



September 2002

An Examination of Sulfur Poisoning on Pd/Ceria Catalysts

T. Luo

University of Pennsylvania

John M. Vohs

University of Pennsylvania, vohs@seas.upenn.edu

Raymond J. Gorte

University of Pennsylvania, gorte@seas.upenn.edu

Follow this and additional works at: http://repository.upenn.edu/cbe_papers

Recommended Citation

Luo, T., Vohs, J. M., & Gorte, R. J. (2002). An Examination of Sulfur Poisoning on Pd/Ceria Catalysts . Retrieved from http://repository.upenn.edu/cbe_papers/43

Postprint version. Published in *Journal of Catalysis*, Volume 210, Issue 2, 10 September 2002, pages 397-404.
Publisher URL: <http://dx.doi.org/10.1006/jcat.2002.3689>

This paper is posted at ScholarlyCommons. http://repository.upenn.edu/cbe_papers/43
For more information, please contact libraryrepository@pobox.upenn.edu.

An Examination of Sulfur Poisoning on Pd/Ceria Catalysts

Abstract

The species formed by exposure of a Pd/ceria catalyst to SO₂ under various conditions have been studied using temperature-programmed desorption (TPD) and FTIR. For adsorption of SO₂ between 298 and 473 K, a molecular SO₂ species adsorbs on the surface, possibly as a surface sulfite; and this species converts to a sulfate above 473 K. Exposure of Pd/ceria to SO₂ at temperatures above 473 K in the presence of O₂ results in the formation of bulk sulfates. These sulfates decompose to form SO₂ and O₂ upon TPD in He, with O₂ and SO₂ peaks at 1023 K assigned to Ce⁺⁴ sulfates and peaks at 1123 K assigned to Ce⁺³ sulfates. When H₂ is present in the TPD carrier gas, the sulfates are reduced and a significant fraction of the sulfur is removed as H₂S, with the rest remaining as Ce₂O₂S. When CO is present in the TPD carrier gas, all of the sulfates are reduced to Ce₂O₂S, with the simultaneous formation of CO₂. The formation of CO₂ from the reduction of the sulfate occurs in the same temperature range as CO₂ production from reduction of Pd/ceria, except that more CO₂ is formed from the sulfur-poisoned catalyst. The implications of these results for understanding oxygen storage capacity (OSC) in automotive, three-way catalysts is discussed.

Keywords

ceria, SO₂, H₂S, cerium sulfate, cerium oxy-sulfide, FTIR, TPD, oxygen storage capacity (OSC)

Comments

Postprint version. Published in *Journal of Catalysis*, Volume 210, Issue 2, 10 September 2002, pages 397-404.
Publisher URL: <http://dx.doi.org/10.1006/jcat.2002.3689>

An Examination of Sulfur Poisoning on Pd/Ceria Catalysts

T. Luo, J. M. Vohs, and R. J. Gorte
Department of Chemical Engineering
University of Pennsylvania
Philadelphia, P.A. 19104 USA

Abstract

The species formed by exposure of a Pd/ceria catalyst to SO₂ under various conditions have been studied using temperature-programmed desorption (TPD) and FTIR. For adsorption of SO₂ between 298 and 473 K, a molecular SO₂ species adsorbs on the surface, possibly as a surface sulfite; and this species converts to a sulfate above 473 K. Exposure of Pd/ceria to SO₂ at temperatures above 473 K in the presence of O₂ results in the formation of bulk sulfates. These sulfates decompose to form SO₂ and O₂ upon TPD in He, with O₂ and SO₂ peaks at 1023 K assigned to Ce⁺⁴ sulfates and peaks at 1123 K assigned to Ce⁺³ sulfates. When H₂ is present in the TPD carrier gas, the sulfates are reduced and a significant fraction of the sulfur is removed as H₂S, with the rest remaining as Ce₂O₂S. When CO is present in the TPD carrier gas, all of the sulfates are reduced to Ce₂O₂S, with the simultaneous formation of CO₂. The formation of CO₂ from the reduction of the sulfate occurs in the same temperature range as CO₂ production from reduction of Pd/ceria, except that more CO₂ is formed from the sulfur-poisoned catalyst. The implications of these results for understanding oxygen storage capacity (OSC) in automotive, three-way catalysts is discussed.

Keywords: ceria, SO₂, H₂S, cerium sulfate, cerium oxy-sulfide, FTIR, TPD, oxygen storage capacity (OSC).

Introduction

Ceria is a crucial component of three-way, automotive, emissions-control catalysts because its redox properties lead to oxygen-storage capacity (OSC) [1]. Since the exhaust in automobiles oscillates between oxidizing and reducing conditions, OSC is necessary for the catalyst to be able to oxidize CO and hydrocarbons in the reducing part of the cycle and to reduce NO under the oxidizing part of the cycle. Ceria, usually in the form of a mixed oxide with zirconia [2-4], performs this function very well. Indeed, the current generation of catalysts would be sufficient to meet very stringent emissions requirements if it were not for the fact that sulfur, present in small amounts in essentially all hydrocarbon fuels, is a serious poison for ceria [5-8].

The typical exhaust currently consists of 5 to 20 ppm of SO₂. At these relatively low concentrations, there is considerable evidence that SO₂ poisons the exhaust catalyst primarily through interactions with ceria and the effect that these interactions have on OSC [5-8]. For example, Beck, et al. reported that just 5 ppm of SO₂ in the exhaust, a level which corresponds to 75 ppm sulfur in the fuel, changed the OSC of an aged catalyst by a factor of two [6]. Similar losses in OSC due to sulfur poisoning were reported by Gandhi and coworkers [9,10]. Finally, the effect of sulfur on OSC as measured by the oxygen sensors that are required for monitoring catalyst performance according to US Federal regulations (OBD-II) is well documented [6,10,11].

The thermodynamics of the Ce-O-S system has been studied rather extensively due to the importance of ceria as a sulfur getter in steel making [12] and as a potential adsorbent for removing H₂S and SO₂ from dilute gaseous streams [13,14]. Under neutral and mildly reducing conditions, the stable species in the presence of sulfur is reported to be Ce₂(SO₄)₃ [15]. Ce, unlike the other rare-earth metals, is not known to form an oxysulfate of the form Ce₂O₂SO₄ [16]. With decreasing O₂ fugacity, Ce₂(SO₄)₃ decomposes, first to CeO₂ and then to Ce₂O₂S [15-18]. However, surprisingly little information is available on the nature of species formed by contacting ceria with H₂S or SO₂ under milder conditions and on the mechanisms by which thermodynamically stable species form.

Some of the more comprehensive adsorption studies for SO₂ on ceria were performed by Lavalley and coworkers [19-22]. For room-temperature adsorption of SO₂ on ceria [19], only surface species, which have been tentatively identified as sulfites or hydrogen sulfites, were observed. For adsorption of SO₂ at 673 K with O₂, sharp bands between 1300 and 1400 cm⁻¹

appeared in the spectrum and were assigned to sulfate groups on the ceria surface. For larger exposures, the main feature in the IR spectrum was a broad band centered near 1160 cm^{-1} , which has been assigned to bulk sulfate formation. The presence or absence of Pt was reported to have little effect on sulfates, showing that ceria is able to oxidize SO_2 without an additional catalyst [21]. Furthermore, the oxidation of SO_2 to SO_4^{2-} occurs on ceria to some extent without the addition of gas-phase O_2 , obviously with the simultaneous reduction of ceria [19]. Finally, bulk sulfates were only formed when the ceria samples were exposed to SO_2 at temperatures above 423 K.

In the work to be described in this paper, we set out to investigate the adsorption and reaction of SO_2 with a Pd-ceria catalyst to gain additional insights into how SO_2 poisons these materials. We will show evidence for various types of surface species based on FTIR and temperature-programmed desorption (TPD) measurements.

Experimental

The TPD experiments were performed in a reactor system that has been described in earlier papers [23,24]. The system is essentially a tubular reactor in which the effluent can be monitored using a quadrupole mass spectrometer. In a typical measurement, 100 mg of sample was placed in the $\frac{1}{4}$ -inch, quartz, tubular reactor, held at atmospheric pressure. For the studies described in this paper, the flow to the reactor was kept constant while increasing the temperature of the reactor at 10 K/min and monitoring the effluent composition. To determine the effect of oxidizing and reducing conditions, the composition of the gas added to the reactor was varied from pure He to He mixed with 5% O_2 , 5% H_2 , or 5% CO . (Note: While TPD in an oxidizing or reducing environment is usually referred to as temperature-programmed oxidation or reduction, we will not distinguish these measurements with a different nomenclature in this paper.) In all cases, the total flow rate of carrier was held at 80 ml/min. The mass spectrometer signal was calibrated with known gas concentrations, enabling us to calculate the absolute coverages corresponding to the TPD signal. It should be pointed out that we were unable to detect SO_3 in any of our measurements. While Pd/ceria should be an excellent catalyst for the oxidation of SO_2 , equilibrium will favor SO_2 over SO_3 at the high temperatures and low partial pressures where SO_2 desorption occurs.

The FTIR spectra were recorded using a Mattson Galaxy FTIR 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 TPD measurements using the same catalysts.

The Pd/ceria catalyst used in this study was prepared in our laboratory using methods identical to those described in previous papers [23-25]. The ceria was formed by thermal decomposition of $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (Alfa Aesar, 99.5%) and was found to have a surface area of approximately $34 \text{ m}^2/\text{g}$. Pd was added to the support by incipient wetness to a final metal loading of 1.0 wt% using aqueous solutions of $\text{Pd}(\text{NH}_3)_4(\text{NO}_3)_2$. After addition of the Pd salt, the catalyst was dried and then calcined at 723 K for approximately 4 hours in air. Since most of the chemistry that we report in this paper is associated with ceria and not Pd, it is important to recognize that 1% Pd corresponds to approximately 0.1 mmol/g. For comparison to the sulfur-poisoned Pd/ceria catalyst, a bulk sample of $\text{Ce}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$, obtained from Alfa Aesar, was also examined as part of this study.

RESULTS

TPD

The TPD results for the bulk sample of $\text{Ce}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$, performed with a pure He carrier gas, are shown in Fig. 1a) and help establish a starting point for understanding SO_2 poisoning of ceria. Decomposition of the sulfate to SO_2 ($m/e = 64$) and O_2 ($m/e = 32$), in a ratio of 2:1, is clearly observed at 1023 K. The amount of SO_2 removed from the sample, 5.5 mmol/g, is within experimental error of the amount expected based on the stoichiometry of the compound. The curves in Fig. 1b) were obtained from the Pd/ceria catalyst after exposing it to flowing He with 1% SO_2 and an excess of O_2 for 20 min at 673 K. The results are virtually identical to those for the bulk sulfate except that the quantity of SO_2 removed from the Pd/ceria catalyst was 2 mmol/g. Since a monolayer of sulfate would correspond to approximately 0.34 mmol/g, assuming a value of 6×10^{18} molecules/ m^2 for the monolayer, the large amount of SO_2 leaving the sample in Fig. 1b) suggests formation of bulk sulfate. This agrees with literature reports that suggest sulfate formation occurs for SO_2 exposure at temperatures above about 473 K in the presence of O_2 [19]. While we do not show results for a pure ceria sample with no Pd, the data were essentially indistinguishable from that shown here. Again, this is in agreement with

literature reports that indicate that the presence of precious metals do not enhance formation of sulfates [20].

In order to observe sulfur species formed under milder conditions, we examined TPD curves for SO₂ adsorption without O₂ at various temperatures, with the results shown in Fig. 2. Fig. 2a) is the result for TPD in a pure He carrier obtained following a 20-min exposure to 1% SO₂ in He at room temperature. The total amount of SO₂ leaving the sample after this exposure was ~0.4 mmol/g, which is close to the monolayer value. Interestingly, approximately half of the SO₂ desorbs below 673 K. Based on the fact that no O₂ desorption occurs simultaneously with the SO₂ desorption below 673 K, we assign this to be molecularly adsorbed SO₂, rather than a sulfate. Obviously, we cannot identify the form of the adsorbed species and these could be sulfites and hydrogen sulfites, as others have suggested [19]. The rest of the SO₂ desorbs in two peaks centered at 1023 and 1123 K. Both of these desorption features are associated with sulfate decomposition, as demonstrated by the simultaneous desorption of O₂. We suggest that the low-temperature peak is associated with Ce⁺⁴ sulfates and the high-temperature peak is due to Ce⁺³ sulfates. This assignment is the result of three observations. First, the ceria in these experiments must be in a reduced form, since formation of sulfates from exposure of ceria to SO₂ requires additional oxygen from the ceria. Second, TPD performed in 5% O₂-95% He, shown in Fig. 2b), give only the low-temperature peak. (In this case, only SO₂ (m/e=64) was monitored since excess O₂ in the gas phase for this experiment prevented us from monitoring m/e =32.) Third, high-temperature thermodynamic data suggest that Ce₂(SO₄)₃ is the only stable form of sulfate at the higher temperatures [15].

Adsorption at 473 K gave results that are virtually indistinguishable from the room-temperature adsorption data, as shown in Fig. 2c). (The desorption of SO₂ below 473 K in this figure is due to the fact that the sample was cooled in flowing SO₂.) However, adsorption at 673 K gave rise to TPD curves that are very different in appearance, as shown in Fig. 2d). First, the amount of SO₂ leaving the sample was ~0.6 mmol/g, an amount larger than that expected for a monolayer but smaller than that observed when adsorption was performed with excess O₂, as in Fig. 1b). The sulfate decomposition peak at 1023 K, associated with Ce⁺⁴, is noticeably larger, implying that oxygen from the ceria lattice has diffused to the surface region, making the surface more “oxidized” than in the case when adsorption is carried out at lower temperatures. Finally, there is an SO₂ desorption feature between 673 and 873 K that was not present when adsorption

was carried out at lower temperatures. The absence of simultaneous O₂ desorption implies that this feature is not associated with a sulfate species, but we can only speculate as to the chemical nature of this surface species.

Fig. 3 shows the TPD curves measured in flowing He following exposure of the sample to 1% SO₂ in He and excess O₂ at room temperature and at 473 K. Fig. 3a), the result obtained following room temperature exposure, is very similar to the result in Fig. 2a), showing that the presence of O₂ has little effect at low temperatures, probably due to the fact that oxidation of reduced ceria is an activated process. The only difference between the two sets of TPD curves in Figs. 2a) and 3a) is the O₂ desorption that occurs just before the onset of sulfate decomposition. This temperature is lower than one would expect for O₂ desorption from the surface of Pd particles but might be due to decomposition of bulk PdO [26]. Following SO₂ adsorption at 473 K in the presence of O₂, the TPD curves in Fig. 3b) show that most of the sulfate decomposes at 1023 K, implying that the ceria surface exists in an oxidized form. In agreement with reports presented by others for the formation of bulk sulfates beginning at 473 K [19], the amount of SO₂ leaving the surface in Fig. 3b), ~0.4 mmol/g, corresponds to slightly more than one monolayer. Exposure to SO₂ in the presence of O₂ at still higher temperatures results only in higher coverages, as shown in Fig. 1b).

It is also interesting to examine desorption under reducing conditions. In Fig. 4, TPD curves are shown following exposure of the Pd/ceria catalyst to SO₂ at 673 K in excess O₂ for 20 min, followed by desorption into a carrier that contained 5% H₂ in He. As discussed earlier, the exposure conditions used to prepare this sample gave rise to a bulk sulfate with a coverage of ~2 mmol/g. The TPD results now show primarily desorption of H₂S ($m/e = 32$ and 34) in a peak centered at 723 K, a much lower temperature than that at which the sulfate decomposes. More interestingly, the amount of H₂S leaving the sample corresponds to only half of the initial coverage of sulfate. This is almost certainly due to the formation of Ce₂O₂S [13]. As demonstration of this fact, an additional TPD experiment was performed immediately after the experiment shown in Fig. 4, but this time the carrier contained 5% O₂ in He. The results are shown in Fig. 5 and demonstrate that the remaining SO₂ could still be removed from the sample under oxidizing conditions, at the normal temperature observed for sulfate decomposition.

To understand the results in Figs. 4 and 5, it is helpful to consider the Ce-O-S phase diagram at 773 K, shown in Fig. 6. The thermodynamic properties, based on data from Kay, et

al. [15], have been extrapolated from high-temperature measurements and should probably be viewed only qualitatively. As mentioned previously, the only stable sulfate formed under oxidizing conditions at high temperatures is $\text{Ce}_2(\text{SO}_4)_3$, and not $\text{Ce}(\text{SO}_4)_2$. The phase diagram also suggests that Ce_2S_3 can only exist at high S_2 pressures. Based on the phase diagram, we assign the peak at $m/e = 64$ in Fig. 4 as resulting from sulfur that is in excess of that needed to form $\text{Ce}_2\text{O}_2\text{S}$. It seems likely that the presence of H_2 , in addition to reducing the ceria, reacts with excess sulfur at the surface to form H_2S . Sulfur from the bulk is unable to react with H_2 and simply decomposes from the sulfate to $\text{Ce}_2\text{O}_2\text{S}$.

When CO is used in place of H_2 as the reducing agent, the results are quite different, as shown in Fig. 7. In Fig. 7a), TPD results are shown for an oxidized Pd/ceria catalyst using a carrier gas that was 5% CO in He. The total amount of CO_2 that desorbed is 1 mmol/g, with CO_2 from the reduction of Pd forming below 450 K and CO_2 from the reduction of ceria forming between 700 and 900 K. Since previous results have shown that a stable carbonate, corresponding to 0.5 mmol CO_2/g , is formed following reduction of Pd/ceria catalysts in CO [23,27], the total amount of oxygen atoms removed from the sample in this experiment could be as high as 1.5 mmol/g. For comparison, complete reduction of a PdO/ CeO_2 catalyst to Pd/ Ce_2O_3 would give 3.0 mmol/g of oxygen.

The analogous TPD results for the Pd/ceria after exposure to SO_2 in excess O_2 are shown in Fig. 7b). (Based on a subsequent SO_2 desorption measurement analogous to those in Fig 5, the SO_2 coverage on the sample in Fig. 7b) was 1.2 mmol/g.) The only product formed on the sulfated catalyst in significant amounts during TPD in CO was CO_2 and this formed in essentially the same temperature regime as that found on the unpoisoned catalyst. However, the sulfur poisoned catalyst showed much larger amounts of CO_2 formation than the fresh catalyst due to the reduction of the sulfate species. The amount of CO_2 formed in Fig. 7b) was approximately 4 mmol/g, an amount which clearly implies reduction of the sulfate ions. It has been reported previously that the amount of oxygen that could be reversibly removed from a Pd/ceria catalyst in a series of CO and O_2 pulses increased after treating the catalyst with SO_2 [24]. The present results confirm that finding and also show that reduction of the sulfate occurs at a similar temperature to that at which the Pd/ceria catalyst is reduced.

FTIR Measurements

The TPD results discussed in the previous section provide only indirect information on the nature of surface species that are formed following exposure of Pd/ceria to SO₂. For example, the observation of sulfate decomposition features following exposure of Pd/ceria to SO₂ at room temperature could be due to sulfates formed at room temperature or to sulfates formed by conversion of adsorbed SO₂ at higher temperatures during the temperature ramp. To gain insights into the nature of the species formed on the surface, we performed DRIFTS measurements under similar conditions to those used in the TPD experiments.

In Fig. 8, spectra were taken after exposing an oxidized Pd/ceria catalyst, shown in Fig. 8a) to 1% SO₂ in He at room temperature, followed by heating in pure flowing He to various temperatures. As shown in the spectrum of Fig. 8b), there is a single band centered at 980 cm⁻¹ following adsorption at room temperature. As the sample is heated, the species responsible for the peak at 980 cm⁻¹ is converted to a species with a strong vibrational band at 1345 cm⁻¹, beginning at approximately 373 K. The conversion of the species at 980 cm⁻¹ to the one at 1345 cm⁻¹ is not reversible upon cooling. The spectra at 373 and 473 K also show bands at ~1210 and 1240 cm⁻¹, which seem to suggest an intermediate species is formed between the high- and low-temperature forms. The peak at 1345 cm⁻¹ has been observed in earlier studies and assigned to a surface sulfate [19-22], a conclusion that is in agreement with our interpretation of the TPD results from the previous section. The FTIR results show conclusively that the surface sulfate did not form below approximately 473 K in our experiments.

The species responsible for the peak at 980 cm⁻¹ is more difficult to assign. Since gas-phase SO₂ has major peaks at 1151 and 1362 cm⁻¹ and gas-phase SO₃ at 1061 and 1391 cm⁻¹, the adsorbed species must be significantly perturbed from simple gas-phase species. Given that the gas-phase SO₂ anion is reported to have a symmetric stretch at 991 cm⁻¹ [28], it is likely that the adsorbed SO₂ takes on a negative charge by interacting with oxygen anions at the ceria surface. Therefore, the assignment of these peaks to sulfites and hydrogen sulfites is reasonable [19].

Fig. 9 shows data from a set of experiments analogous to those described in Fig. 2. Here, the sample was exposed to 1% SO₂ in He for 20 min at the indicated temperature and then flushed with He before taking the spectrum. The results are virtually identical to those in Fig. 8, showing that the temperature at which exposure takes place is not crucial. One point worth noting in the spectrum shown in Fig. 9d) is that no new features are observed for adsorption of

SO₂ at 673 K. Based on the results from our TPD experiments in Fig. 2d), we expected to observe a feature that could be associated with the high-temperature, molecularly adsorbed form of SO₂ between 673 and 873 K. Also, given that bulk sulfates show intense absorption in a broad region centered at 1160 cm⁻¹, very little bulk sulfate is formed upon adsorption in the absence of O₂. This agrees with the relatively low coverages observed in the TPD following adsorption in the absence of O₂.

To determine what changes occur on the surface during reduction of the sulfate, we examined a sulfated surface after treatment in either CO or H₂. Since the data for the two reductants is similar, we only show results for CO reduction. Initially, the Pd/ceria catalyst was exposed to 1% SO₂ in excess O₂ at 673 K, cooled to room temperature, and finally heated in 5% CO to various temperatures. The spectra recorded from this surface at room temperature and after heating in CO to 623 K were essentially identical, so that only the spectrum taken after heating to 623 K in CO is shown, Fig. 10a). This spectrum is indicative of bulk sulfates [19]. After reduction in CO at 773 and 973 K, we observed removal of the sulfate bands, with the simultaneous formation of new features at 1160, 1385, and 1440 cm⁻¹, which we tentatively assign to lattice stretches of Ce₂O₂S.

Discussion

The TPD and FTIR results reported here demonstrate the rich chemistry involved with sulfur interactions on ceria-supported catalysts. Indeed, it is somewhat surprising how easily the various Ce-O-S compounds convert from one compound to another. At temperatures below 473 K, we have shown that SO₂ adsorbs primarily in a molecular form, possibly as sulfites and hydrogen sulfites [19]. These are oxidized to sulfates at higher temperatures and the sulfates are stable to above 850 K in oxidizing and neutral environments. Under reducing conditions, the sulfates can be reduced to Ce₂O₂S above 673 K. The oxysulfide can also be reoxidized to the sulfate.

There are apparent discrepancies between this work and model studies performed by Overbury, et al. [29] and by Rodriguez, et al. [30], which can probably be explained by the types of samples used and the experimental conditions employed [31]. Overbury, et al. examined adsorption on ceria films deposited in vacuum and did not observe significant sulfate formation on their oxidized sample. They also reported dissociation to the sulfide at room temperature on reduced samples. Research from our laboratory has shown that ceria is very structure sensitive

and that single crystals and ceria films that have been annealed to high temperature are much less easily reduced than ceria powders that have not been heated to high temperature. Therefore, their failure to see sulfates is likely due to differences in the properties of ceria powders and the ceria films used in their study. Sample dependences and experimental conditions may also explain why Rodriguez, et al. observed sulfate formation at room temperature. Finally, we note that a recent XPS studies of SO₂ adsorption on ceria films performed in our laboratory showed excellent agreement with the data we report in this paper [32]. Of course, the idea that SO₂ adsorption on ceria is structure sensitive raises interesting questions about the nature of the surface of ceria powders and the types of sites that are present for interacting with SO₂.

In agreement with our previous CO-O₂ pulse study on Pd/ceria [23], we again observe a significant *increase* in the amount of oxygen that can be removed from a Pd/ceria catalyst after poisoning with sulfur, due to oxidation and reduction of sulfates. Surprisingly, the reduction of cerium sulfates occurs in the same temperature range observed for reduction of ceria. The implications of this result for understanding Oxygen Storage Capacity (OSC) and for the characterization methods that we use to compare materials are most significant. Clearly, it is well established that sulfur poisons the OSC of ceria-supported metals [5-10]. However, the temperature-programmed reduction and pulse-reactor studies that are commonly used to measure OSC must be looked at carefully.

It is useful to examine how OSC is measured in those situations where a decrease in OSC was reported due to the presence of SO₂. Beck and Sommers measured oxygen uptake and release in a gaseous mixture that simulated a real exhaust environment [7]. A key point to notice is that the gas mixture in their study oscillated from oxidizing to reducing conditions by switching from 0.2% O₂ to 1.0% O₂ every 0.5 sec, while maintaining a steady concentration of 10% H₂O and 10% CO₂. Likewise, Hepburn, et al., who also reported that CO-O₂ pulse studies were an unreliable measure of OSC, used a pulse-flame-combustor method in which H₂O and CO₂ are again major gas-phase components above the catalyst [10]. Based on the fact that ceria-supported metals are active for a number of reactions that are important in the catalytic converter, including water-gas shift (WGS) [33,34], steam reforming [34,35], and CO₂ reforming [23], it seems very likely that H₂O and CO₂ are key components in the reaction mixture and that understanding their role is necessary for understanding OSC. Based on the fact that there appears to be a good correlation between OSC and steady-state, water-gas-shift rates on Pd/ceria [36], it

seems likely that the role of ceria in OSC may be more as a promoter of certain reactions than as a true oxygen “capacitor”.

While the present study has provided information on several important species that are formed following exposure of ceria to SO₂, there is still much to learn concerning how the various species transform to other species. There must be intermediate stages between Ce₂O₂S and cerium sulfates. In another example, the mechanism for the formation of H₂S upon heating cerium sulfates in H₂ must involve a complex set of elementary reaction steps. Clearly, the Ce-O-S system involves fascinating chemistry and much work is needed to fully understand the catalytic chemistry of this system.

Conclusion

SO₂ poisoning of ceria-supported catalysts involves formation of a complex set of compounds. Depending on the conditions used for exposing these catalysts to SO₂, one can form molecularly adsorbed species (sulfites?), sulfates, and Ce₂O₂S. Much of the complexity of this system can be understood from the Ce-O-S phase diagram. Depending on the adsorption temperature and the amount of O₂ present, both surface and bulk cerium compounds can be formed. The decomposition of bulk and surface sulfates to SO₂ and O₂ occurs in a relatively narrow temperature range and can be easily identified in TPD. The reduction of sulfates to Ce₂O₂S in the presence of CO is relatively facile and occurs in the same temperature range observed for reduction of a normal Pd/ceria catalyst. Reduction of the sulfates with H₂ results in a mixture of H₂S desorption and Ce₂O₂S formation. The complexity of this system suggests that there is still much to be learned about the effects of SO₂ on oxygen-storage capacity in automotive, three-way catalysts.

Acknowledgements

The authors gratefully acknowledge support from the DOE, Basic Energy Sciences, Grant # DE-FG03-85-13350 and from the Coordinating Research Council, Inc.

References

- 1) Yao, H. C., and Yao, Y. F. Y., *J. Catal.*, **86**, 254 (1984).
- 2) Nunan, J. G., Williamson, W. B., and Robota, H. J., *SAE Paper # 960798* (1996).
- 3) Yao, M. H., Baird, R. J., Kunz, F. W., and Hoost, T. E., *J. Catal.*, **166**, 67 (1997).
- 4) Bunluesin, T., Gorte, R. J., and Graham, G. W., *Appl. Catal. B*, **14**, 105 (1997).
- 5) Beck, D. D., Sommers, J. W., and Dimaggio, C. L., *Appl. Catal. B*, **3**, 205 (1994).
- 6) Beck, D. D., Sommers, J. W., and DiMaggio, C. L., *Appl. Catal. B*, **11**, 273 (1997).

- 7) Beck, D. D., and Sommers, J. W., *Appl. Catal. B.*, **6**, 185 (1994).
- 8) Beck, D. D., *Catalyst Deactivation*, **111**, 21 (1997).
- 9) Gandhi, H. S., presented at the CRC Auto/Oil Symposium, Dearborn, MI, (1997).
- 10) Hepburn, J. S., Dobson, D. A., Hubbard, C. P., Guidberg, S. O. Thanasiu, E., Watkins, W. L., Burns, B. D., and Gandhi, H. S., *SAE Paper # 942057* (1994).
- 11) Rieck, J. S., Collins, N. R., and Moore, J. S., *SAE Paper # 980665* (1998).
- 12) Kilbourn, B. T., *Cerium: A Guide to its Role in Chemical Technology*, (Molycorp, Inc., Fairfield, NJ, 1992) pp. 10-17.
- 13) Zeng, Y., Kaytakoglu, S., and Harrison, D. P., *Chem. Eng. Sci.*, **55**, 4893 (2000).
- 14) Akyurtlu, J. F., and Akyurtlu, A., *Chem. Eng. Sci.*, **54**, 2991 (1999).
- 15) Kay, D. A. R., Wilson, W. G., and Jalan, V., *J. Alloys & Comp.*, **192**, 11 (1993).
- 16) Dwivedi, R. K., and Kay, D. A. R., *Metall. Trans. B*, **15B**, 523 (1984).
- 17) Fruehan, R. J., *Metall. Trans. B*, **10B**, 143 (1979).
- 18) Akila, R., Jacob, K. T., and Shukla, A. K., *Metall. Trans. B*, **18B**, 163 (1987).
- 19) Waqif, M., Bazin, P., Saur, O., Lavalley, J. C., Blanchard, G., and Touret, O., *Appl. Catal. B*, **11**, 193 (1997).
- 20) Bazin, P., Saur, O., Lavalley, J. C., Blanchard, G., Visciglio, V., Touret, O., *Appl. Catal. B.*, **13**, 265 (1997)
- 21) Bazin, P., Saur, O., Lavalley, J. C., Le Govic, A. M., and Blanchard, G., *Stud. Surf. Sci. Catal.*, **116**, 571 (1998).
- 22) Waqif, M., Pieplu, A., Saur, O., Lavalley, J. C., Blanchard, G., *Solid State Ionics*, **95**, 163 (1997).
- 23) Sharma, S., Hilaire, S., Vohs, J. M., Gorte, R. J., and Jen, H.-W., *J. Catal.*, **190**, 199 (2000).
- 24) Hilaire, S., Sharma, S., Gorte, R. J., Vohs, J. M., and Jen, H.-W., *Catal. Lett.*, **70**, 131 (2000).
- 25) Wang, X., and Gorte, R. J., *Catal. Lett.*, **73**, 15 (2001).
- 26) Putna, E. S., Vohs, J. M., and Gorte, R. J., *Surf. Sci.*, 391, L11778 (1997).
- 27) Hilaire, S., Wang, X., Luo, T., Gorte, R. J., and Wagner, J., *Applied Catalysis A*, **215**, 271 (2001).
- 28) Forney, D., Kellogg, C.B., Thompson, W.E., and Jacox, M.E., *J. Chem. Phys.*, **113**, 86 (2000).
- 29) Overbury, S. H., Mullins, D. R., Huntley, D. R., Kundakovic, L., *J. Phys. Chem. B*, **103**, 11308 (1999).
- 30) Rodriguez, J. A., Jirsak, T., Freitag, A. Hanson, J. C., Larese, J. Z., and Chaturvedi, S., *Catal. Lett.*, **62**, 113 (1999).
- 31) Cordatos, H., Bunluesin, T., Stubenrauch, J., Vohs, J. M., and Gorte, R. J., *J. Phys. Chem.*, **100**, 785 (1996).
- 32) Ferrizz, R., Gorte, R. J., and Vohs, J. M., *Catal. Lett.*, in press.
- 33) Barbier, J., and Duprez, D., *Appl. Catal. B*, **4**, 105 (1994).
- 34) Whittington, B. I., Jiang, C. J., and Trimm, D. L., *Catal. Today*, **26**, 41 (1995).
- 35) Craciun, R., Shereck, B., and Gorte, R. J., *Catal. Lett.*, **51**, 149 (1998).
- 36) Bunluesin, T., Gorte, R. J., and Graham, G. W., *Appl. Catal. B*, **15**, 107 (1998).

Figure Captions

- Fig. 1. TPD results using a He carrier gas for the following samples: (a) bulk $\text{Ce}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$; (b) Pd/Ceria after exposure to 1% SO_2 and excess O_2 at 673 K for 20 min.
- Fig. 2. TPD results using a He carrier gas for a Pd/ceria catalyst after 20-min exposure to 1% SO_2 in pure He. The exposure temperature in each of the curves was as follows: (a) 298 K; (c) 473 K; (d) 673 K. In (b), the exposure was the same as in (a) but the carrier gas in TPD contained 5% O_2 in He.
- Fig. 3. TPD results using a He carrier gas for a Pd/ceria catalyst following exposure to 1% SO_2 in excess O_2 for 20 min at: (a) 298 K; (b) 473 K.
- Fig. 4. TPD curves for a Pd/ceria catalyst after exposure to 1% SO_2 in excess O_2 at 673 K for 20 min. The carrier gas contained 5% H_2 in He.
- Fig. 5. TPD curves obtained immediately after the experiment shown in Fig. 4, using a carrier containing 5% O_2 in He.
- Fig. 6. Phase diagram for Ce-O-S system at 773 K. The data used in the calculation was obtained from reference [15].
- Fig. 7. TPD curves for a Pd/ceria catalyst using a carrier that was 5% CO in He. (a) Results for an oxidized Pd/ceria catalyst. (b) Data for the same catalyst after exposure to 1% SO_2 with excess O_2 at 673 K for 20 min.
- Fig. 8. DRIFTS spectra of a Pd/ceria catalyst after the following treatments: (a) oxidized Pd/ceria at 298 K; Pd/ceria after exposure to 1% SO_2 in He at 298 K for 20 min at (b) 298 K; (c) 373 K; (d) 473 K; (e) 573 K; and (f) 673 K.
- Fig. 9. DRIFTS spectra of a Pd/ceria catalyst: (a) before SO_2 exposure at 298 K; (b) after 20-min exposure to 1% SO_2 in He at 298 K; (c) after 20-min exposure to 1% SO_2 in He at 473 K; (d) after 20-min exposure to 1% SO_2 in He at 673 K.
- Fig.10. DRIFTS spectra of a Pd/ceria catalysts after 20-min exposure to 1% SO_2 in excess O_2 , followed by heating in 5% CO taken in mixture of 5% CO in He at: (a) 623 K; (b) 773 K; (c) 973 K.