam dosers to maintain a low base pressure. The pressure in front of the dosers was estimated to be approximately 20 times higher than the chamber pressure. All exposures quoted in this manuscript were determined using this factor. TPD measurements were carried out with a linear heating rate of 12 K/s.

The oxide substrates consisted of 3 mm diameter disks of α-$Al_2O_3(0001)$ and an α-$Al_2O_3(0001)$-supported zirconia thin film. The sapphire crystal was obtained from Crystal Systems Inc. The α-$Al_2O_3(0001)$-supported, zirconia substrate was prepared by spray pyrolysis of a 1 M, aqueous solution of $ZrO(NO_3)_2$ (Johnson Matthey) onto an α-$Al_2O_3(0001)$ crystal. The solution was sprayed at a flow rate of 0.5 ml/min for 20 min, using N_2 as the carrier gas, while holding the crystal at 650 K. After the zirconia was deposited, the sample was placed in an oven and held at 1000 K for 2 h in air. This procedure produced a polycrystalline zirconia film $\sim$ 10 μm thick, which XRD showed had a tetragonal structure. The oxide crystals were mounted on a Ta foil, enabling them to be resistively heated up to 1400 K. A thermocouple was attached to the back side of each sample and used to monitor the temperature.

After cleaning the substrates by Ar^+ ion bombardment (1.5 kV, 5 μA sample current) at room temperature, they were annealed in 5×10^{-8} Torr of $^{16}O_2$ at 1270 K for 10 min, then oxidized in 5×10^{-8} Torr of $^{16}O_2$ at 770 K for 30 min. Finally, ceria or Rh films were vapor deposited onto these substrates. Ceria films were prepared by evaporating Ce metal (Johnson Matthey, 99.9%) onto the substrate in the presence of 10^{-7} Torr of either $^{16}O_2$ or $^{18}O_2$ (Matheson, 98.5 at% ^{18}O). During ceria deposition, the substrate temperature was held at 570 K. Following ceria deposition, the samples were oxidized in 10^{-7} Torr of either $^{16}O_2$ or $^{18}O_2$ for 15 min at 670 K to ensure complete oxidation of the Ce metal. The coverage of the CeO_2 films, as determined by a quartz-crystal, film-thickness monitor, was maintained at 1×10^{16} CeO_2/cm^2, corresponding to an average film thickness of $\sim$ 4.0 nm.

In order to study the reactivity of the ceria thin films, 1×10^{15} Rh/cm^2 was deposited onto some of the ceria films by vapor deposition. After deposition, the sample was heated to 800 K to form Rh particles. Based on dispersion measurements, the average Rh particles size was estimated to be $\sim$ 3.0 nm.

3. Results and discussion

3.1. $^{16}O/^{18}O$ exchange in CeO_2/α-$Al_2O_3(0001)$

Previously, TPD data for O_2 from polycrystalline, ceria films on α-$Al_2O_3(0001)$ were shown to exhibit two features [20]: a broad peak centered at 1000 K due to the desorption of weakly bound oxygen and a high-temperature signal due to the onset of bulk reduction of the ceria lattice at 1300 K. The bulk reduction occurs at the same temperature observed for O_2 desorption from $CeO_2(111)$ [20]. It is important to notice, however, that the low-temperature state is not observed in TPD data from the single-crystal surface. In the case of the ceria thin film, the low-temperature desorption state can be repopulated by oxidizing in O_2 at temperatures above 400 K.

Isotopically labeled $^{18}O_2$ was used to distinguish whether the low-temperature O_2 desorption resulted from adsorbed, molecular oxygen or lattice oxygen. A CeO_2 film supported on α-$Al_2O_3(0001)$ was initially produced by vapor deposition of Ce metal onto the substrate in the presence of 10^{-7} Torr of $^{18}O_2$, as described in section 2. TPD data obtained from the freshly prepared film indicated that it was only partially labeled with ^{18}O. The low-temperature O_2 desorption feature for this film contained $^{16}O_2$, $^{16}O^{18}O$ and $^{18}O_2$, with the mixed isotope being the primary product. ^{16}O impurities are likely introduced by Ce metal source or from background water in the vacuum system. In order to increase the isotopically labeled oxygen content, the film was exposed repeatedly to $\sim$100 L (1 L (langmuir) $= 10^{-6}$ Torr s $= 3.7 \times 10^{14}$ molecules/cm^2) $^{18}O_2$ at 670 K, followed by flashing to 1300 K. The TPD data obtained following five of these O_2 adsorption–desorption cycles are shown in figure 1a. Notice that roughly equal amounts of $^{18}O_2$ and $^{16}O^{18}O$ (the ratio of peak areas of $^{18}O_2$ to $^{16}O^{18}O$ is 0.7) are observed, with essentially no $^{16}O_2$.

After preparing the ^{18}O-labeled film, TPD experiments were performed in which the film was reoxidized with $^{16}O_2$ following each heating cycle. The isotopic composition of desorbed O_2 measured in the first run after switching to $^{16}O_2$ was similar to that shown in figure 1a. The fact that most of the oxygen desorbed as $^{18}O_2$ and $^{18}O^{16}O$ following adsorption of $^{16}O_2$ demonstrates that the adsorbed oxygen is not molecular but, rather, results from recombination of lattice oxygen. Repeated adsorption–desorption cycles with $^{16}O_2$ resulted in a transition in the isotopic makeup of the low-temperature O_2. Figure 1b displays desorption data obtained after seven oxidation–reduction cycles. Here, the ratio of $^{16}O_2$ to $^{16}O^{18}O$ is 2.4, while virtually no $^{18}O_2$ is observed.

In a previous study, the amount of O_2 contained in the low-temperature TPD feature was estimated to be less than 5% of the total oxygen content of the film based on a comparison of peak areas with TPD data from a Rh film [20]. (Complete reduction of CeO_2 to Ce_2O_3 would remove 25% of the oxygen; our estimate that less than 5% is actually removed is consistent with the results for the ceria–zirconia film, to be described in the next section.) The fact that only a small fraction of the oxygen in the ceria film desorbs, in conjunction with the fact that relatively few oxidation–reduction cycles were necessary to significantly change the isotopic composition of the

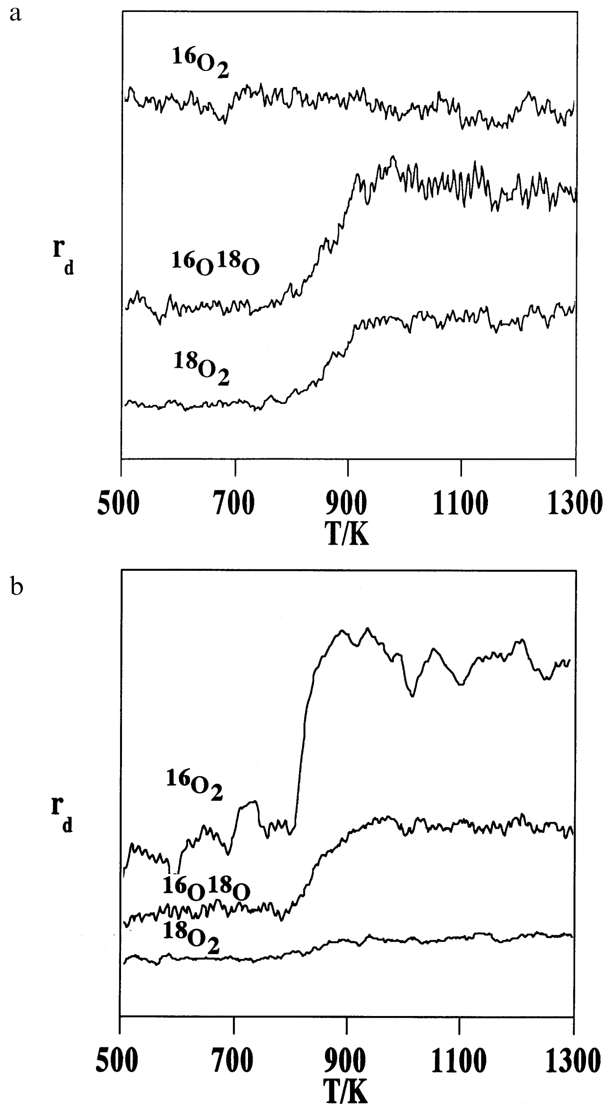

Figure 1. O_2 TPD data for a ceria film with 10^{16} CeO_2/cm^2, supported on α-$Al_2O_3(0001)$, prepared by vapor deposition of Ce metal in 10^{-7} Torr oxygen, as described in the text. (a) The film was prepared in $^{18}O_2$, followed by five adsorption–desorption cycles in $^{18}O_2$. (b) The TPD data was measured after seven additional adsorption–desorption cycles were performed with $^{16}O_2$.

TPD features, suggests that rapid exchange of the desorbing oxygen with oxygen in the bulk of the ceria film does not occur. This is somewhat surprising given that ceria is a reasonably good oxygen ion conductor in the temperature range at which oxygen desorption occurs [22]. It does, however, suggest that there are separate oxygen reservoirs which do not exchange with each other. Two possible explanations are as follows: (1) Only surface oxygen desorbs and this oxygen cannot exchange with the oxygen in the bulk film. (2) The "film" is actually made up of active and inactive crystallites, and the inactive crystallites are only spectators in the adsorption–desorption measurements. Other possibilities could be offered, and a complete understanding of this phenomenon may help explain the reasons for loss of oxygen-storage capacity in ceria.

3.2. $CeO_2/ZrO_2/\alpha$-$Al_2O_3(0001)$

TPD experiments were also performed for ceria films supported on zirconia to determine whether the beneficial effects of zirconia could be observed using our methods. The support consisted of a 10 μm, polycrystalline film of zirconia, with tetragonal structure, supported on an α-$Al_2O_3(0001)$ crystal. In a set of control experiments, oxygen desorption was not observed during TPD for the pure zirconia, up to 1400 K, in agreement with the expectation that zirconia is not reducible.

A ceria film, labeled with ^{18}O, was deposited onto the zirconia support using a procedure identical to that for the ceria film on α-$Al_2O_3(0001)$. The TPD data for this film are shown in figure 2a. As with the alumina-supported ceria, the onset of oxygen desorption begins at 800 K. However, there are two important differences between the alumina- and zirconia-supported ceria. First, approximately five times more O_2 desorbs below 1300 K from the zirconia-supported film compared to the alumina-supported film, even though the ceria coverage was the same. (The scale in figure 1 is four times more sensitive than that in figure 2.) Using the estimate for the alumina-supported ceria that approximately 5% of the oxygen desorbed at lower temperatures, 25% of the oxygen in the ceria/zirconia film desorbs at lower temperatures. Removal of 25% of the oxygen corresponds to a complete reduction from CeO_2 to Ce_2O_3. The increased extent of ceria reduction is consistent with reports of enhanced reducibility for mixed oxides of ceria and zirconia [13–19]. In mixed oxides, the increased reducibility is usually associated with the formation of solid solutions, which could also occur at the surface of our samples during ceria deposition. (Attempts to use Auger electron spectroscopy to look for mixing of the oxide phases suggested that this did not occur on a macroscopic scale based on the complete disappearance of the zirconia Auger peaks following deposition of ceria.) Alternatively, the zirconia support may simply decrease ceria crystallite size, alter ceria crystallite morphology, or increase ceria surface area.

A second important difference in the TPD results for ceria/alumina and ceria/zirconia is that $^{16}O_2$ is the primary desorption product for the zirconia-supported film, even after repeated adsorption–desorption cycles with $^{18}O_2$. For the alumina support, deposition of Ce in $^{18}O_2$, followed by five cycles of exposure to $^{18}O_2$ and flashing to 1300 K, gave a surface for which 65% of the oxygen which desorbed at low temperatures was ^{18}O. In contrast, for the zirconia-supported film, the same procedure yielded only 22% ^{18}O, in spite of the fact that five times as much oxygen could be exchanged during each adsorption–desorption cycle. The continued predominance of the $^{16}O_2$ signal after repeated oxidation cycles

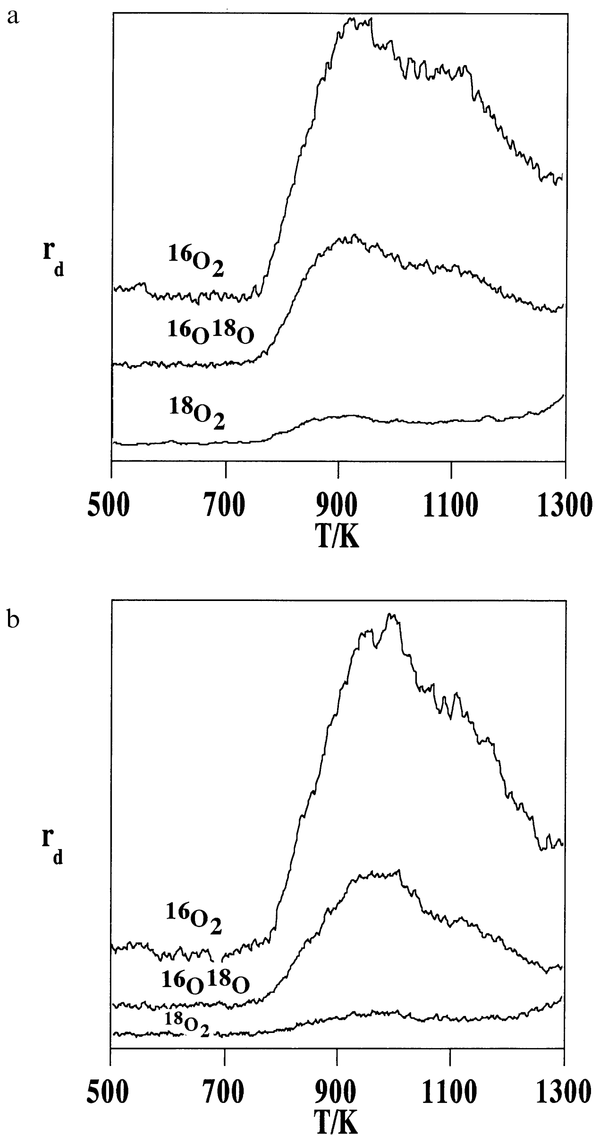

Figure 2. O_2 TPD data for a ceria film, 10^{16} CeO_2/cm^2, supported on polycrystalline zirconia. The preparations for (a) and (b) are exactly the same as in figure 1.

in $^{18}O_2$ indicates that ^{16}O from the zirconia substrate undergoes substantial exchange with ^{18}O in the CeO_2 film. Complete removal of residual ^{18}O was also slow. Following the TPD experiment depicted in figure 2a, seven adsorption–desorption cycles with $^{16}O_2$ were performed; the results, shown in figure 2b, were very similar to those shown in figure 2a. This again implies that there is a large reservoir of oxygen involved in the exchange process. Since zirconia can be an oxygen-ion conductor in the temperature regime used in the TPD experiments [22], it is likely that oxygen exchange occurs between the ceria film and the zirconia support and that oxygen from the zirconia substrate communicates with the oxygen reservoir observed in the desorption experiments.

The involvement of weakly held oxygen in ceria/zirconia for reaction with reductants on supported metals was also examined. Following deposition of 1×10^{15} Rh/cm^2 onto the ceria/zirconia and subsequent exposure to 10 L of CO, it was found that a significant fraction of the adsorbed CO reacted with the lattice oxygen to form CO_2 during TPD. Therefore, as in the ceria/alumina case [20], the weakly held oxygen can be associated with reactions on supported-metal catalysts.

3.3. Oxidation of ceria by water

Ceria is known to play a role in the water–gas-shift reaction in automotive catalysis [1–8]. A possible mechanism for the role of ceria involves oxidation of reduced ceria by water, followed by the ceria-mediated oxidation of CO adsorbed on the supported, precious metals [8]. To investigate this possibility, the following

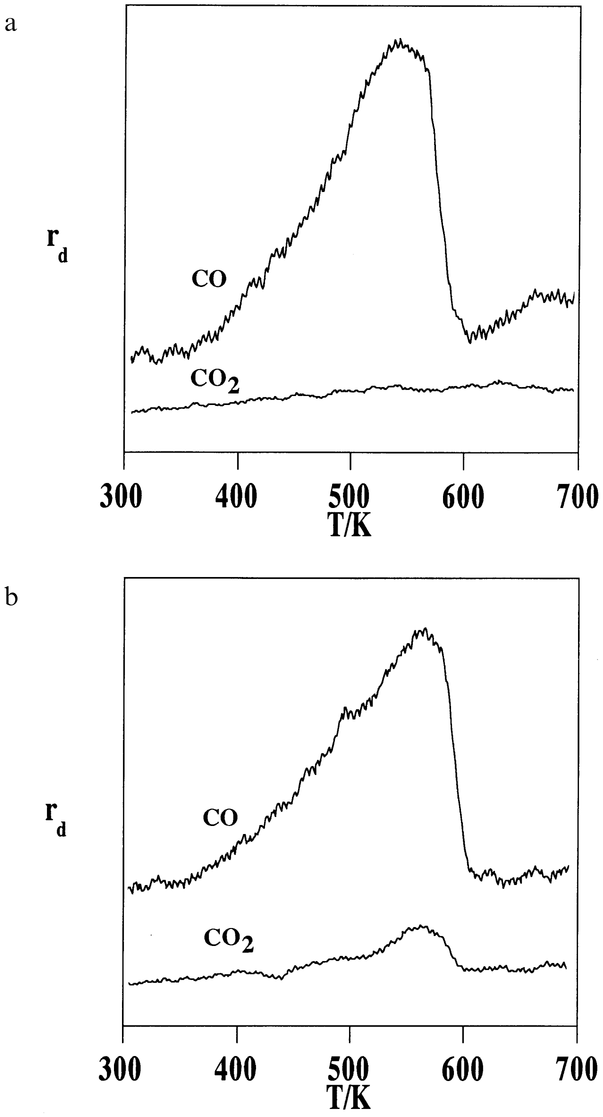

Figure 3. TPD data following a saturation exposure of CO to Rh particles at 300 K on the ceria/zirconia film. (a) The sample was first reduced by heating in CO. (b) The sample in (a) was reoxidized by heating in 10^{-7} Torr of water.

set of experiments were performed. A sample consisting of Rh on the ceria/zirconia support was initially reduced by annealing at 673 K in 5×10^{-8} Torr of CO for 10 min. This was followed by a CO TPD experiment, the results of which are shown in figure 3a. Only CO desorbed from the surface, confirming that the ceria film was significantly reduced by annealing in CO.

Exposure of the reduced catalyst to water at 300 K had little effect. Following exposure to 10^{-7} Torr of water for 15 min at 300 K, the TPD results were essentially identical to that depicted in figure 3a. Exposure of the reduced catalyst to water at elevated temperatures gave a very different result. Figure 3b shows the results for a CO TPD experiment after the reduced sample was exposed to 10^{-7} Torr of water for 15 min at 670 K. In this case, 10% of the adsorbed CO was oxidized to CO_2, demonstrating that water can be used to reoxidize the ceria film at catalytically relevant temperatures.

4. Summary

The O_2 TPD results for ceria films on α-Al_2O_3(0001) and polycrystalline zirconia demonstrate that the support can strongly influence the amount of weakly bound oxygen. Studies with isotopically labeled oxygen suggest that only a fraction of the oxygen in the alumina-supported ceria is active, while labile exchange of oxygen occurs in the zirconia-supported ceria. Finally, the promotional effect of ceria for the water–gas-shift reaction was demonstrated in the observation that reduced ceria could be oxidized by water at slightly elevated temperatures.

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