A mechanistic study of sulfur poisoning of the water–gas-shift reaction over Pd/ceria

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The effect of sulfur on the water–gas-shift (WGS) activity of Pd/ceria catalysts has been studied using steady-state rate measurements, pulse-reactor studies, and FTIR. After exposing Pd/ceria to SO_2 at 673 K in an oxidizing environment, the WGS rates dropped to a value close to that observed on Pd/alumina. Both pulse-reactor and FTIR measurements showed that cerium sulfates can be readily reduced by CO and re-oxidized by O_2 at 723 K; however, unlike reduced ceria, the Ce_2O_2S formed by reduction of the sulfates cannot be re-oxidized by H_2O or CO_2. The implications of these measurements for understanding the oxygen-storage capacity (OSC) of three-way catalysts are discussed.

KEY WORDS: ceria; SO_2; cerium sulfate; water–gas shift; oxygen storage capacity (OSC).

1. Introduction

Ceria plays a crucial role in automotive, three-way, emissions-control catalysis because of its oxygen-storage capacity (OSC) [1]. Ceria takes up oxygen under fuel-rich reducing conditions and releases oxygen during fuel-lean oxidizing conditions. In modern catalysts, ceria is stabilized by mixing it with zirconia, so that the OSC properties can be maintained for long periods of time [2–4]. However, ceria is susceptible to sulfur poisoning. With the current levels of sulfur in gasoline, the typical exhaust has 5–20 ppm of SO_2. At these relatively low concentrations, SO_2 poisons the exhaust catalyst primarily through interactions with ceria and the effect that these interactions have on OSC [5–8].

On first examination, OSC appears to be a simple property that should be easily measured by determining the amount of oxygen that can be reversibly removed from a catalyst. Indeed, it is common practice to measure OSC simply by titration with CO and O_2. However, Hepburn and co-workers reported "that the CO/O_2 titration method was unable to differentiate between catalysts which displayed greatly different transient performances on a vehicle" [9]. In our laboratory, we have found that exposing a Pd/ceria catalyst to SO_2 can actually *increase* the amount of oxygen which can be reversibly removed in both $CO–O_2$ pulse studies and in temperature-programmed reduction measurements with CO [10]. These observations suggest that further investigations are necessary for understanding the role of ceria in automotive catalysts and for understanding the nature of sulfur poisoning of OSC.

The species formed by exposure of ceria to SO_2 have been studied rather thoroughly [11–18]. Below approximately 473 K, SO_2 adsorbs molecularly, possibly as a sulfite [18]. At higher temperatures, this surface species is oxidized to Ce^{3+} and Ce^{4+} sulfates [18], using either molecular O_2 from the gas phase or by reduction of CeO_2. If ceria is exposed to SO_2 in an oxidizing environment at above 473 K, both surface and bulk sulfates are formed. The sulfates are easily reduced to Ce_2O_2S, which in turn can be easily re-oxidized back to the sulfate, explaining the apparent increase in OSC that is observed in $CO–O_2$ pulse studies of SO_2-poisoned catalysts [10]. Under oxidizing conditions, the sulfate is stable to approximately 1073 K, above which temperature the sulfate decomposes to SO_2 and O_2 [18]. When the sulfate is reduced in H_2, some H_2S is formed along with Ce_2O_2S.

In two previous studies from our laboratory, a correspondence was noted between OSC and the activity of the catalyst for the water–gas-shift (WGS) reaction [10,19]. First, using model Pd/ceria catalysts for which the Pd–ceria interfacial contact area was fixed, it was demonstrated that high-temperature calcination of ceria, which is known to irreversibly deactivate OSC, also deactivated the WGS reaction. Second, exposure of a Pd/ceria catalyst to SO_2, which is known to poison OSC, also severely poisoned the WGS reaction rate [10].

It has been proposed that the WGS reaction on Pd/ceria occurs through a redox mechanism as shown below [20]:

$$CO + \sigma \rightarrow CO_{ad} \tag{1}$$

$$H_2O + Ce_2O_3 \rightarrow 2CeO_2 + H_2 \tag{2}$$

$$CO_{ad} + 2CeO_2 \rightarrow CO_2 + Ce_2O_3 + \sigma \tag{3}$$

According to this picture, CO adsorbs on transition metal sites (σ) and reacts with oxygen from the ceria,

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which in turn is re-oxidized by H_2O. For our purposes here, it should be noted that H_2O, which is present in large concentrations in the exhaust stream, affects the oxidation state of the ceria. The role of sulfur in this reaction mechanism has not been extensively investigated. Therefore, the present study was instituted to determine the relationship between SO_2 poisoning of Pd/ceria and the WGS reaction using pulse-reactor studies and FTIR. We show that the results on fresh Pd/ceria are consistent with the above redox mechanism, but that the poisoned catalyst, while easily reduced by CO, can be re-oxidized by water only with difficulty.

2. Experimental

The catalysts used in this study were prepared at the University of Pennsylvania. The ceria support was prepared by decomposing $Ce(NO_3)_3{\cdot}6H_2O$ (Alfa Aesar, 99.5%) in air to give a pure ceria with a surface area of $\sim 35\,m^2/g$ [21], while the γ-Al_2O_3 was used as received from Alfa Aesar. Pd was added to a level of 1 wt% to the supports by wet impregnation of $Pd(NH_3)_4(NO_3)_2$ (Aldrich 99.99%). The samples were then calcined in air to 873 K for 4 h and reduced under reaction conditions. Poisoned samples in this study were exposed to a mixture of 1% SO_2 in He and pure O_2, in a ratio of 1 : 1 at 673 K, conditions that earlier studies had demonstrated lead to formation of $Ce(SO_4)_2$ [16,18].

Steady-state WGS reaction rates were measured in a $\frac{1}{4}$-inch, Pyrex tubular reactor using approximately 0.10 g of catalyst. Water was introduced by saturation of a He carrier gas flowing through a de-ionized water saturator. While the reactor pressure was always atmospheric, the partial pressures of CO, H_2O, and He were controlled by adjusting the relative flow rates of each component. The rates reported in this study were collected with partial pressures for CO and H_2O of 25 torr, with conversions of CO and H_2O kept well below 10%, so that differential conditions could be assumed. Before analyzing the products, we always allowed the reaction to run for at least 30 min to avoid potential transients associated with catalyst conditioning. The concentration of the effluent from the reactor was determined using an on-line gas chromatograph, SRI8610C, equipped with a Hayesep Q column and a TCD detector.

The transient-pulse experiments were performed using a system that has been described previously [18,22]. Computer-controlled switching valves allowed the composition of reactants admitted to a tubular reactor to undergo step changes. The product gases leaving the reactor could be analyzed by an on-line quadrupole mass spectrometer. Integration of the partial pressures as a function of time allowed accurate determination of the amounts of oxygen that could be added or removed at different temperatures. The carrier gas was pure He, with relatively dilute amounts of CO (5% in He), O_2 (7% in He), CO_2 (5% in He) and H_2O (2% in He) added in the pulses. The amount of catalyst used was 1.0 g.

The FTIR spectra were recorded using a Mattson Galaxy instrument with a diffuse-reflectance attachment, Collector II^{TM} provided by Spectra-Tech Inc. The FTIR experiments were performed under flow conditions similar to those in pulse measurement using the same catalysts.

3. Results

Figure 1 shows steady-state reaction rates for the WGS reaction with 25 torr each of CO and H_2O under

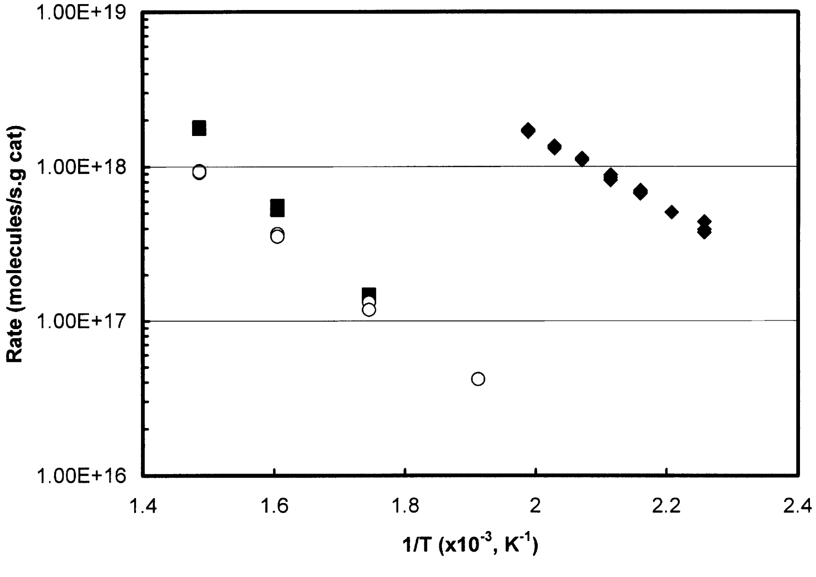

Figure 1. Arrhenius plot for the WGS reaction over ◆ fresh Pd/ceria, ■ SO_2-poisoned Pd/ceria, and ○ Pd/alumina. Data were collected under differential reaction conditions with 25 torr of both CO and H_2O.

differential conditions on a Pd/ceria catalyst, before and after it had been poisoned by SO_2. Data for the Pd/alumina catalyst is shown on the same plot for comparison. Under these conditions, rates were found to be stable for a period of at least several hours [23]. Because the reaction rates on the poisoned Pd/ceria and Pd/alumina were much lower than that on the fresh Pd/ceria, it was necessary to perform the rate measurements at a higher temperature. However, extrapolating rates to 500 K shows that the fresh Pd/ceria is at least 50 times as active as the other two samples at this temperature. The activation energy on the fresh Pd/ceria, 45 kJ/mol, is also much lower than on the poisoned Pd/ceria, 80 kJ/mol, or the Pd/alumina, 65 kJ/mol.

The most striking aspect of these data is how similar the rates are on the poisoned Pd/ceria and the Pd/alumina catalysts. Since our earlier studies showed that poisoning conditions used here leave the Pd unaffected and only transform the ceria to the sulfate [10], the rates on the poisoned Pd/ceria likely reflect the activity of Pd itself. The similarity in the rates observed on Pd/alumina support this conclusion. The higher rates on the fresh Pd/ceria are due to the ceria-mediated process discussed in section 1.

The proposed mechanism for the WGS reaction implies that redox processes are crucial. Therefore, we examined the oxidation and reduction of the fresh and poisoned Pd/ceria catalysts using pulse-reactor studies.

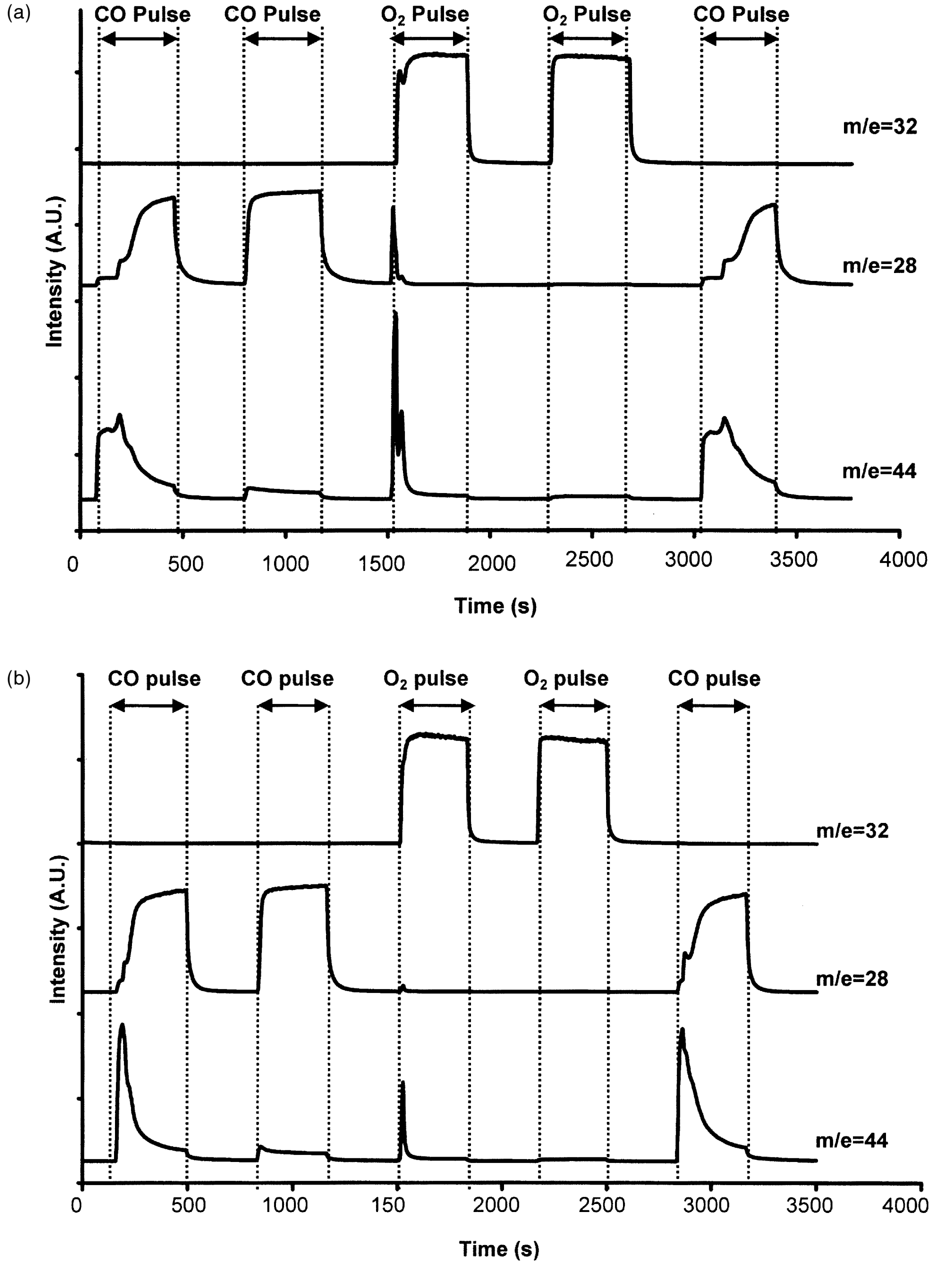

Figure 2. Pulse measurements on (a) fresh and (b) SO_2-poisoned Pd/ceria catalysts at 723 K. The data are for two pulses of CO ($m/e = 28$), followed by two pulses of O_2 ($m/e = 32$) and another of CO. Formation of CO_2 ($m/e = 44$ and 28) is observed.

In figure 2(a), results are shown for a series of CO and O_2 pulses on the fresh Pd/ceria at 723 K. Starting with an oxidized catalyst, approximately 500 μmol/g of CO reacts to CO_2 in the initial CO pulse. Introduction of a second CO pulse gave only small amounts of additional CO_2. Since the maximum amount of CO_2 that could form by reduction of PdO on a 1 wt% catalyst is less than 100 μmol/g, most of the CO_2 is formed from oxygen originating in the ceria. Since complete reduction of CeO_2 to Ce_2O_3 should provide 2900 μmol/g, reduction of the ceria is incomplete. After the two CO pulses, two O_2 pulses were introduced. In the first O_2 pulse, a sharp CO_2 ($m/e = 44$ and 28) spike, corresponding to ~300 μmol/g of CO_2, was observed. Similar results were obtained in previous CO–O_2 pulse studies, where the CO_2 was assigned to carbonate decomposition based on FTIR data [20,22]. Clearly 300 μmol/g is too large an amount to be due to CO adsorption on the Pd, but is close to the amount expected for a monolayer coverage on ceria assuming 6×10^{18} CO_3^{2-}/m^2 in a monolayer [20]. It appears that carbonates only form on the reduced ceria and re-oxidation of the ceria releases CO_2 corresponding to one monolayer of carbonate. Additional O_2 has no effect on the sample and the final CO pulse shows that the sample returned to its initial state at the end of the pulse sequence.

The analogous CO–O_2 pulse data for the poisoned Pd/ceria catalyst are shown in figure 2(b). Again, the

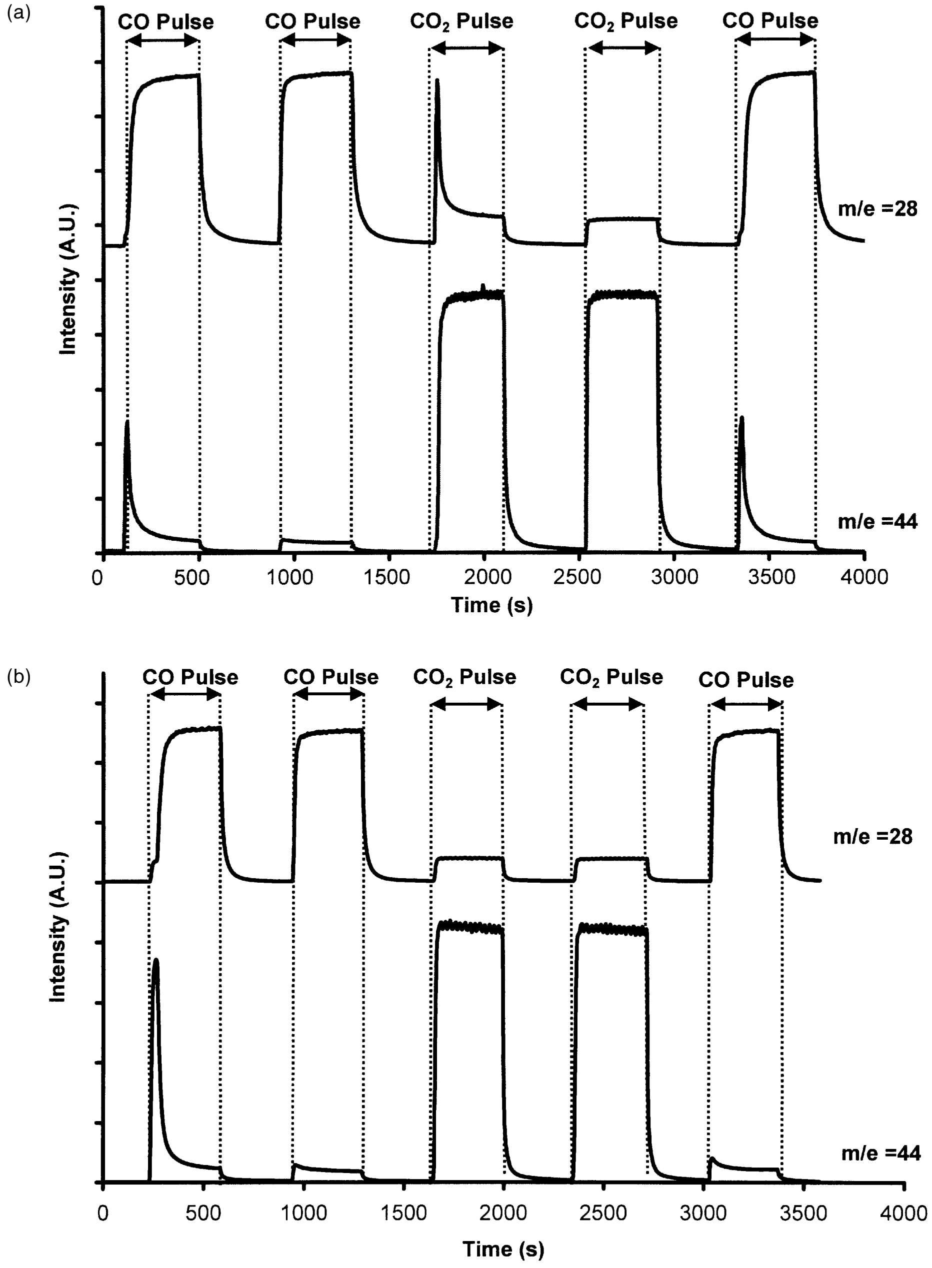

Figure 3. Pulse measurements on (a) fresh and (b) SO_2-poisoned Pd/ceria catalysts at 723 K. The data are for two pulses of CO ($m/e = 28$), followed by two pulses of CO_2 ($m/e = 44$ and 28) and another of CO.

first pulse of CO causes the formation of 500 μmol/g of CO_2, an amount that can only be explained by reduction of the support. While this result is similar to that observed on the fresh catalyst, only a small amount of CO_2, 30 μmol/g, is formed during the subsequent O_2 pulse. Again, this is in agreement with previous reports, where it was suggested that the carbonate could not be formed on the surface of Ce_2O_2S [10]. The small quantity of CO_2 that does form during the O_2 pulse may be due to incomplete poisoning of the sample or adsorption of CO on the Pd. Finally, the formation of large amounts of CO_2 in the final CO pulse demonstrates that the redox process on the poisoned catalyst remains reversible.

Since molecular O_2 is a very strong oxidant, we next probed the fresh and poisoned Pd/ceria catalyst with the weaker oxidants, CO_2 and H_2O, again at 723 K. The results for CO–CO_2 pulses on the fresh catalyst are given in figure 3(a) and agree very well with previous reports [22]. Starting with a catalyst that had been exposed to a series of CO and CO_2 pulses that are not shown, the first CO pulse shows significant CO_2 formation, ~200 μmol/g. Upon introduction of CO_2 to the reduced sample, approximately 200 μmol/g of CO is formed at the leading edge of the CO_2 pulse. (While there is a significant peak at $m/e = 28$ in the mass spectrum of CO_2, the ratio of peaks at $m/e = 28$ and 44 shows that much of the product in the leading edge

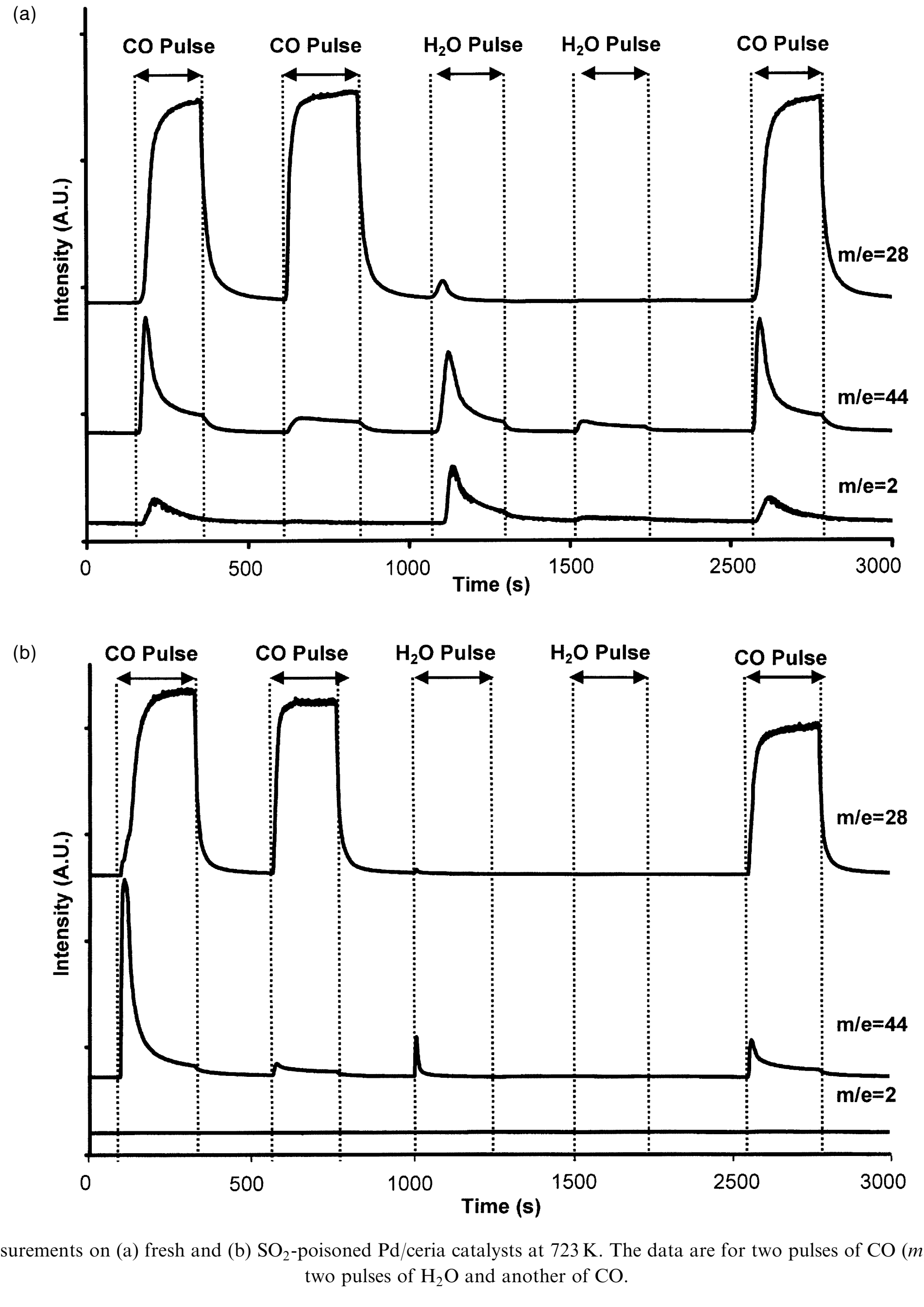

Figure 4. Pulse measurements on (a) fresh and (b) SO_2-poisoned Pd/ceria catalysts at 723 K. The data are for two pulses of CO ($m/e = 28$), followed by two pulses of H_2O and another of CO.

of the CO_2 pulse must be CO.) Finally, the CO_2 formation during the final CO pulse demonstrates that the sample had been oxidized by CO_2.

Data for the CO–CO_2 pulse sequence on the poisoned Pd/ceria at 723 K are shown in figure 3(b), starting this time from a partially oxidized catalyst in order to demonstrate that the catalyst was reducible. As in figure 2(b), exposure to CO produced a large amount of CO_2, $\sim$400 μmol/g in this particular experiment. However, on this sample, there is no evidence for CO production upon exposure of the catalyst to CO_2 and negligible amounts of CO_2 are formed in the final CO pulse. Assuming that the reduced catalyst in this case is Ce_2O_2S, CO_2 is unable to re-oxidize this to the sulfate.

Finally, the CO–H_2O pulse data at 723 K are reported in figure 4, although the $m/e = 18$ peak is not shown because of the difficulty of monitoring water with a mass spectrometer. In figure 4(a), starting from a fresh Pd/ceria catalyst oxidized in water, $\sim$200 μmol/g of CO_2 and $\sim$100 μmol/g of H_2 are formed during the first CO pulse that is shown. When this reduced catalyst was exposed to 2% H_2O in He, an additional 150 μmol/g of CO_2 and 250 μmol/g of H_2 were formed at the leading edge of the water pulse. Finally, the last CO pulse shows that the sequence is repeatable. The interpretation of at least certain aspects of these data is clear based on the results in figures 2(a) and 3(a). In the initial CO pulse, CO_2 is formed primarily by reduction of ceria. Since the reduction of ceria by CO is accompanied by the formation of surface carbonates, it is tempting to suggest that H_2 formation results from decomposition of hydroxyls that become unstable on the reduced ceria surface or in the presence of carbonates. The formation of CO_2 in the first H_2O pulse is due to re-oxidation of ceria, which in turn destabilizes the carbonate, as discussed in the interpretation of figure 2(a). The oxidation of ceria by H_2O obviously requires the production of H_2.

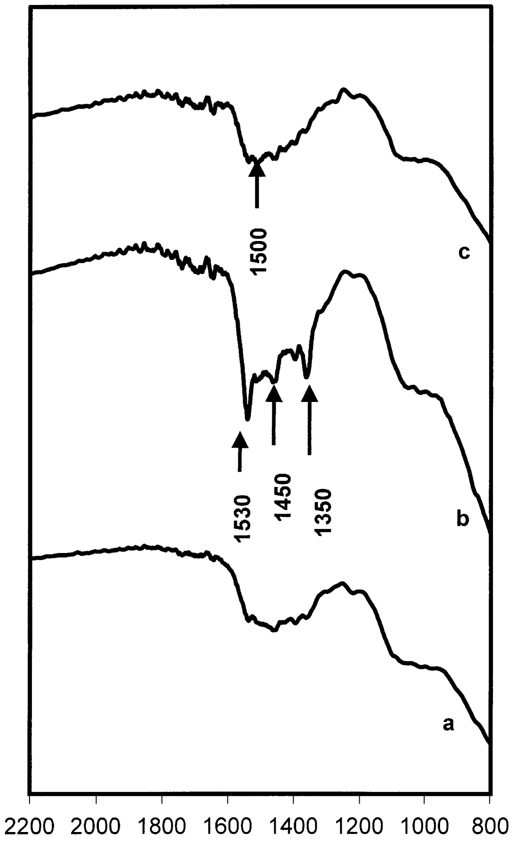

Figure 5. FTIR data for a Pd/ceria catalyst at 573 K after the following treatments: (a) after oxidation in O_2; (b) after exposure to 25 torr CO; and (c) after exposure to 25 torr H_2O.

The FTIR data in figure 5 help confirm this interpretation and is similar to that reported elsewhere [20]. Due to the fact that the hydroxyl region showed only broad bands, only the spectral region from the carbonates is given here. The spectrum of the fresh, oxidized Pd/ceria catalyst is shown in figure 5(a). Only broad features are observed between 1300 and 1700 cm^{-1}. Upon exposure to 25 torr of CO at 573 K, sharp peaks are observed at 1350, 1450, and 1530 cm^{-1}, which have earlier been assigned to surface carbonates [20]. Finally, heating the sample in 25 torr of H_2O at 573 K produces a sample that gives a spectrum without carbonate features, figure 5(c).

The CO–H_2O pulse data from the poisoned sample at 723 K are displayed in figure 4(b). Starting again with the oxidized catalyst in order to demonstrate reducibility, a significant fraction of the first CO pulse reacts to CO_2

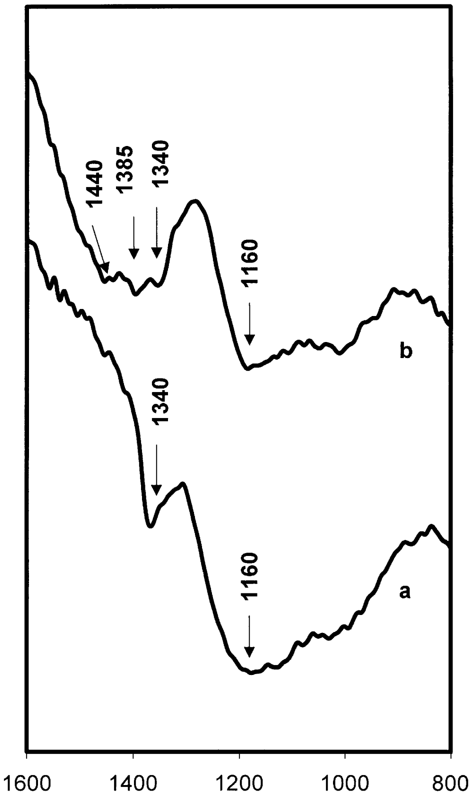

Figure 6. FTIR data for an SO_2-poisoned Pd/ceria catalyst (a) after oxidation in O_2 and (b) after exposure to 25 torr CO at 773 K.

to reduce the sample. However, exposure of the reduced catalyst to H_2O results in the formation of only trace amounts of CO_2 and no H_2. The final CO pulse also leads to low CO_2 levels, possibly resulting from oxygen diffusion from the bulk. Comparing these data to the fresh Pd/ceria, it is clear that H_2O is much less able to oxidize the poisoned catalyst. FTIR data, shown in figure 6, confirm that the sulfate is easily reduced by CO at moderate temperatures. The spectrum in figure 6(a), produced by exposing Pd/ceria to 1% SO_2 at 673 K, is indicative of bulk sulfates [18]. After heating this sample in CO at 773 K, the spectrum changes to that shown in figure 6(b), which has been assigned as resulting from partial reduction of the sulfate to the oxysulfide. Heating this sample in 25 torr H_2O caused negligible changes in the spectrum.

4. Discussion

The results reported here on the fresh Pd/ceria catalyst strongly support the redox mechanism for the WGS reaction. The similarities between the CO–O_2, CO–CO_2, and CO–H_2O pulses imply that CO easily reduces the catalyst, and that the reduced Pd/ceria can in turn be re-oxidized by O_2, CO_2, and H_2O. Because the amounts of oxygen transferred are significantly larger than the number of Pd atoms in the sample, the redox process must involve ceria. The formation of carbonates on the reduced ceria and the decomposition of those carbonates upon oxidation of the ceria are consistent with this picture.

The poisoned sample, which is probably best described as Pd supported on $Ce(SO_4)_2$ [18], remains easily reduced by CO, but is not as easily re-oxidized as the fresh Pd/ceria. It is easy to understand this based on energetic arguments by considering the reactions in table 1 with their standard enthalpy changes. The reaction enthalpies show that re-oxidation of Ce_2O_3 by any of the three potential oxidants, O_2, CO_2, and H_2O, is exothermic. Re-oxidation of Ce_2O_2S by O_2 is also energetically downhill, but re-oxidation by CO_2 and H_2O are energetically uphill. Obviously, one should consider the free energies, rather than the enthalpies, to determine whether or not a reaction will proceed. (We did not do so because free energy data are difficult to obtain for all of the compounds in table 1 and may in any case be somewhat unreliable [24,25].) Since there are ceria phases with average oxidation states between +3 and +4 [26] and since redox properties of ceria are sensitive to crystallite size and structure [27], the enthalpies shown may not be entirely relevant to the reactions observed in the pulse studies anyway. Still, the enthalpy changes for the above reactions make it easy to rationalize the experimental data.

Table 1
Standard enthalpies of possible redox reactions in this study[a]

Reaction	ΔH° (kJ/mol)	
$Ce_2O_3 + 0.5O_2 = 2CeO_2$	−380	(4)
$Ce_2O_3 + H_2O = 2CeO_2 + H_2$	−139	(5)
$Ce_2O_3 + CO_2 = 2CeO_2 + CO$	−97	(6)
$0.2Ce_2O_2S + 0.5O_2 = 0.1Ce(SO_4)_2 + 0.3CeO_2$	−222	(7)
$0.2Ce_2O_2S + H_2O = 0.1Ce(SO_4)_2 + 0.3CeO_2 + H_2$	+19.78	(8)
$0.2Ce_2O_2S + CO_2 = 0.1Ce(SO_4)_2 + 0.3CeO_2 + CO$	+60.94	(9)

[a] These data are taken from the *CRC HandBook of Chemistry and Physics*, 72nd edition.

The more difficult question regards how to explain the effect of sulfur on OSC, given that Ce_2O_2S can be readily oxidized by O_2 and reduced by CO. One possibility is that the rate of oxidation and reduction of the poisoned catalyst is too slow. Light-off measurements for CO oxidation on fresh and poisoned Pd/ceria have shown an upward shift in temperature for the poisoned catalyst [10]. However, at temperatures that are more typical of automotive exhaust conditions, above 673 K, the oxidation and reduction on both fresh and poisoned catalyst appear to be very rapid based on our pulse measurements. We suggest that the rate of these reactions in the catalytic converter is probably not limited by surface reactions.

The major change we observed on the poisoned catalyst compared to the fresh catalyst involved the WGS reaction. The relevance of WGS to OSC is not immediately obvious, given that the WGS reaction does not change the exhaust stream from reducing to oxidizing. The WGS reaction simply exchanges one mole of CO for one mole of H_2. However, a closer examination suggests that WGS could be critical for OSC. First, H_2 is a more effective reductant for NO. Second, oxygen sensors respond more effectively and quickly to H_2 than they do to CO [28]. The response of the oxygen sensors is obviously crucial to the measured OSC.

In those cases where a decrease in OSC due to the presence of SO_2 has been reported, H_2O and CO_2 are always present in significant quantities. For example, in the work of Beck and Sommers [7], oxygen uptake and release were measured upon changing the gas stream from oxidizing to reducing; but a steady concentration of 10% H_2O and 10% CO_2 was maintained throughout the cycle. Likewise, Hepburn *et al.* used a pulse flame combustor method in which H_2O and CO_2 are again major gas-phase components above the catalyst [9]. Obviously, H_2O and CO_2 are present in all engine tests where the effect of sulfur-containing fuels is monitored.

The pulse studies provide some mechanistic details about the nature of the surface under WGS reaction conditions. In addition to confirming the overall redox nature of the reactions, the results confirm the presence of carbonate species on reduced ceria and the decomposition of the carbonate upon oxidation. The formation of H_2 during the CO pulse is also of interest since it is doubtful that one could have adsorbed water at 723 K without gas-phase water present. Because the amount of H_2 formed during the CO pulse is more than the amount of Pd on the sample, the hydrogen must be associated with ceria, probably as a hydroxyl. The fact that it leaves the surface during reduction by CO implies that surface hydroxyls take part in the reaction in some manner. Clearly, this will be an interesting point to explore.

5. Conclusion

The high WGS activity of Pd/ceria is due to a redox process in which the catalyst is reduced by CO and oxidized by H_2O. Exposing Pd/ceria to SO_2 under oxidizing conditions causes formation of $Ce(SO_4)_2$ and blocks the WGS activity enhancement associated with ceria. Reduction of the sulfate remains facile; however, while Ce_2O_2S can be re-oxidized easily by O_2, Ce_2O_2S is not readily re-oxidized by H_2O.

Acknowledgments

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