



February 2003

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## Recommended Citation

Luo, T., & Gorte, R. J. (2003). A Mechanistic Study of Sulfur Poisoning of the Water-Gas-Shift Reaction Over Pd/Ceria. Retrieved from [http://repository.upenn.edu/cbe\\_papers/57](http://repository.upenn.edu/cbe_papers/57)

Postprint version. Published in *Catalysis Letters*, Volume 85, Issues 3-4, February 2003, pages 139-146. The original publication is available at [www.springerlink.com](http://www.springerlink.com).

Publisher URL: <http://dx.doi.org/10.1023/A:1022125209602>

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## Keywords

ceria, SO<sub>2</sub>, cerium sulfate, water-gas shift, oxygen storage capacity (OSC)

## Comments

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## **A Mechanistic Study of Sulfur Poisoning of the Water-Gas-Shift Reaction Over Pd/Ceria.**

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### **Abstract**

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<sub>2</sub> 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<sub>2</sub> at 723 K; however, unlike reduced ceria, the Ce<sub>2</sub>O<sub>2</sub>S formed by reduction of the sulfates cannot be re-oxidized by H<sub>2</sub>O or CO<sub>2</sub>. The implications of these measurements for understanding oxygen-storage capacity (OSC) of three-way catalysts are discussed.

**Keywords:** ceria, SO<sub>2</sub>, cerium sulfate, water-gas shift, oxygen storage capacity (OSC).

**Short Title:** Sulfur Poisoning of on Pd/ceria

## 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 to 20 ppm of SO<sub>2</sub>. At these relatively low concentrations, SO<sub>2</sub> 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<sub>2</sub>. However, Hepburn and coworkers reported “that the CO/O<sub>2</sub> 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<sub>2</sub> can actually *increase* the amount of oxygen which can be reversibly removed in both CO-O<sub>2</sub> 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<sub>2</sub> have been studied rather thoroughly [11-18]. Below approximately 473 K, SO<sub>2</sub> adsorbs molecularly, possibly as a sulfite [18]. At higher temperatures, this surface species is oxidized to Ce<sup>+3</sup> and Ce<sup>+4</sup> sulfates [18], using either molecular O<sub>2</sub> from the gas phase or by reduction of CeO<sub>2</sub>. If ceria is exposed to SO<sub>2</sub> in an oxidizing environment at above 473 K, both surface and bulk sulfates are formed. The sulfates are easily reduced to Ce<sub>2</sub>O<sub>2</sub>S, which in turn can be easily reoxidized back to the sulfate, explaining the apparent increase in OSC that is observed in CO-O<sub>2</sub> pulse studies of SO<sub>2</sub>-poisoned catalysts [10]. Under oxidizing conditions, the sulfate is stable to approximately 1073 K, above which temperature the sulfate decomposes to SO<sub>2</sub> and O<sub>2</sub> [18]. When the sulfate is reduced in H<sub>2</sub>, some H<sub>2</sub>S is formed along with Ce<sub>2</sub>O<sub>2</sub>S.

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<sub>2</sub>, 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]:



According to this picture, CO adsorbs on transition-metal sites ( $\sigma$ ) and reacts with oxygen from the ceria, which in turn is re-oxidized by H<sub>2</sub>O. For our purposes here, it should be noted that H<sub>2</sub>O, 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<sub>2</sub> poisoning of Pd/ceria and the WGS reaction using pulse-reactor studies and FTIR. We will 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.

## Experimental

The catalysts used in this study were prepared at the University of Pennsylvania. The ceria support was prepared by decomposing Ce(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O (Alfa Aesar, 99.5%) in air to give a pure ceria with a surface area of ~35 m<sup>2</sup>/g [21], while the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> 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<sub>3</sub>)<sub>4</sub>(NO<sub>3</sub>)<sub>2</sub> (Aldrich 99.99%). The samples were then calcined in air to 873 K for 4 hrs and reduced under reaction conditions. Poisoned samples in this study were exposed to a mixture of 1% SO<sub>2</sub> in He and pure O<sub>2</sub>, in a ratio of 1:1 at 673 K, conditions which earlier studies had demonstrated lead to formation of Ce(SO<sub>4</sub>)<sub>2</sub> [16,18].

Steady-state WGS reaction rates were measured in a ¼-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<sub>2</sub>O, 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<sub>2</sub>O

of 25 torr, with conversions of CO and H<sub>2</sub>O 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 on 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<sub>2</sub> (7% in He), CO<sub>2</sub> (5% in He) and H<sub>2</sub>O (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 FTIR with a diffuse-reflectance attachment, Collector II<sup>TM</sup> provided by Spectra-Tech Inc. The FTIR experiments were performed under flow conditions similar to those in pulse measurement using the same catalysts.

## Results

Fig. 1 shows steady-state reaction rates for the WGS reaction with 25 torr each of CO and H<sub>2</sub>O under differential conditions on a Pd/ceria catalyst, before and after it had been poisoned by SO<sub>2</sub>. 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 this 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 the Introduction.

The proposed mechanism for WGS 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. In Fig. 2a), results are shown for a series of CO and O<sub>2</sub> pulses on the fresh Pd/ceria at 723 K. Starting with an oxidized catalyst, approximately 500 μmol/g of CO reacts to CO<sub>2</sub> in the initial CO pulse. Introduction of a second CO pulse gave only small amounts of additional CO<sub>2</sub>. Since the maximum amount of CO<sub>2</sub> that could form by reduction of PdO on a 1-wt% catalyst is less than 100 μmol/g, most of the CO<sub>2</sub> is formed from oxygen originating in the ceria. Since complete reduction of CeO<sub>2</sub> to Ce<sub>2</sub>O<sub>3</sub> should provide 2900 μmol/g, reduction of the ceria is incomplete. After the two CO pulses, two O<sub>2</sub> pulses were introduced. In the first O<sub>2</sub> pulse, a sharp CO<sub>2</sub> (m/e=44 and 28) spike, corresponding to ~300 μmol/g of CO<sub>2</sub>, was observed. Similar results were obtained in previous CO-O<sub>2</sub> pulse studies, where the CO<sub>2</sub> was assigned to carbonate decomposition based on FTIR data [20,22]. 300 μmol/g is clearly 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  $6 \times 10^{18}$  CO<sub>3</sub><sup>2-</sup>/m<sup>2</sup> in a monolayer [20]. It appears that carbonates only form on the reduced ceria and re-oxidation of the ceria releases CO<sub>2</sub> corresponding to one monolayer of carbonate. Additional O<sub>2</sub> 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<sub>2</sub> pulse data for the poisoned Pd/ceria catalyst is shown in Fig. 2b). Again, the first pulse of CO causes the formation of 500 μmol/g of CO<sub>2</sub>, 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<sub>2</sub>, 30 μmol/g, is formed during the subsequent O<sub>2</sub> 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<sub>2</sub>O<sub>2</sub>S [10]. The small quantity of CO<sub>2</sub> that does form during the O<sub>2</sub> 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<sub>2</sub> in the final CO pulse demonstrates that the redox process on the poisoned catalyst remains reversible.

Since molecular O<sub>2</sub> is a very strong oxidant, we next probed the fresh and poisoned Pd/ceria catalyst with the weaker oxidants, CO<sub>2</sub> and H<sub>2</sub>O, again at 723 K. The results for CO-CO<sub>2</sub> pulses on the fresh catalyst are given in Fig. 3a) and agree very well with previous reports

[22]. Starting with a catalyst that had been exposed to a series of CO and CO<sub>2</sub> pulses that are not shown, the first CO pulse shows significant CO<sub>2</sub> formation, ~200 μmol/g. Upon introduction of CO<sub>2</sub> to the reduced sample, approximately 200 μmol/g of CO is formed at the leading edge of the CO<sub>2</sub> pulse. (While there is a significant peak at m/e=28 in the mass spectrum of CO<sub>2</sub>, the ratio of peaks at m/e=28 and 44 shows that much of the product in the leading edge of the CO<sub>2</sub> pulse must be CO.) Finally, the CO<sub>2</sub> formation during the final CO pulse demonstrates that the sample had been oxidized by CO<sub>2</sub>.

Data for the CO-CO<sub>2</sub> pulse sequence on the poisoned Pd/ceria at 723 K are shown in Fig. 3b), starting this time from a partially oxidized catalyst in order to demonstrate that the catalyst was reducible. As in Fig. 2b), exposure to CO produced a large amount of CO<sub>2</sub>, ~ 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<sub>2</sub> and negligible amounts of CO<sub>2</sub> are formed in the final CO pulse. Assuming that the reduced catalyst in this case is Ce<sub>2</sub>O<sub>2</sub>S, CO<sub>2</sub> is unable to re-oxidize this to the sulfate.

Finally, the CO-H<sub>2</sub>O pulse data at 723 K are reported in Fig. 4, although the m/e=18 peak is not shown because of the difficulty of monitoring water with a mass spectrometer. In Fig. 4a), starting from a fresh Pd/ceria catalyst oxidized in water, ~200 μmol/g of CO<sub>2</sub> and ~100 μmol/g of H<sub>2</sub> is formed during the first CO pulse that is shown. When this reduced catalyst was exposed to 2% H<sub>2</sub>O in He, an additional 150 μmol/g of CO<sub>2</sub> and 250 μmol/g of H<sub>2</sub> 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 this data are clear based on the results in Fig. 2a) and 3a). In the initial CO pulse, CO<sub>2</sub> 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<sub>2</sub> formation results from decomposition of hydroxyls that become unstable on the reduced ceria surface or in the presence of carbonates. The formation of CO<sub>2</sub> in the first H<sub>2</sub>O pulse is due to re-oxidation of ceria, which in turn destabilizes the carbonate, as discussed in the interpretation of Fig. 2a). The oxidation of ceria by H<sub>2</sub>O obviously requires the production of H<sub>2</sub>.

The FTIR data in Fig. 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 Fig. 5a). Only broad features are observed between 1300 and 1700 cm<sup>-1</sup>.



Upon exposure to 25 torr of CO at 573 K, sharp peaks are observed at 1350, 1450, and 1530  $\text{cm}^{-1}$ , which have earlier been assigned to surface carbonates [20]. Finally, heating the sample in 25 torr of  $\text{H}_2\text{O}$  at 573 K produces a sample that gives a spectrum without carbonate features, Fig. 5c).

The CO- $\text{H}_2\text{O}$  pulse data from the poisoned sample at 723 K is displayed in Fig. 4b). Starting again with the oxidized catalyst in order to demonstrate reducibility, a significant fraction of the first CO pulse reacts to  $\text{CO}_2$  to reduce the sample. However, exposure of the reduced catalyst to  $\text{H}_2\text{O}$  results in the formation of only trace amounts of  $\text{CO}_2$  and no  $\text{H}_2$ . The final CO pulse also leads to low  $\text{CO}_2$  levels, possibly resulting from oxygen diffusion from the bulk. Comparing this data to the fresh Pd/ceria, it is clear that  $\text{H}_2\text{O}$  is much less able to oxidize the poisoned catalyst. FTIR data, shown in Fig. 6, confirm that the sulfate is easily reduced by CO at moderate temperatures. The spectrum in Fig. 6a), produced by exposing Pd/ceria to 1%  $\text{SO}_2$  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 Fig. 6b), which has been assigned as resulting from partial reduction of the sulfate to the oxysulfide. Heating this sample in 25 torr  $\text{H}_2\text{O}$  caused negligible changes in the spectrum.

## 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- $\text{O}_2$ , CO- $\text{CO}_2$ , and CO- $\text{H}_2\text{O}$  pulses imply that CO easily reduces the catalyst, and that the reduced Pd/ceria can in turn be re-oxidized by  $\text{O}_2$ ,  $\text{CO}_2$ , and  $\text{H}_2\text{O}$ . 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  $\text{Ce}(\text{SO}_4)_2$  [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  $\text{Ce}_2\text{O}_3$  by any of the three potential oxidants,  $\text{O}_2$ ,  $\text{CO}_2$ , and  $\text{H}_2\text{O}$ , is exothermic. Re-oxidation of  $\text{Ce}_2\text{O}_2\text{S}$  by  $\text{O}_2$  is also energetically downhill, but re-oxidation by  $\text{CO}_2$  and  $\text{H}_2\text{O}$  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 is 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 above 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.

The more difficult question regards how to explain the effect of sulfur on OSC, given that  $\text{Ce}_2\text{O}_2\text{S}$  can be readily oxidized by  $\text{O}_2$  and reduced by  $\text{CO}$ . One possibility is that rate of oxidation and reduction of the poisoned catalyst is too slow. Light-off measurements for  $\text{CO}$  oxidation on fresh and poisoned  $\text{Pd/ceria}$  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  $\text{CO}$  for one mole of  $\text{H}_2$ . However, a closer examination suggests that WGS could be critical for OSC. First,  $\text{H}_2$  is a more effective reductant for  $\text{NO}$ . Second, oxygen sensors respond more effectively and quickly to  $\text{H}_2$  than they do to  $\text{CO}$  [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  $\text{SO}_2$  has been reported,  $\text{H}_2\text{O}$  and  $\text{CO}_2$  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%  $\text{H}_2\text{O}$  and 10%  $\text{CO}_2$  was maintained throughout the cycle. Likewise, Hepburn, et al. used a pulse-flame-combustor method in which  $\text{H}_2\text{O}$  and  $\text{CO}_2$  are again major gas-phase components above the catalyst [9]. Obviously,  $\text{H}_2\text{O}$  and  $\text{CO}_2$  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<sub>2</sub> 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<sub>2</sub> 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.

### Conclusion

The high water-gas-shift (WGS) activity of Pd/ceria is due to a redox process in which the catalyst is reduced by CO and oxidized by H<sub>2</sub>O. Exposing Pd/ceria to SO<sub>2</sub> under oxidizing conditions causes formation of Ce(SO<sub>4</sub>)<sub>2</sub> and blocks the WGS activity enhancement associated with ceria. Reduction of the sulfate remains facile; however, while Ce<sub>2</sub>O<sub>2</sub>S can be re-oxidized easily by O<sub>2</sub>, Ce<sub>2</sub>O<sub>2</sub>S is not readily re-oxidized by H<sub>2</sub>O.

### Acknowledgements

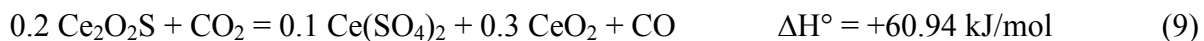
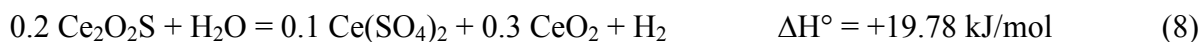
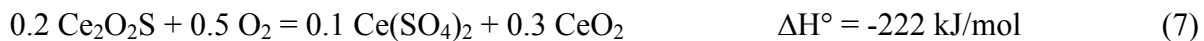
This work was supported by the DOE, Basic Energy Sciences, Grant #DE-FG03-85-13350. We thank Dr. X. Wang for his help in collecting the WGS rate data.

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- Fig. 1. Arrhenius plot for the WGS reaction over  $\blacklozenge$  fresh Pd/ceria,  $\blacksquare$  SO<sub>2</sub>-poisoned Pd/ceria, and  $\circ$  Pd/alumina. Data were collected under differential reaction conditions with 25 torr of both CO and H<sub>2</sub>O.
- Fig. 2. Pulse measurements on a) fresh and b) SO<sub>2</sub>-poisoned Pd/ceria catalysts at 723 K. The data are for two pulses of CO (m/e = 28), followed by two pulses of O<sub>2</sub> (m/e = 32) and another of CO. Formation of CO<sub>2</sub> (m/e = 44 and 28) is observed.
- Fig. 3. Pulse measurements on a) fresh and b) SO<sub>2</sub>-poisoned Pd/ceria catalysts at 723 K. The data are for two pulses of CO (m/e = 28), followed by two pulses of CO<sub>2</sub> (m/e = 44 and 28) and another of CO.
- Fig. 4. Pulse measurements on a) fresh and b) SO<sub>2</sub>-poisoned Pd/ceria catalysts at 723 K. The data are for two pulses of CO (m/e = 28), followed by two pulses of H<sub>2</sub>O and another of CO.
- Fig. 5. FTIR data for a Pd/ceria catalyst at 573 K after the following treatments: a) after oxidation in O<sub>2</sub>; b) after exposure to 25 torr CO; and c) after exposure to 25 torr H<sub>2</sub>O.
- Fig. 6. FTIR data for an SO<sub>2</sub>-poisoned Pd/ceria catalyst a) after oxidation in O<sub>2</sub> and b) after exposure to 25 torr CO at 773 K.

**Table 1** Standard Enthalpies of Possible Redox Reactions in this Study.\*

\*This data is taken from the CRC HandBook of Chemistry and Physics, 72th Edition.

Fig. 1

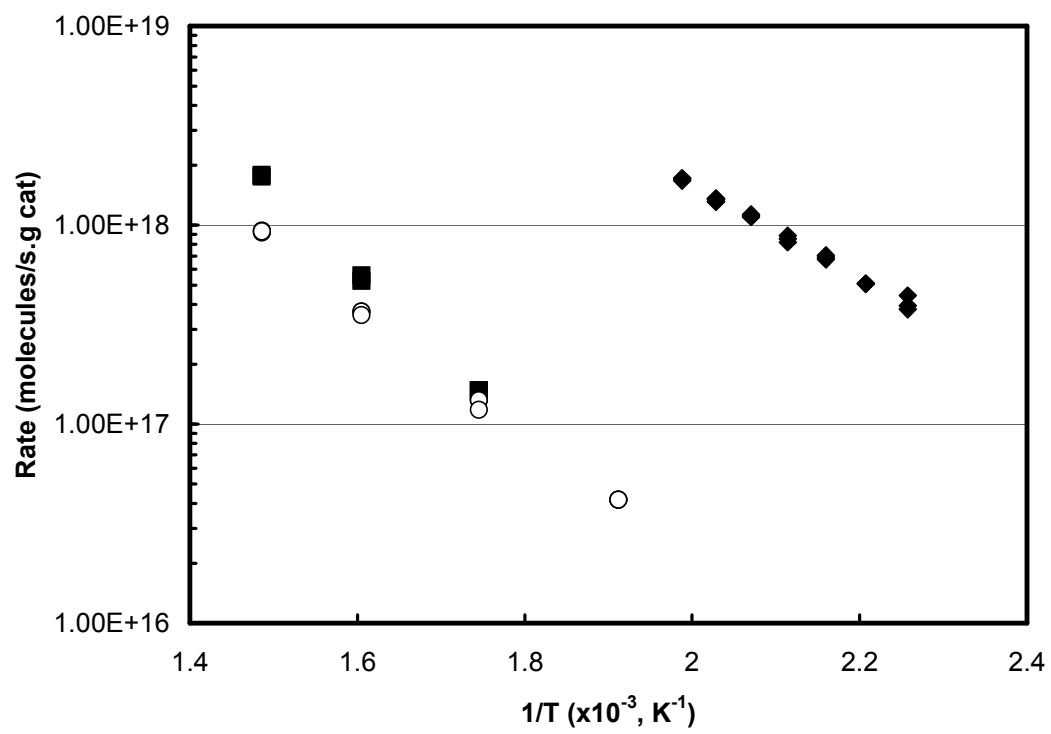


Fig. 2a)

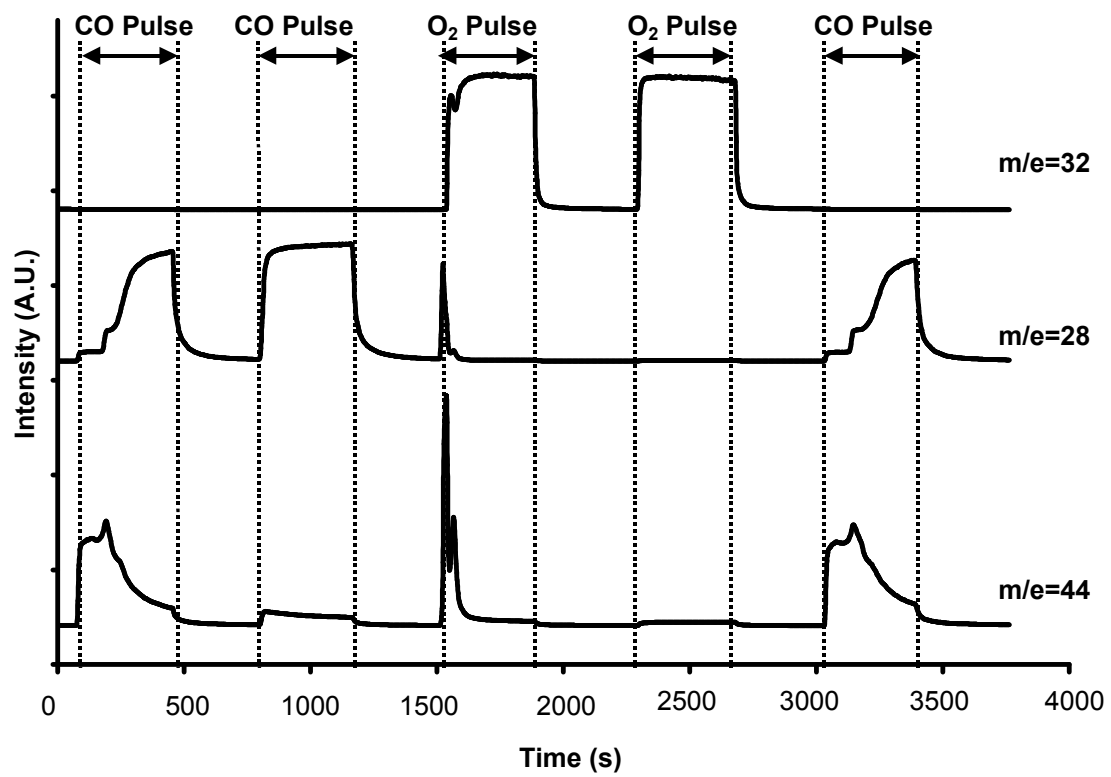


Fig. 2b)

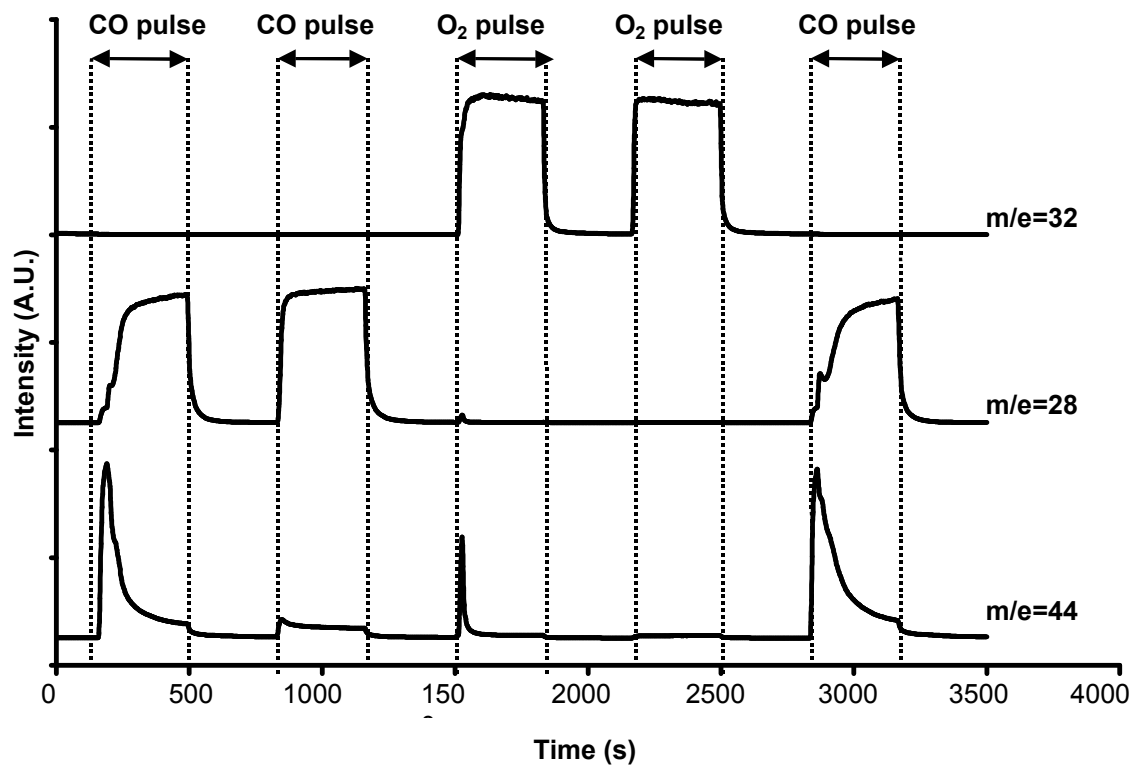




Fig. 3a)

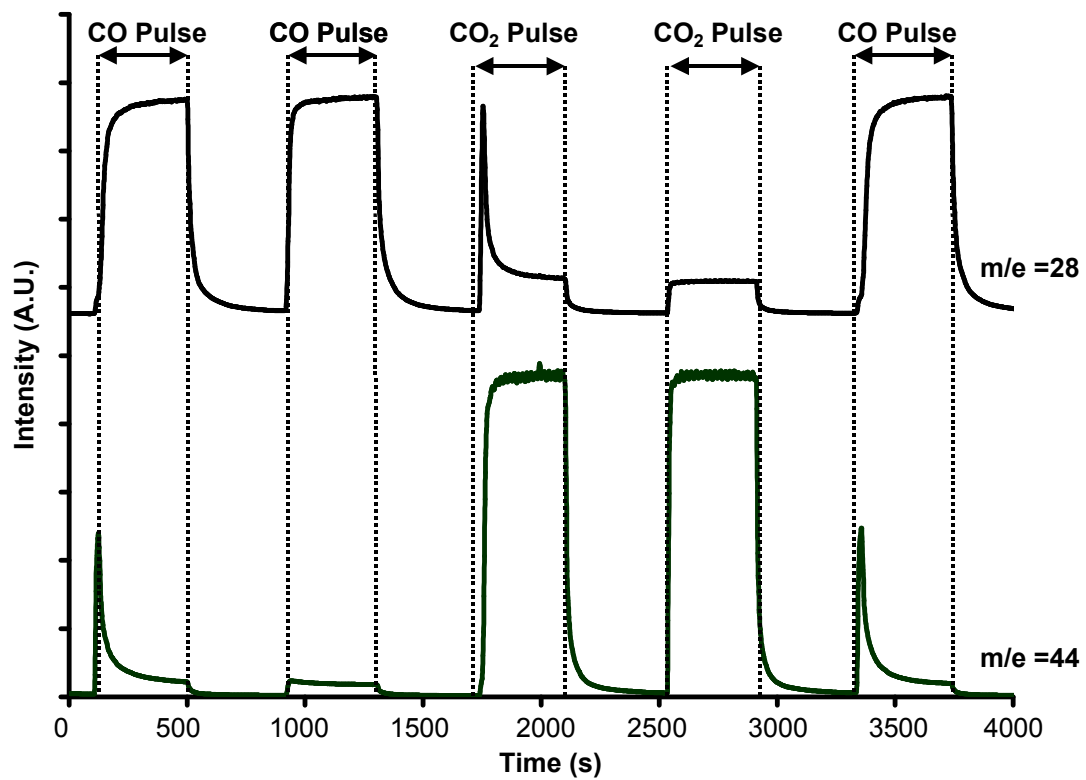


Fig. 3b)

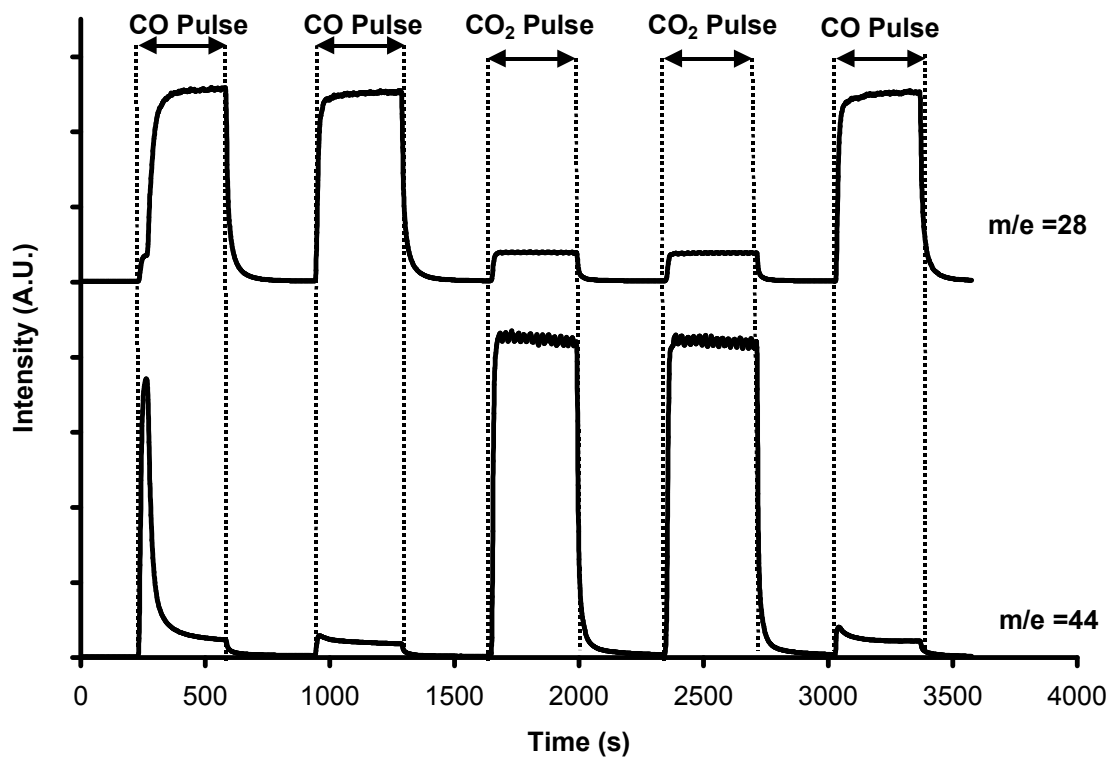


Fig. 4a)

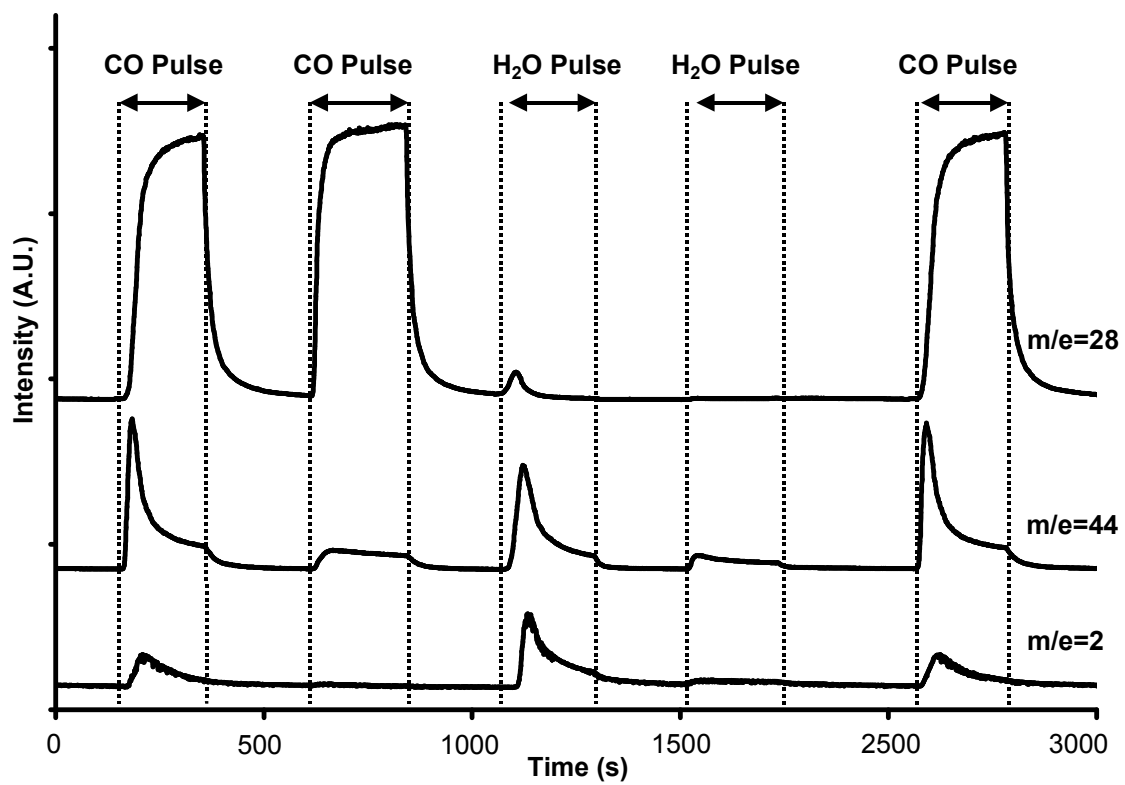


Fig. 4b)

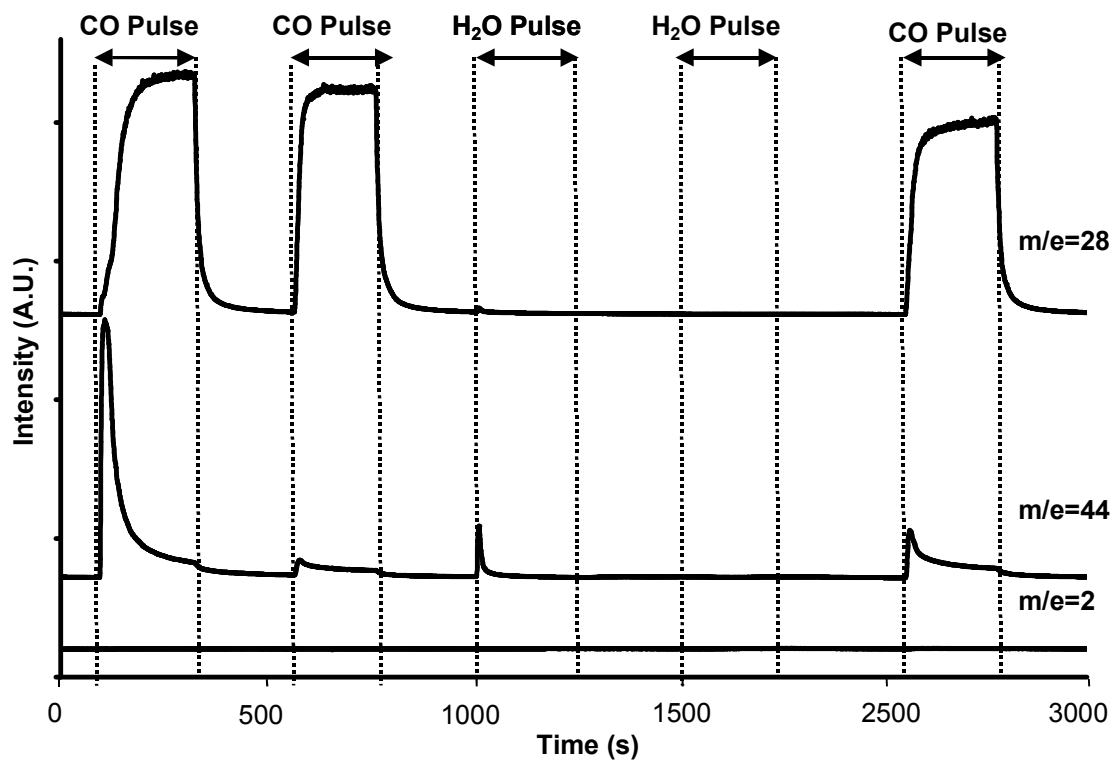


Fig. 5

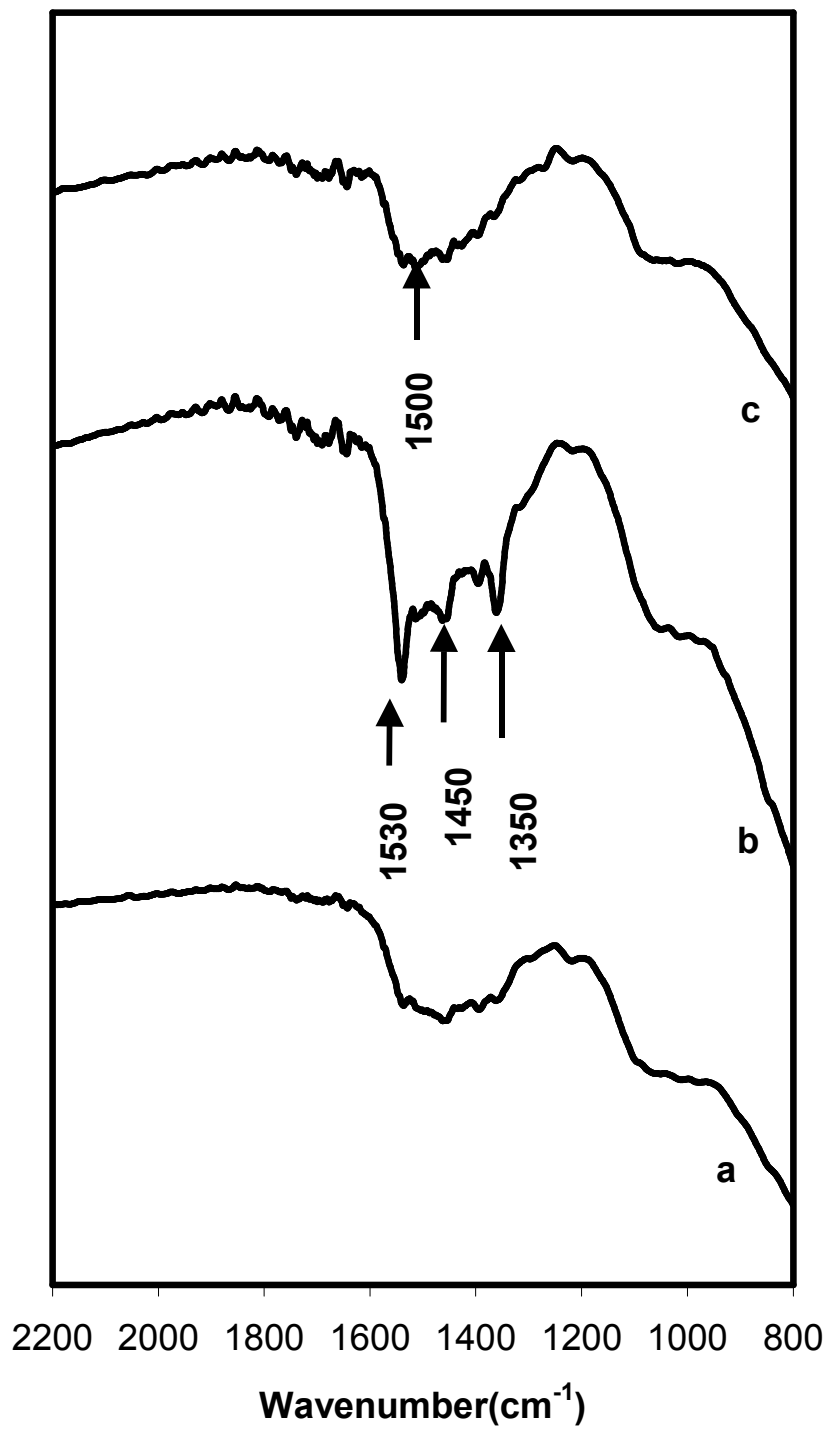


Fig. 6

