A calorimetric study of oxygen-storage in Pd/ceria and Pd/ceria–zirconia catalysts

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Heats of adsorption were measured calorimetrically for O_2 adsorption on reduced Pd/alumina, Pd/ceria, and Pd/ceria–zirconia catalysts, all with 1 wt% Pd. Significantly more O_2 adsorbed on the ceria-containing catalysts due to oxidation of the support. For Pd/alumina, the heats were found to be between 180 and 220 kJ/mol, only slightly higher in magnitude than the heat of reaction for bulk oxidation of Pd. However, the heats of adsorption for both ceria and ceria–zirconia were also $\sim$200 kJ/mol, much lower than the heat of reaction for Ce_2O_3 oxidation to CeO_2, but in reasonable agreement with estimates from O_2 desorption studies on model ceria films. The implications of these results for understanding oxygen-storage properties on ceria-based catalysts are discussed.

KEY WORDS: oxygen storage; three-way catalysts; O_2 adsorption; calorimetry; Pd; ceria; ceria–zirconia

1. Introduction

Ceria is an important component in automotive, emissions-control catalysis, primarily because of its ability to store and release oxygen [1–8]. Oxygen storage is crucial for controlling the ratio of oxidants and reductants in the exhaust, so that CO and hydrocarbons can be oxidized simultaneously with the reduction of NO. However, the redox properties of pure ceria are known to degrade with time in the automotive exhaust environment. To stabilize the oxygen-storage properties, ceria is usually included as a mixed oxide with zirconia [9–18]. The details of how ceria performs its role as an oxygen-storage component and the mechanism by which zirconia stabilizes the redox properties of ceria are not well understood.

There is strong evidence that the redox properties of ceria are structure sensitive and that the active form of oxygen is weakly bound relative to normal lattice oxygen [19–24]. In studies of model, ceria-supported metals designed to ensure that the interfacial contact between the metal and the oxide was constant, it was demonstrated that heating the ceria film above 1270 K in air caused severe deactivation for CO oxidation [22], the water–gas-shift reaction [23], and the steam-reforming reaction [24]. Temperature-programmed desorption (TPD) studies of CO from Pd particles on ceria showed significant amounts of CO_2 formation on the active catalysts, with no CO_2 formation on deactivated materials [19]. Finally, an investigation of O_2 desorption from ceria films on α-$Al_2O_3(0001)$ provided evidence for a low-temperature state centered at $\sim$1000 K which did not exist on a $CeO_2(111)$ single crystal [20]. A similar, low-temperature feature was found for ceria films on a polycrystalline zirconia surface, with the additional observation that enough O_2 desorbed from the ceria on zirconia by 1300 K to account for complete reduction to Ce^{3+} [21]. In contrast, the extent of reduction for the ceria film on α-$Al_2O_3(0001)$ was only 20% by this temperature.

In the present study, we set out to investigate the redox properties of ceria and ceria–zirconia powders calorimetrically. In agreement with the earlier TPD studies, we demonstrate that the heat of adsorption for oxygen on the reduced, ceria-supported catalysts is much lower than the tabulated heat of reaction for Ce_2O_3 going to CeO_2.

2. Experimental

The apparatus and procedures used in the calorimetric measurements have been described elsewhere [25–27]. Briefly, the instrument is home-built using thermopiles from International Thermal Instruments, Del Mar, CA. Between 2 and 2.5 g of the oxidized catalyst were loaded into the cubically shaped, sample cells; the catalyst was then reduced *in situ* at 750 K by repeatedly increasing the pressure to 10 Torr of H_2, followed by evacuation. After placing the sample cell into the calorimeter, the instrument was heated to $\sim$510 K. The heat that evolved upon dosing the samples with O_2 pulses was measured up to the point at which gas-phase oxygen remained above the sample.

All three samples used in this study had a Pd loading of 1 wt% and have been described in earlier pulse studies [28,29]. The supports were γ-Al_2O_3, CeO_2, and a $50:50$ CeO_2–ZrO_2 mixed oxide. The γ-Al_2O_3 was obtained from Alfa Aesar; and the ceria and ceria–zirconia supports were prepared from aqueous solutions of $Ce(NO_3)_3$, with or without $Zr(NO_3)_2 \cdot xH_2O$, by drying and calcining in air to 673 K. The surface areas of the ceria and the ceria–zirconia were determined to be $\sim$30 m^2/g. In earlier studies with alternating CO and O_2 pulses [28,29], the concentrations of oxygen atoms that could be added and removed, reversibly, at 670 K are listed in table 1.

Table 1
Comparison of oxygen adsorption capacities from calorimetry and pulse-reaction studies.

Catalyst	Pulse-reactor studies (μmol O atoms/g)	Calorimetric coverages (μmol O atoms/g)
Pd/γ-Al_2O_3	50	40
Pd/CeO_2	500	300
Pt/CeO_2–ZrO_2	500	420

3. Results and discussion

The heats of adsorption for all three samples are plotted as a function of the amount of O_2 adsorbed in figure 1. It is immediately apparent that the amount of oxygen that could adsorb was much lower on the Pd/alumina sample, with saturation occurring at a coverage of 20 μmol O_2/g (40 μmol O/g) compared to values of 150 μmol O_2/g on Pd/ceria and 210 μmol O_2/g on Pd/ceria–zirconia. For comparison, complete oxidation of the Pd to PdO would require 48 μmol of O_2/g, and bulk oxidation of Ce_2O_3 to CeO_2 in pure ceria would require 1450 μmol O_2/g. It is also certainly not surprising that the ceria-containing catalysts should take up more oxygen, given that ceria is added to automotive catalysts for providing oxygen-storage capacity. As shown in table 1, the oxygen uptakes in the calorimetric study follow the same trends observed in the pulse-reactor study, although the calorimetric values are somewhat lower in all cases. The differences in the values may be due to the fact that catalysts are reduced in flowing CO in the pulse measurements, rather than by just backfilling the samples with H_2, or to the fact that reoxidation is performed at ~670 K in the pulse studies, while adsorption occurred at ~510 K in the calorimetric measurements. In either case, it seems clear that the calorimetric and the pulse-reactor measurements are probing similar adsorption states.

Before discussing the absolute values for the heats of adsorption, it is important to remember that these are nonequilibrium measurements [26,27]. For pulse adsorption into a bed of catalyst, it is likely that adsorption is rapid compared to diffusion of gas into the catalyst bed and then into the catalyst particles themselves. Since adsorption of O_2 is irreversible at 510 K and coverages below saturation, it may not be possible for the oxygen atoms, once adsorbed, to migrate to higher energy sites. If the sticking coefficient is high, adsorption of the first pulse will saturate the top of the catalyst bed, with subsequent pulses saturating the next layers. The practical implication of this is that one probably cannot measure differential heats as a function of coverage. Rather, the measured "differential" heats should be considered to be "integral" heats of adsorption averaged over some part of the catalyst bed. For this reason, the apparent differential heats averaged over all pulses is probably the most meaningful value to take away from the measurements, rather than attempting to interpret the results in terms of a distribution of energies.

The values for the heats of adsorption on Pd/alumina start at ~220 kJ/mol and fall to 180 kJ/mol at the saturation coverage of 20 μmol/g. Values in this range agree well with bulk thermodynamics and observations from O_2 TPD studies on various types of model Pd catalysts [30–36]. First, the heat of formation of PdO at standard conditions is −172 kJ/mol, based on one mole of O_2. Clearly, the saturation coverage is well below the quantity of O_2 required for complete oxidation of Pd, 48 μmol/g. From TPD studies, it appears reasonable that surface oxygen is more strongly bound than bulk oxygen. On Pd(111), O_2 desorbs in a single peak between 800 and 900 K [31,32], while an additional desorption feature at ~700 K, associated with higher oxygen coverages and possibly a bulk-like oxide, is observed on Pd(100) and Pd(110) [33–36]. Finally, a TPD study of O_2 from small Pd particles deposited on α-Al_2O_3(0001) demonstrated that oxygen adsorption depends on particle size, with smaller particles adsorbing oxygen more strongly [30]. The re-

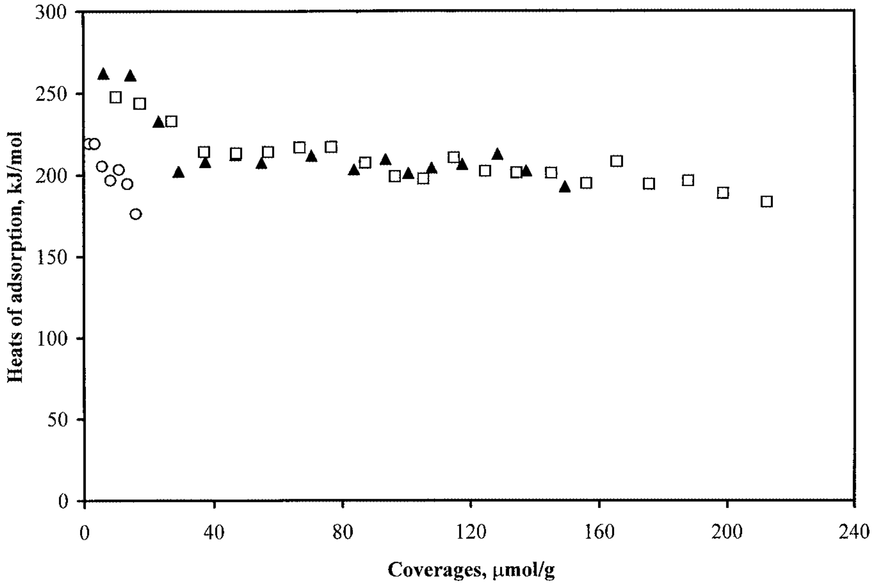

Figure 1. Calorimetric results for O_2 adsorption at 510 K for 1 wt% Pd on alumina (○), ceria (▲), and (□) ceria–zirconia.

sults of that study showed a peak desorption temperature of $\sim$920 K for 1.6 nm particles and $\sim$850 K for 9.1 nm particles at a saturation coverage [30]. All of this suggests that calorimetrically measured heats of adsorption of $\sim$200 kJ/mol are reasonable and consistent with what is known about O_2 adsorption on Pd from the literature.

The measured heats on the Pd/ceria and Pd/ceria–zirconia catalysts are similar. At very low coverages, the heats are approximately 250 kJ/mol, but the values quickly fall to between 200 and 210 kJ/mol. We believe the low-coverage values may result from residual hydrogen in the catalyst; experiments in which we evacuated H_2 from the sample at 510 K, rather than 750 K as in the reported results, gave rise to significantly higher initial heats. It is also safe to conclude that most of the adsorption on the Pd/ceria and Pd/ceria–zirconia catalysts is associated with oxidation of ceria. Even complete oxidation of Pd to PdO can account for only a fraction of the O_2 adsorbed in these catalysts. Given that the heat of adsorption for O_2 adsorption on Pd/alumina is so close to the values on the ceria-containing catalysts, heats associated with oxidation of Pd cannot significantly affect the conclusions anyway. Therefore, the heat of oxidation for ceria and the ceria–zirconia mixed oxide is $\sim$200–210 kJ/mol.

There are several interesting conclusions that can be reached from these results. First, the binding of the active oxygen in pure ceria and in the mixed oxide is similar. While the mixed oxide is known to have much better oxygen-storage properties than pure ceria, this is due primarily to the stability of the mixed oxide following harsh treatment. High-temperature treatment causes ceria to lose its oxygen-storage properties and its abilities to enhance CO oxidation, the water–gas-shift reaction, and the steam-reforming reaction [22–24]. We have found that a fresh ceria-supported catalyst shows similar properties to catalysts prepared using ceria–zirconia as the support so long as they are not calcined above 1270 K [22].

Using heats of formation at standard conditions, one finds that enthalpy of oxidation for Ce_2O_3 according to reaction (1) below should be 760 kJ/mol [37].

$$2Ce_2O_3 + O_2 \rightleftharpoons 4CeO_2 \qquad (1)$$

Before addressing the implications of and possible reasons for the difference between the bulk thermodynamic data and the measured binding energies, it important to establish that the calorimetric data is reasonable. Figure 2 shows TPD data, taken from the literature, for O_2 desorption from 9.1 nm, Pd particles on α-Al_2O_3(0001) [30], from a 4.0 nm film of ceria on α-Al_2O_3(0001) [20], and from a 4.0 nm film of ceria on polycrystalline zirconia [21]. Based on the fact that the peak temperatures for all three model catalysts are similar, it is indeed reasonable that the heats of adsorption are similar. Furthermore, the calculated activation energy for a peak temperature of 1000 K, assuming a normal value for the pre-exponential of the desorption rate constant, is 260 kJ/mol. Given that adsorption may be activated and the pre-exponential may deviate from the "normal" value, the agreement between the TPD results and the calorimetry results is remarkable.

As noted in previous publications, the active form of ceria has oxygen that is loosely bound compared to oxygen in ceria that has been calcined to high temperatures. No oxygen desorption was observed below 1300 K for a CeO_2(111) single crystal [21]. The CeO_2(111) was also completely inactive for transferring oxygen to a supported metal. Even for the ceria film on α-Al_2O_3(0001) in figure 2, the amount of O_2 that desorbed below 1300 K corresponded to only 20% of that necessary to completely reduce the Ce^{4+} to Ce^{3+} and isotope-exchange measurements showed that remaining oxygen did not exchange with the more weakly held oxygen [22]. In contrast, heating the ceria film supported on zirconia to 1300 K released enough O_2 to account for complete reduction [22]. In of this suggests that there must be at least two types of oxygen in ceria, that high-temperature calcinations eliminate the weakly bound form of oxygen, and that zirconia tends to maintain the weakly bound oxygen.

The evidence indicates that structural differences in ceria are responsible for differences in its reducibility. Certainly, high-temperature calcinations cause changes in the crystallite size [19,22]. Recent measurements on ceria–zirconia mixed oxides suggest that these are not solid solutions [38]. Rather, it appears that zirconia directs the structure of ce-

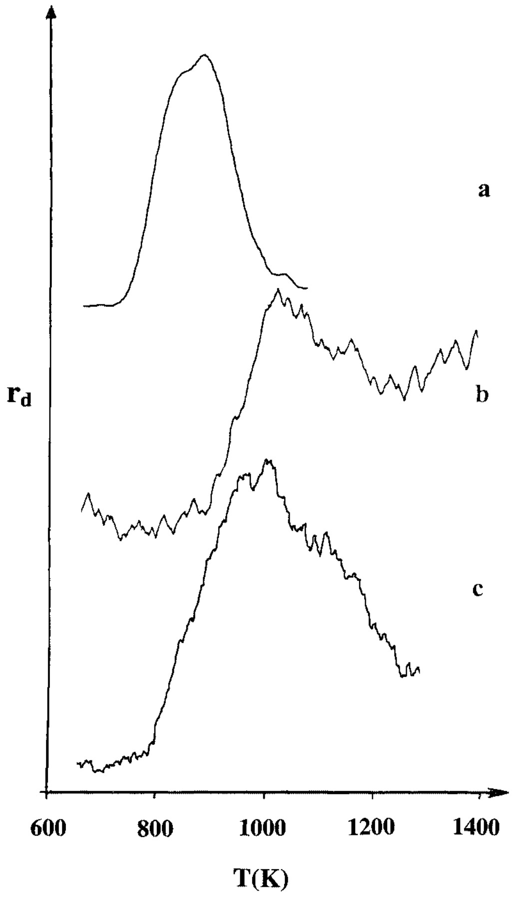

Figure 2. TPD curves for O_2 desorption from the following model catalysts: (a) Pd/α-Al_2O_3(0001) [30], (b) ceria/α-Al_2O_3(0001) [20], and (c) ceria–zirconia [21].

ria that is in contact with it and that this influence on ceria structure maintains the reducibility of ceria [39,40]. Several explanations have been offered to explain the structure sensitivity of ceria. First, it has been suggested that the active form of oxygen is present as defects in the fluorite structure of CeO_2 [41]. For example, since the fluorite structure is relatively open, there is room for oxygen anions to exist outside the simple-cubic, oxygen sublattice. Indeed, evidence for oxygen defects has been found in neutron-scattering measurements [41]. Another possible explanation is based on the fact that complete reduction of the cubic CeO_2 to hexagonal Ce_2O_3 requires a significant structural rearrangement. It is possible that this structural rearrangement is prevented in small crystallites and by the structure-directing properties of zirconia. Partial reduction of cubic CeO_2 occurs before the structural transformation and intermediate phases are known [42–44]. However, a definitive explanation for the oxygen binding energy to be so much lower in active forms of ceria is unknown at this time. It does seem clear that a weakly bound form of oxygen is most important in oxygen storage and this form of oxygen is crucial for understanding many of the catalytic properties of ceria.

Finally, one of the interesting observations from the calorimetric results is that the binding energy for oxygen on ceria is very similar to that for oxygen on typical catalytic metals, like Pd, Pt, and Rh. Many groups have observed that TPD measurements of CO from metals supported on ceria show desorption of CO_2 at very low temperatures, similar indeed to the temperatures at which CO_2 forms when CO and oxygen are coadsorbed on the metals [45]. Since oxygen transfer from the active form of ceria to the precious metal is almost thermally neutral, it is possible that precious metal is indeed oxidized by the underlying ceria. Even if reaction occurs at the periphery between the precious metal and the ceria, the similarity in binding energy helps to explain the ease with which oxygen from ceria reacts with reductants on the metal.

4. Summary

Calorimetric studies demonstrate that the enthalpy change for reoxidation of the active form of ceria is much smaller in magnitude than the standard heat of reaction for oxidation of Ce_2O_3 to CeO_2, but is similar to the heat of adsorption for O_2 on Pd.

Note added in proof

M.Y. Smirnov and G.W. Graham have just demonstrated that Pd films are indeed oxidized by their ceria–zirconia supports after heating in vacuum to above 470 K [46]. The ease with which Pd is oxidized and ceria reduced implies that there cannot be a large enthalpic barrier for oxygen transfer from ceria to Pd, completely consistent with our calorimetric measurements.

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