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## TPD and XPS Investigation of the Interaction of SO<sub>2</sub> with Model Ceria Catalysts

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### Keywords

ceria, SO<sub>2</sub>, cerium sulfate, TPD, XPS

### Comments

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## TPD and XPS Investigation of the Interaction of SO<sub>2</sub> with Model Ceria Catalysts

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### Abstract

The interaction of SO<sub>2</sub> with model thin film ceria catalysts was studied using temperature programmed desorption (TPD) and X-ray photoelectron spectroscopy (XPS). During TPD of ceria samples that had been exposed to SO<sub>2</sub> at room temperature, SO<sub>2</sub> desorbed in peaks centered at 473, 883 and 963 K. The lower temperature peak is associated with molecularly adsorbed SO<sub>2</sub>, while the higher temperature peaks are due to decomposition of adsorbed sulfates. XPS results show that at room temperature a small fraction of the adsorbed SO<sub>2</sub> is oxidized to SO<sub>4</sub><sup>2-</sup> using oxygen supplied by the ceria. This reaction also results in partial reduction of the ceria surface. High coverages of surface sulfate species could be produced by exposing the ceria samples to mixtures of SO<sub>2</sub> and O<sub>2</sub> at 573 K. In addition to producing gaseous SO<sub>2</sub>, thermal decomposition of surface sulfates at temperatures above 823 K resulted in the formation of an oxy-sulfide (Ce<sub>2</sub>O<sub>2</sub>S) on the ceria surface.

**Keywords:** ceria, SO<sub>2</sub>, cerium sulfate, TPD, XPS.

## Introduction

Ceria is an important component in the three-way catalyst for automotive emissions control, where its ability to store and release oxygen is utilized to maintain the gas phase composition in a narrow operating window in which the simultaneous conversion of CO, hydrocarbons, and NO<sub>x</sub> can take place [1-5]. Unfortunately, this important oxygen storage function is poisoned by exposure of the ceria to sulfur containing compounds [6-8]. Current automotive fuels contain up to 300 ppm of sulfur and after combustion, the engine exhaust typically contains up to 20 ppm of SO<sub>2</sub>. This concentration is sufficient to have a deleterious effect on the oxygen storage capacity of the ceria, which in turn adversely affects the performance of the catalytic converter. Recently enacted government regulations in the United States and Europe will require a substantial reduction in fuel sulfur content. Even small amounts of sulfur, however, will over time result in loss of oxygen storage capacity. For example, Beck et al. have shown that at SO<sub>2</sub> levels of only 5 ppm, the oxygen storage capacity of an aged catalyst is still reduced by more than 50% [8]. Hence, the sulfur poisoning of ceria will continue to be an important issue in environmental catalysis, as we strive to achieve lower levels of automotive emissions.

Conventional wisdom places cerium sulfate as the prime culprit for ceria deactivation [9-10-11]. Cerium sulfate is thought to "lock" the cerium cations in the +3 oxidation state and thereby disrupt the Ce<sup>4+</sup>/Ce<sup>3+</sup> redox cycle that is needed for oxygen storage. Although the effects of SO<sub>2</sub> exposure on the oxygen storage properties of ceria are well documented [6-11], surprisingly little is known about the adsorption and reaction of SO<sub>2</sub> on ceria and the thermodynamic properties of cerium sulfates. In one of the few detailed studies of the adsorption of SO<sub>2</sub> on high surface area ceria catalysts, Waqif et al. showed using FTIR that SO<sub>2</sub> can react on ceria at temperatures as low as 298 K to form a surface sulfate species. These sulfates were found to be stable up to 973 K [10]. Recently, several studies of the interaction of SO<sub>2</sub> with low surface area model ceria catalysts have also appeared in the literature. Rodriguez et al. have used photoemission and XANES to study the adsorption and reaction of SO<sub>2</sub> on ceria thin films supported on Pt(111) and ceria powders [12]. They reported that SO<sub>2</sub> reacts at room temperature on ceria to form sulfates, but in contrast to the Waqif et al. study, they concluded that the

sulfates decompose and desorb as SO<sub>2</sub> at temperatures between 353 and 698 K. Overbury et al. have used TPD to study the interaction of SO<sub>2</sub> with ceria thin films [13]. They found that upon heating SO<sub>2</sub>-dosed, epitaxial CeO<sub>2</sub>(111) films supported on Ru(0001), SO<sub>2</sub> desorbs between room temperature and 598 K. XPS results reported in the same study, however, did not provide any evidence for the formation of sulfates on the ceria surface.

Although the previous fundamental surface science studies provide some insight into the interaction of SO<sub>2</sub> with both ceria powders and thin films, questions still remain concerning the conditions under which SO<sub>2</sub> reacts on ceria to form sulfates and more importantly the thermal stability of these species. In order to provide additional insight into the formation and thermal stability of sulfates on ceria we have used TPD in combination with XPS to probe the adsorption and reaction of SO<sub>2</sub> on model ceria catalysts composed of polycrystalline ceria thin films supported on tantalum foil and on Mo(100). The results obtained in this study show that the coverage of surface sulfates produced by exposure of ceria to SO<sub>2</sub> is dependent on both temperature and the presence of gas phase oxygen. Once formed the sulfates are thermally stable up to temperatures approaching 973 K.

## **Experimental**

Temperature programmed desorption (TPD) experiments were conducted in a small, high vacuum chamber designed for expedient exchange of samples and rapid evacuation of reactant gases. This TPD system had a base pressure of approximately  $5 \times 10^{-8}$  Torr, and was equipped with a VGQ mass spectrometer, and two variable leak valves for exposing the sample to reactant gases. The ceria samples used in the TPD studies consisted of polycrystalline films supported on a tantalum foil and were prepared by spray pyrolysis of an aqueous cerium nitrate solution. Following film deposition, the sample was dried at 573 K and then mounted on a sample manipulator that was attached to the vacuum system. The sample could be resistively heated and the temperature was monitored with a chromel-alumel thermocouple spot-welded to the back of the tantalum foil sample holder. Once in vacuum the cerium nitrate film was converted to CeO<sub>2</sub> by annealing at 773 K for 1 hour in  $5 \times 10^{-5}$  Torr of O<sub>2</sub>. TPD experiments were also

performed with a  $\text{Ce}(\text{SO}_4)_2$  thin film. The  $\text{Ce}(\text{SO}_4)_2$  film was prepared by spraying an aqueous solution of cerium sulfate onto a tantalum foil followed by drying at 573 K. During each TPD experiment the sample was heated at a rate of 4 K/sec and m/e values of 80, 64, 48, and 32 were monitored.

X-ray photoelectron spectroscopy (XPS) experiments were conducted in an ultra-high vacuum chamber (base pressure of  $2 \times 10^{-10}$  Torr) equipped with a hemispherical electron energy analyzer and x-ray source. The sample studied using XPS consisted of a polycrystalline ceria thin film that was vapor-deposited onto a Mo(100) single crystal. The Mo(100) single crystal was mounted on a UHV sample manipulator and could be resistively heated. The temperature was monitored using a chromel-alumel thermocouple attached to the back surface of the sample. Prior to film deposition the Mo(100) crystal was cleaned by sputtering  $\text{Ar}^+$  ions and then annealed at 1173 K. Ceria film growth was achieved by exposing the Mo(100) surface held at 450 K to a flux of cerium atoms in a  $\text{O}_2$  background of  $1 \times 10^7$  Torr. A home built electron-beam evaporative cerium source was used to provide the flux of cerium atoms and a quartz crystal, film thickness monitor adjacent to the sample was used to determine the film thickness. The ceria films used in this study had a thickness of approximately 40 nm. XPS analysis showed that ceria films produced using this deposition procedure were fully oxidized, and completely covered the Mo(100) surface. Reference XPS spectra of a bulk cerium sulfate ( $\text{Ce}(\text{SO}_4)_2$ , Alpha Aesar) and highly reduced ceria were also collected. The cerium sulfate sample was identical to that used in the TPD studies, while the reduced ceria sample consisted of a  $\text{CeO}_2(111)$  single crystal that had been sputtered with  $\text{Ar}^+$  ions.

## Results

The adsorption and reaction of  $\text{SO}_2$  on ceria was initially studied using TPD. Prior to each TPD run, the ceria film was heated to 973 K in  $5 \times 10^{-5}$  Torr  $\text{O}_2$ , and then annealed at 773 K for 5 minutes in this same  $\text{O}_2$  background. This pre-treatment was used to ensure a sulfur-free, oxidized ceria surface. The sample was then exposed for 10 minutes to a gas mixture that contained  $3 \times 10^{-5}$  Torr of  $\text{O}_2$  and  $3 \times 10^{-5}$  Torr of  $\text{SO}_2$ . The sample temperature was held at either 298 or 573 K during exposure to the  $\text{SO}_2$ -containing gas. Following exposures at 573 K the sample was allowed to cool to room

temperature in the SO<sub>2</sub>-rich gas at which point the system was evacuated. The results of these TPD experiments are presented in Figure 1.

Curve a in Figure 1 was obtained from a ceria sample that was exposed to SO<sub>2</sub> and O<sub>2</sub> at room temperature. Similar results were obtained from a sample that was exposed to only SO<sub>2</sub> at this temperature. Sulfur dioxide desorption is detected as a large peak centered at approximately 473 K. This peak is most likely due to desorption of molecularly adsorbed SO<sub>2</sub>. Additionally, two smaller overlapping SO<sub>2</sub> desorption features are observed at 883 and 963 K. Since it is unlikely that molecularly adsorbed SO<sub>2</sub> would be stable to these high temperatures, these species are tentatively assigned to more strongly bound surface sulfates. This assignment is consistent with that reported by Waqif et al. who used FTIR and TGA to characterize the interaction of SO<sub>2</sub> with ceria powders [10]. In that study it was found that cerium sulfates decomposed between 823 and 973 K. TPD has also been used in our laboratory to study the reaction of SO<sub>2</sub> with ceria powders and gave a similar result [14]. Additional support for this assignment is provided by curve c in Figure 1 which corresponds to the SO<sub>2</sub> desorption as a function of temperature from a thin film of Ce(SO<sub>4</sub>)<sub>2</sub>. As noted above, this sample was prepared by spraying an aqueous solution of Ce(SO<sub>4</sub>)<sub>2</sub> onto a tantalum foil substrate. Note that decomposition of the bulk sulfate and evolution of SO<sub>2</sub> occurs at 1023 K. The somewhat lower decomposition temperature in the case the ceria film may reflect differences in the thermal stability of surface versus bulk sulfate species.

One would expect that that in addition to SO<sub>2</sub>, sulfate decomposition would produce some O<sub>2</sub>. The m/e 32 signal did contain a broad peak near 900 K. Unfortunately, exposure of the sample in 10<sup>-5</sup> torr of O<sub>2</sub> during synthesis of the ceria film and again during SO<sub>2</sub> exposure resulted in a high background level of O<sub>2</sub> in the chamber. This caused the m/e 32 spectrum to be of very poor quality. It was, therefore, not possible to quantify the amount of O<sub>2</sub> produced during sulfate decomposition.

Curve b in Figure 1 was obtained from a ceria sample prepared in the same manner as that in curve a, except that the exposure to SO<sub>2</sub> and O<sub>2</sub> was carried out at a sample temperature of 573 K. For this sample, SO<sub>2</sub> desorption was detected over the same temperature ranges as that for the sample dosed at 298 K; however, the relative intensities of the peaks are somewhat different. Dosing at the higher temperature

produced an increase in the intensity of the high-temperature peaks at 883 and 963 K which result from decomposition of surface sulfates, relative to the low-temperature peak due to desorption of molecularly adsorbed SO<sub>2</sub>. This result demonstrates that formation of the surface sulfates is a thermally activated process. In a separate set of TPD experiments with ceria powders it was shown that the increase in the area of the high-temperature peaks requires the sample to be exposed to both O<sub>2</sub> and SO<sub>2</sub> at 573 K [14]. This result is again consistent with the conclusion that the high-temperature peaks are due to decomposition of sulfate species.

The results presented in Figure 1 indicate that several different sulfur-containing species can be formed on the ceria surface: one that desorbs at low temperature that is most likely molecularly adsorbed SO<sub>2</sub> and one or possibly two species that decompose between 770 and 1020 K which are most likely sulfate species. In order to further identify the various adsorbed sulfur containing species, XPS spectra of an SO<sub>2</sub>/O<sub>2</sub> dosed ceria film were collected as a function of the sample annealing temperature. XPS spectra of a freshly prepared ceria film prior to exposure to SO<sub>2</sub> and a reference spectrum of bulk Ce(SO<sub>4</sub>)<sub>2</sub> were also collected.

The S(2p) XPS spectra of a ceria film dosed with SO<sub>2</sub> and O<sub>2</sub> as a function of the sample annealing temperature are displayed in Figure 2. For comparison purposes the S(2p) spectrum of bulk Ce(SO<sub>4</sub>)<sub>2</sub> is contained in part a of the figure and is composed of two overlapping peaks centered at 168.8 and 167.5 eV which correspond to the S(2p<sub>1/2</sub>) and S(2p<sub>3/2</sub>) spin-orbit states, respectively. These peak positions are consistent with those reported in the literature for cerium sulfate [12,15] and correspond to sulfur atoms with an oxidation state of +6. A curve resolution of the spectrum is included in the figure.

The spectra in part b of Figure 2 were obtained from a ceria film that had been dosed with 3×10<sup>-5</sup> Torr of O<sub>2</sub> and 3×10<sup>-5</sup> Torr of SO<sub>2</sub> at 298 K. The spectrum obtained immediately after dosing clearly contains multiple peaks and as shown in the figure, it can be fit using two separate S(2p) doublets. One of the doublets has peaks located at the same energies as those in the spectrum of Ce(SO<sub>4</sub>)<sub>2</sub>, i.e. 168.8 and 167.5 eV. Thus, a fraction of the adsorbed SO<sub>2</sub> is oxidized to sulfate. The second doublet is located at lower energy and has peaks centered at 166.0 and 167.3 eV. These peak positions are consistent with those reported in the literature for S<sup>+4</sup> [12,15]. These peaks can,



therefore, be assigned to either molecularly adsorbed  $\text{SO}_2$  or  $(\text{SO}_3)^{2-}$  species. Assuming that  $\text{SO}_2$  interacts with exposed  $\text{O}^{2-}$  anions on the ceria surface, molecularly adsorbed  $\text{SO}_2$  and a surface sulfite  $((\text{SO}_3)^{2-})$  are essentially the same species. In the remainder of the paper we will refer to this species as molecularly adsorbed  $\text{SO}_2$ .

Briefly annealing the  $\text{SO}_2/\text{O}_2$ -dosed sample to 823 and then 923 K produced dramatic changes in the S(2p) spectrum. These include the near disappearance of the peaks due to molecularly adsorbed  $\text{SO}_2$  and the emergence of a new doublet between 158 and 163 eV. The disappearance of the peaks due to adsorbed  $\text{SO}_2$  upon heating to 923 K is consistent with the TPD data in Figure 1, which shows that  $\text{SO}_2$  desorbs in a peak centered at 473 K which has a broad tail that extends up to approximately 873 K. Concomitant with the loss of intensity of peaks due to adsorbed  $\text{SO}_2$  was an increase in the intensity of the peaks due to adsorbed sulfate. This result demonstrates that a fraction of the adsorbed  $\text{SO}_2$  is oxidized to sulfate upon heating. The oxygen required for this reaction must be supplied by the ceria support. The S(2p) features that emerge at lower binding energies upon heating to 923 K can be fit to a doublet with peaks centered at 161.3 and 160.0 eV. These peak positions are consistent with those reported in the literature for  $\text{S}^{2-}$  [15-17] and, therefore, indicate the formation of a surface cerium sulfide.

Heating the  $\text{SO}_2/\text{O}_2$ -dosed sample to 1123 K produced a significant decrease in the intensity of the S(2p) doublet due to surface sulfate species. This feature is now barely resolvable from the baseline in the spectrum. This is consistent with the TPD data, and allows the  $\text{SO}_2$  desorption peaks between 773 and 1023 K to be assigned to decomposition of surface sulfates. In contrast to the sulfate peaks, the sulfide peaks decreased only slightly in intensity upon heating to 1123 K. Since the sulfide peaks emerge in the same temperature range in which sulfate decomposition occurs, a fraction of the surface sulfates must react with the substrate to form cerium sulfide or cerium oxy-sulfide, rather than decomposing to produce gaseous  $\text{SO}_2$ . The surface sulfide species was found to be very stable and could only be removed by annealing in  $5 \times 10^{-5}$  Torr of  $\text{O}_2$  at 973 K.

In addition to S(2p), O(1s) and Ce(3d) XPS spectra of the  $\text{SO}_2/\text{O}_2$ -dosed ceria sample were collected. Following exposure to  $\text{SO}_2/\text{O}_2$  at 298 K the O(1s) spectrum contained two peaks centered at 529.2 and 531.1 eV which can be assigned to the ceria

substrate and adsorbed  $\text{SO}_x$  species, respectively. Unfortunately, it was not possible to distinguish between molecularly adsorbed  $\text{SO}_2$  and sulfate in the O(1s) spectrum. Heating to 823 K produced only a slight decrease in the intensity of the O(1s) peak due to the adsorbed  $\text{SO}_x$  species. A small O(1s) peak due to  $\text{SO}_x$  was still present upon heating to 923 K. This peak, however, was no longer detected after heating to 1123 K. These results are again consistent with the TPD data.

Figure 3 displays the Ce(3d) XPS spectrum of the  $\text{SO}_2/\text{O}_2$ -dosed sample as a function of annealing temperature. For comparison purposes, the Ce(3d) spectrum of the ceria film prior to exposure to  $\text{SO}_2/\text{O}_2$  and of a highly reduced  $\text{CeO}_2(111)$  single crystal surface are also displayed in the figure. The spectrum of the clean ceria film is indicative of  $\text{Ce}^{+4}$  [18-22]. Based on the work of Creaser et al. [20] and Pfau et al. [21-22] this spectrum can be assigned as follows. The peaks labeled u are due to  $3d_{3/2}$  spin-orbit states, and those labeled v are the corresponding  $3d_{5/2}$  states [20-21]. The u<sup>'''</sup>/v<sup>'''</sup> doublet is due to the primary photoemission from  $\text{Ce}^{+4}$ . The u/v and u<sup>''</sup>/v<sup>''</sup> doublets are shakedown features resulting from transfer of one or two electrons from a filled O 2p orbital to an empty Ce 4f orbital. The spectrum of the highly reduced  $\text{CeO}_2(111)$  surface is indicative of  $\text{Ce}^{+3}$  [18-22]. The u<sup>'</sup>/v<sup>'</sup> doublet in this spectrum is due to primary photoemission from  $\text{Ce}^{+3}$ , and the u<sup>0</sup>/v<sup>0</sup> doublet is a shakedown feature resulting from transfer of one electron from a filled O 2p orbital to a Ce 4f orbital during photoemission from  $\text{Ce}^{+3}$  [20-21].

Exposure of the ceria sample to  $\text{SO}_2$  and  $\text{O}_2$  at 298 K produced several changes in the Ce(3d) spectrum relative to that of the clean ceria support, the most noticeable being the emergence of peaks at 886 and 904 eV. These peak positions correspond to those for the u<sup>'</sup>/v<sup>'</sup> doublet in the spectrum of  $\text{Ce}^{+3}$  on the highly reduced  $\text{CeO}_2(111)$  surface. The corresponding u<sup>0</sup>/v<sup>0</sup> doublet for  $\text{Ce}^{+3}$  cannot be resolved due to overlap with the u/v doublet of  $\text{Ce}^{+4}$ . The presence of features attributable to  $\text{Ce}^{+3}$  is consistent with the S(2p) spectrum and demonstrates that  $\text{SO}_2$  reacts with surface lattice oxygen forming adsorbed sulfate and reducing a fraction of the surface cerium cations from  $\text{Ce}^{+4}$  to  $\text{Ce}^{+3}$ .

Heating the  $\text{SO}_2/\text{O}_2$ -dosed sample from 298 to 823 K produced a significant increase in the intensity of the u<sup>'</sup>/v<sup>'</sup> peaks attributed to  $\text{Ce}^{3+}$  photoemission. This trend continued upon heating to 923 K and is indicative of the reaction of additional adsorbed

SO<sub>2</sub> with surface lattice oxygen to form sulfate. Even after heating to 1123 K, a temperature sufficient to cause decomposition of the adsorbed sulfate, the features due to Ce<sup>+3</sup> persist in the spectrum. The spectrum obtained after heating to this temperature is clearly due to a mixture of Ce<sup>+3</sup> and Ce<sup>+4</sup> cations. Thus, the sulfide formed at high temperature contains Ce<sup>+3</sup>. Since this species is formed on the surface of an oxide it is most likely an oxysulfide of cerium, such as Ce<sub>2</sub>O<sub>2</sub>S, which is known to be a stable compound [23].

## Discussion

The TPD and XPS results described above present a relatively clear picture of the adsorption and reaction of SO<sub>2</sub> on ceria. Sulfur dioxide adsorbs molecularly on CeO<sub>2</sub> at 298 K. In addition to the molecular species, the XPS results show that a fraction of the adsorbed SO<sub>2</sub> is oxidized to SO<sub>4</sub><sup>2-</sup>. The source of the oxygen required for this reaction is the ceria surface. This is reflected in the Ce(3d) spectrum obtained after exposure of the sample to SO<sub>2</sub>, that shows partial reduction of the ceria surface and the presence of Ce<sup>3+</sup> cations. Thus, even at room temperature the ceria film is able to donate oxygen for reaction with adsorbed SO<sub>2</sub> to form sulfate.

Upon heating, the SO<sub>2</sub> either desorbs intact between 373 and 673 K or reacts with surface oxygen forming additional adsorbed sulfate and further reducing the ceria. Evidence for this thermal conversion of SO<sub>2</sub> to sulfate is presented in Figure 2, which shows the emergence of the S(2p) doublet indicative of cerium sulfate at 168 eV upon heating to 823 K. At this temperature, the sulfate is the predominant surface species. The selectivity for the two competing reaction pathways for adsorbed SO<sub>2</sub>, i.e. desorption or reaction to sulfate, appears to be determined by the availability of surface lattice oxygen. Both the TPD and XPS results show that the surface sulfates decompose in the temperature range of 823 to 1123 K. This produces gaseous SO<sub>2</sub> and results in the formation of a surface cerium sulfide species as evidenced by the emergence of a S(2p) doublet at 160.0 and 161.3 eV in the XPS spectrum. Decomposition of the sulfate and formation of the sulfide does not result in reoxidation of the ceria surface, suggesting the formation of a cerium (III) sulfide, such as Ce<sub>2</sub>O<sub>2</sub>S.

Another interesting feature of the TPD results is that the SO<sub>2</sub> desorption peaks between 823 to 1123 K are significantly more intense following exposure to SO<sub>2</sub> and O<sub>2</sub> at 573 K than after exposure at 298 K. This demonstrates that the formation of the surface sulfate species is activated and is enhanced by the presence of gas phase oxygen. Based on the results obtained in this study it is not possible to determine if sulfate formation at 573 K involves reaction of adsorbed SO<sub>2</sub> directly with gaseous O<sub>2</sub>, or proceeds via reaction with lattice oxygen that is continually re-supplied via reaction of the ceria surface with the O<sub>2</sub>.

Examination of the high-temperature SO<sub>2</sub> desorption feature due to sulfate decomposition in the TPD data (see Figure 1) reveals that it is composed of two distinct peaks at 883 and 963 K. These peaks are approximately equal in intensity for the room temperature-dosed sample, while the 883 K peak is more intense for the ceria sample dosed with SO<sub>2</sub> and O<sub>2</sub> at 573 K. Since it is clear that both of these peaks are due to sulfate decomposition, this result suggests that sulfates are present on the surface in more than one chemical environment. Note that the XPS results show that the sulfated surfaces are always partially reduced. Thus, it is possible that both Ce<sup>3+</sup> and Ce<sup>4+</sup> sulfates are formed and that these two species have slightly different thermal stabilities. Indeed, at high temperatures only the Ce<sup>+3</sup> sulfate is reported to be stable [23].

It is useful to compare the results obtained in this study with those reported in previous studies of the adsorption and reaction of SO<sub>2</sub> on model ceria catalysts. As noted above, Overbury et al. have used TPD and XPS to characterize the interaction of SO<sub>2</sub> with highly-ordered CeO<sub>2</sub>(111) films as a function of coverage, temperature, and degree of oxidation of the ceria [13]. During TPD following exposure of CeO<sub>2</sub>(111) to SO<sub>2</sub> at temperatures up to 398 K, SO<sub>2</sub> desorption was detected as a broad peak spanning from room temperature to 498 K. The high-temperature SO<sub>2</sub> peaks obtained in the present study, which are due to sulfate decomposition, were not observed. This result indicates that sulfates were not formed on the CeO<sub>2</sub>(111) surface following SO<sub>2</sub> exposure in ultra-high vacuum. This conclusion is also consistent with the XPS results for SO<sub>2</sub>-dosed CeO<sub>2</sub>(111) reported by Overbury et al. which did not provide any evidence for sulfate formation.

Although the results of Overbury et al. appear to be at odds with those reported here for the reaction of SO<sub>2</sub> on ceria to form surface sulfates, it is well known that the catalytic activity and oxygen transport properties of ceria are structure-sensitive [18,24-29]. Previous studies of ceria single crystals and ceria thin films annealed at high temperatures (i.e. > 1200 K) have shown that these samples are nearly inert [18,25-28], while polycrystalline ceria samples that have not been annealed at high temperature and ceria in contact with zirconia, display enhanced oxygen transport properties [24-29]. Note that the films used in this study fall in this later category. Thus, the differences obtained in the Overbury et al. study and those reported here are most likely due to the different model systems that were employed.

There is better agreement between the results obtained in the present study and those reported by Rodriguez et al. who used photoemission, XANES, and TPD to characterize the interaction of SO<sub>2</sub> with 30 Å polycrystalline ceria films supported on Pt(111) and with ceria powders [12]. In the Rodriguez et al. study it was suggested that exposure of the ceria samples to SO<sub>2</sub> at room temperature produced only surface sulfate species. This result is similar to that obtained here except that the samples used in the Rodriguez et al. appear to be more reactive than those used in our study and produced higher concentrations of surface sulfates at lower temperatures. This may be due to the fact that the samples used by Rodriguez et al. were supported on a Pt(111) single crystal. Rodriguez et al. also concluded that SO<sub>2</sub> desorption which occurred at temperatures below 698 K was due to sulfate decomposition. Our results suggest that this is most likely not the case and that the SO<sub>2</sub> product between 298 and 773 K during TPD is due to desorption of molecularly adsorbed SO<sub>2</sub>. It appears that Rodriguez et al. only heated their samples to roughly 700 K and were, therefore, unable to observe sulfate decomposition which occurs between 823 to 1123 K.

The results of the present study are in reasonably good agreement with those reported by Waqif et al. who used IR spectroscopy to study the sulfation of ceria powders [10]. Although it was found that sulfate formation did not take place to any appreciable extent upon exposure of ceria powders to SO<sub>2</sub> at room temperature, high coverages of surface sulfates were produced following exposure to SO<sub>2</sub>/O<sub>2</sub> mixtures at 673 K. This result is similar to that obtained in the present study. They also observed the formation of

some sulfate species upon exposure to only SO<sub>2</sub> at this temperature. As was the case in the present study, Waqif et al. also found that surface sulfates decomposed upon heating to approximately 875 K.

Finally, it is worth noting that the results in the present study for the interaction of SO<sub>2</sub> with low surface area ceria thin films are in good agreement with recent flow reactor TPD and FTIR studies of the reaction of SO<sub>2</sub> on high surface area Pd/ceria catalysts that have been carried out in our labs [14]. The details of these studies will be reported in a separate paper. These studies showed that molecularly adsorbed SO<sub>2</sub> was the primary surface species after exposure of the Pd/ceria catalyst to SO<sub>2</sub> at room temperature and that thermal conversion of SO<sub>2</sub> to sulfate occurred between 473 and 573 K. Bulk sulfates were formed during exposure to mixtures of SO<sub>2</sub> and O<sub>2</sub> at 673 K. During TPD in flowing He, SO<sub>2</sub> and O<sub>2</sub> desorption resulting from sulfate decomposition occurred at temperatures near 970 K.

## **Conclusions**

The XPS and TPD results obtained in this study show that ceria samples exposed to SO<sub>2</sub> at 298 K are primarily covered with molecularly adsorbed SO<sub>2</sub>. Reaction of SO<sub>2</sub> with oxygen supplied via the ceria to form adsorbed sulfate species also occurs to a small extent at this temperature. Upon heating, molecularly adsorbed SO<sub>2</sub> either desorbs intact or reacts with the ceria to form additional surface sulfates. High concentrations of surface sulfates can be produced by exposing ceria films to mixtures of SO<sub>2</sub> and O<sub>2</sub> at 573 K. Adsorbed sulfates on ceria are stable up to 823 K, and decompose producing gaseous SO<sub>2</sub> and a surface cerium oxy-sulfide upon heating to temperatures between 823 and 1023 K.

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## References

- 1 H.S. Gandhi and M. Shelef, *Stud. Surf. Sci. Catal.* 30 (1987) 199.
- 2 B. Harrison, A.F. Diwell and C. Hallett, *Platinum Metals Rev.* 32 (1988) 73.
- 3 K. Otsuka, M. Hatano and A. Morikawa, *J. Catal.* 79 (1983) 493.
- 4 K.C. Taylor, *Catal. Rev.* 35 (1993) 457.
- 5 H.C. Yao and Y.F.Y. Yao, *J. Catal.* 86 (1984) 254.
- 6 M. Boaro, C. de Leitenburg, G. Dolcetti, A. Trovarelli and M. Graziani, *Topics in Catal.* 16/17 (2001) 299.
- 7 D.D. Beck, J.W. Sommers and C.L. DiMaggio, *Appl. Catal. B* 3 (1994) 205.
- 8 D.D. Beck, J.W. Sommers and C.L. DiMaggio, *Appl. Catal. B* 11 (1997) 273.
- 9 T.J. Truex, *Soc. Automot. Eng.*, [Spec. Publ.] SP SP-1459 (1999) 173.
- 10 M. Waqif, P. Bazin, O. Saur, J.C. Lavalley, G. Blanchard and O. Touret, *Appl. Catal. B Env.* 11 (1997) 193.
- 11 D.D. Beck, M.H. Krueger and D.R. Monroe, SAE Paper No. 910844 (1991) 386.
- 12 J.A. Rodriguez, T. Jirsak, A. Freitag, J.C. Hanson, J.Z. Larese and S. Chaturvedi, *Catal. Lett.* 62 (1999) 113.
- 13 S.H. Overbury, D.R. Mullins, D.R. Huntley and L.J. Kundakovic, *J. Phys. Chem. B* 103 (1999) 11308.
- 14 T. Luo, J.M. Vohs and R.J. Gorte, to be submitted
- 15 B.J. Lindberg, K. Hamrin, G. Johansson, U. Gelius, A. Fahlmann, C. Nordling and K. Siegbahn, *Phys. Scr.* 1 (1970) 277.
- 16 H. Binder, *Z. fur Naturforsch B*28 (1973) 256.
- 17 R.B. Shalvoy, G.B. Fisher and P.J. Stiles, *Phys. Rev.* B15 (1977) 1680.
- 18 J. Stubenrauch and J.M. Vohs, *J. Catal.* 159 (1996) 50.
- 19 M. Romeo, K. Bak, J. El Fallah, F. le Normand and L. Hilaire, *Surf. Interface Anal.* 20 (1993) 508.

- 20 D.A. Creaser and P.G. Harrison, *Catal. Lett.* 23 (1994) 13.
- 21 A. Pfau and K.D. Schierbaum, *Surf. Sci.* 321 (1994) 71.
- 22 A. Pfau, K.D. Schierbaum and W. Gopel, *Surf. Sci.* 331 (1995) 1479.
- 23 D.A.R. Kay, W.G. Wilson and V. Jalan, *J. Alloys & Comp.* 192 (1993) 11.
- 24 R.M. Ferrizz, T. Egami and J.M. Vohs, *Surf. Sci.* 465 (2000) 127.
- 25 H. Cordatos, T. Bunluesin, J. Stubenrauch, J.M. Vohs and R.J. Gorte, *J. Phys. Chem.* 100 (1996) 785.
- 26 H. Cordatos, D. Ford and R.J. Gorte, *J. Phys. Chem.* 100 (1996) 18128.
- 27 E.S. Putna, J.M. Vohs and R.J. Gorte, *J. Phys. Chem.* 100 (1996) 17862.
- 28 A. Trovarelli, *Catal. Rev.* 38 (1996) 439.
- 29 E.S. Putna, T. Bunluesin, X.L. Fax, R.J. Gorte, J.M. Vohs, R.E. Lakis and T. Egami, *Catal. Today* 50 (1999) 343.



## Figure Captions

- Figure 1:** SO<sub>2</sub> TPD spectra from a CeO<sub>2</sub> sample following exposure to SO<sub>2</sub> and O<sub>2</sub> at (a) room temperature and (b) 573 K. (c) SO<sub>2</sub> TPD spectrum obtained from a bulk cerium sulfate film.
- Figure 2:** S(2p) XP spectra for (a) a bulk cerium sulfate film and (b) a ceria thin film that had been exposed to SO<sub>2</sub> and O<sub>2</sub> at room temperature, and then heated to the given temperature.
- Figure 3:** Ce(3d) XP spectra for (a) an oxidized ceria thin film that had been (b) subsequently exposed to SO<sub>2</sub> and O<sub>2</sub> at room temperature and then heated to the given temperatures. (c) Ce(3d) XP spectrum of a highly reduced CeO<sub>2</sub>(111) surface.

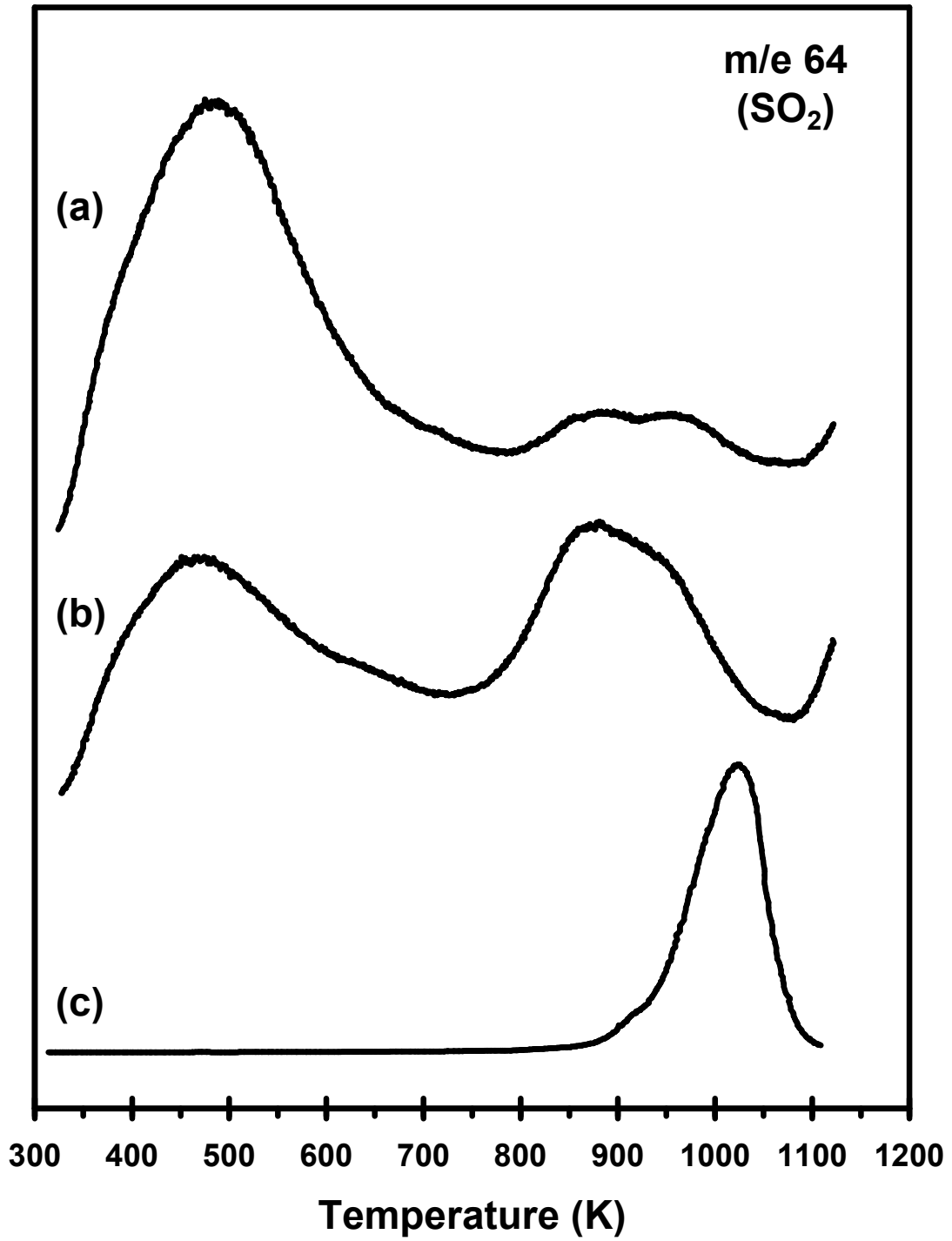


Figure 1

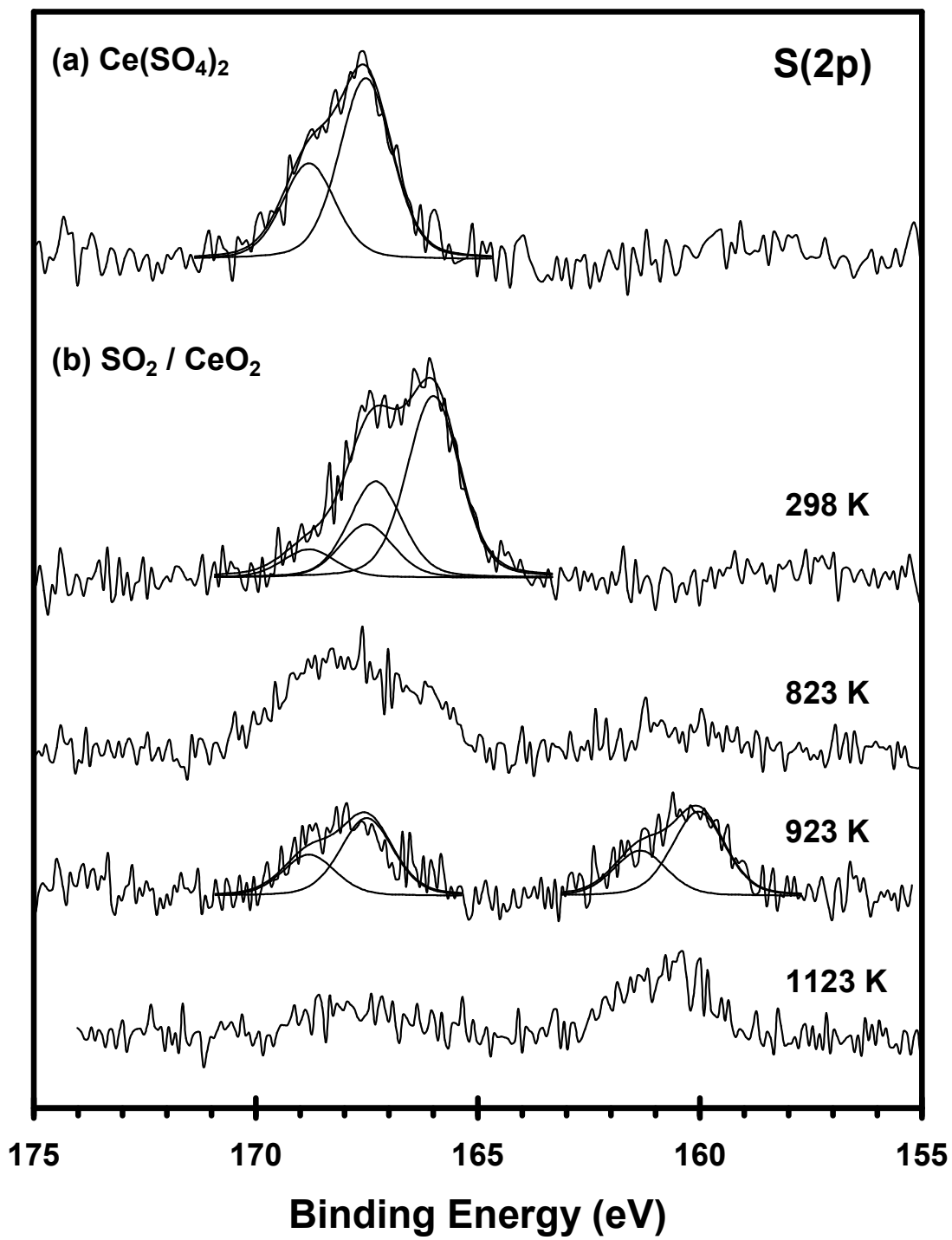


Figure 2

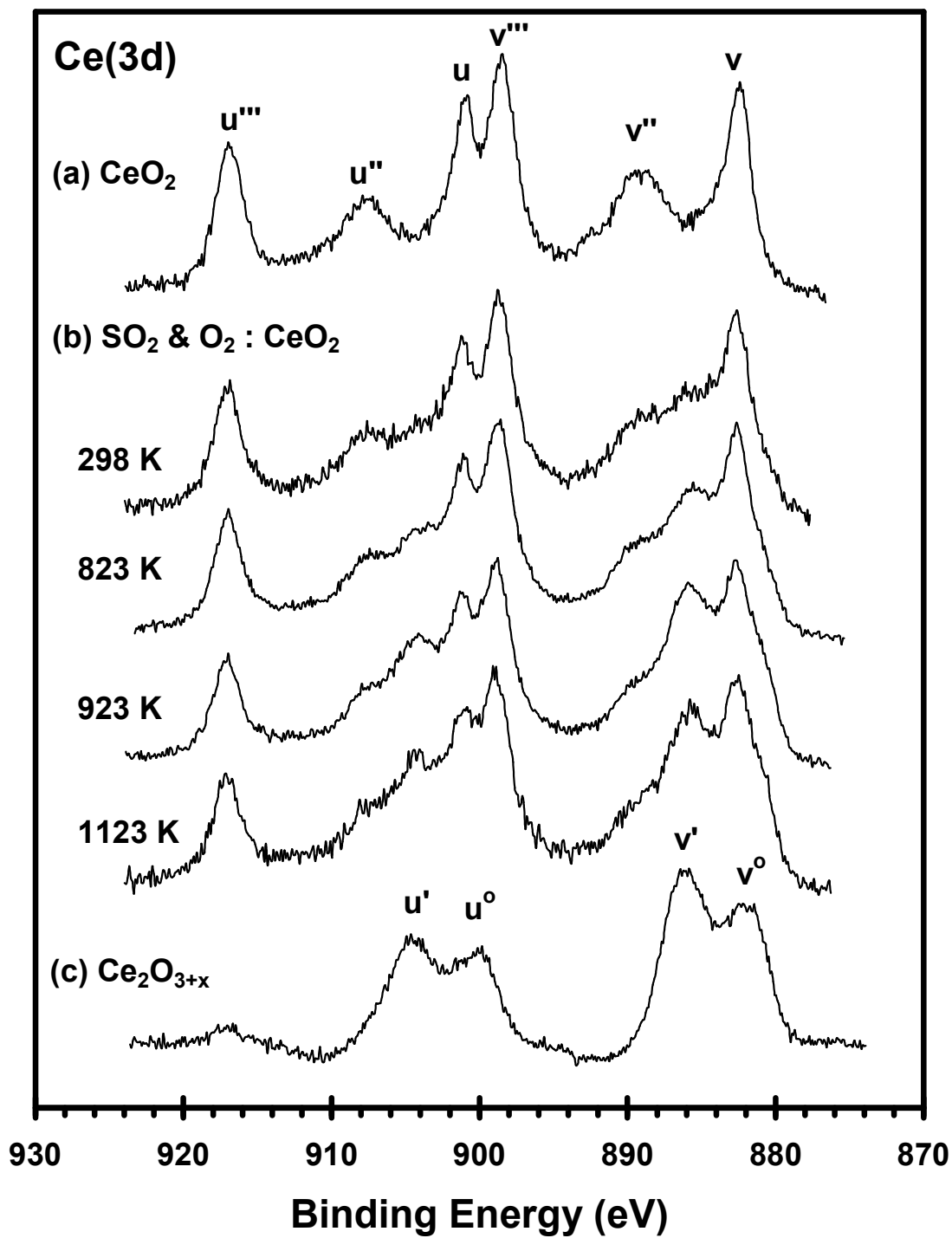


Figure 3