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Characterization of SO_2-Poisoned Ceria-Zirconia Mixed Oxides

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Keywords

Zirconia, Ceria, SO2, Sulfate, H2S, Oxygen Storage Capacity, FTIR, TPD

Comments

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Abstract

CeO_2, ZrO_2, and a series of $Ce_xZr_{1-x}O_2$ catalysts with 1 wt% Pd were exposed to fixed exposures of SO_2 under oxidizing environments and then characterized by FTIR, pulse-reactor studies with CO and O_2, and temperature-programmed desorption (TPD). For exposures above 473 K, sulfates were formed on all of the materials; however, the results are consistent with the formation of bulk sulfates on CeO_2 and only surface sulfates on ZrO_2. For the mixed oxides, the quantity of sulfates formed at 673 K increased linearly with the Ce content. In TPD, the sulfates on ZrO_2 were stable to higher temperatures than those formed on CeO_2, which decomposed in a well-defined peak between 900 and 1050 K. The sulfates on both oxides were reduced by CO above 750 K. Even though XRD patterns for the mixed oxide were significantly different from that of the physical mixture, the TPD and pulse-reactor results were similar to what would be expected for physical mixtures of CeO_2 and ZrO_2, suggesting that sulfate species are associated with individual metal cations. Finally, pulse-reactor studies with CO and O_2 at 873 K show that the sulfates can be reversibly reduced and oxidized on both CeO_2 and ZrO_2, so that sulfur poisoning gives rise to an apparent increase in oxygen storage, demonstrating that this method is not acceptable for measurement of this quantity.

Key Words: zirconia, ceria, SO_2, sulfate, H_2S, Oxygen Storage Capacity, FTIR, TPD

Introduction

Ceria is a crucial component of three-way, automotive, emissions-control catalysts because its redox properties provide oxygen-storage capacity (OSC) [1]. While the OSC properties in early ceria-containing catalysts were prone to deactivate during high-temperature aging [2], the redox properties of ceria in modern catalysts are stabilized and improved by the addition of zirconia. The ceria-zirconia mixed oxide has been shown to be very durable, even in the high-temperature, hydrothermal environment of the catalytic converter [3]. Indeed, the current generation of these mixed oxide, three-way catalysts would be sufficient to meet very stringent emissions requirements if it were not for the fact that sulfur, generally present in all commercially available fuels, poisons the properties of ceria [4-10].

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

It is of interest to know how the presence of zirconia affects the interaction of sulfur with ceria in the mixed oxides that are usually used for oxygen storage, but relatively few reports have been published describing these interactions. In a study from our laboratory, it was shown that pre-exposure of either Pd/ceria or Pd/ceria-zirconia catalysts to 20 ppm of SO_2 at 673 K resulted in large upward shifts in the WGS light-off curves, demonstrating that the catalyst properties of both ceria and ceria-zirconia are affected in a similar manner [10]. Bazin, et al examined catalysts made from ceria, zirconia, and ceria-zirconia using infrared spectroscopy and thermogravimetry following exposure to SO_2 [12]. They reported that bulk sulfates formed on ceria but only surface sulfates were observed on pure zirconia. Their results also suggested that sulfates on the ceria-zirconia mixed oxide were more easily reduced than sulfates on pure ceria. Deshmukh, et al reported that the effect of SO_2 on CO oxidation was much less pronounced for

$Ce_{0.75}Zr_{0.25}O_2$ than for CeO_2 and that the mixed oxide is more resistant to morphological change than is ceria [13]. Nelson, et al examined the effect of SO_2 exposure on the microstructure of ceria and ceria-zirconia mixed oxides and reported that the mixed oxide showed improved sulfur tolerance [14]. Most recently, Liu, et al suggested that the stability of sulfate groups on ceria increases upon formation of solid solutions with zirconia [15].

In the present paper, we investigated the adsorption and reaction of SO_2 with Pd/ZrO_2 and a set of $Pd/Ce_xZr_{1-x}O_2$ catalysts in order to better understand the effect of zirconia on sulfur tolerance. The results suggest that the sulfur chemistry of ceria and zirconia in the mixed oxides were only weakly affected by the presence of the other oxide under the conditions of our study.

Experimental

The catalysts used in these experiments were 1-wt% Pd supported on CeO_2, $Ce_{0.25}Zr_{0.75}O_2$, $Ce_{0.5}Zr_{0.5}O_2$, $Ce_{0.25}Zr_{0.75}O_2$ and ZrO_2. CeO_2 and ZrO_2 were prepared by thermal decomposition of the nitrate salts, $Ce(NO_3)_3{\cdot}6H_2O$ (Alfa Aesar, 99.5%) and $ZrO(NO_3)_2{\cdot}xH_2O$ (Alfa Aesar, 99.9%), at 873 K. Two types of ceria-zirconia mixed oxides were prepared. In the first type, aqueous solutions of $Ce(NO_3)_3{\cdot}6H_2O$ and $ZrO(NO_3)_2{\cdot}xH_2O$ were mixed, dried at 343 K for 4 h, and finally heated in air to 873 K. These samples are designated as $Ce_xZr_{(1-x)}O_2$(N). In the second set of samples, designated $Ce_xZr_{(1-x)}O_2$(C), aqueous solutions of the two metal-oxide salts were mixed with citric acid to promote formation of the solid solution. The solutions with citric acid were also dried at 343 K for 4 hours and calcined in air to 873 K for 4 h.

For all the data shown in this study, Pd was added to each of the supports by wet impregnation of $Pd(NH_4)_3(NO_3)_2$, after which each catalyst was dried, calcined for 2 h in flowing air at 873 K, and pressed into wafers. While sulfates were observed on these supports even when Pd was not added, the addition of precious metal promoted the oxidation and reduction kinetics, increasing the amounts of material that formed.

The surface areas of each oxide, determined by BET measurements of N_2 at 78 K, are shown in Table 1. The effect of different preparation methods on the structure of the mixed oxides was also investigated by X-ray diffraction. In Fig.1, XRD patterns are shown of the ZrO_2, CeO_2, a 50:50 physical mixture of CeO_2 and ZrO_2, $Ce_{0.5}Zr_{0.5}O_2$(N), and $Ce_{0.5}Zr_{0.5}O_2$(C). ZnO was added to each sample to provide an internal reference at 37.35 degrees 2θ. The pattern for CeO_2, Fig. 1a), shows the expected cubic phase, with broad peaks due to the small crystallite sizes in the sample, while the XRD pattern for ZrO_2, Fig. 1b), shows a mixture of tetragonal and monoclinic phases. As expected, the diffraction pattern for the physical mixture, Fig. 1c), exhibits peaks associated with both of the pure compounds. The XRD pattern for $Ce_{0.5}Zr_{0.5}O_2$(N), Fig. 1d), is significantly different from that of the physical mixture; however, the asymmetry of peak near 29 degrees 2θ suggests that this sample is not a single-phase solid solution. The XRD pattern of $Ce_{0.5}Zr_{0.5}O_2$(C), Fig. 1e), shows a more symmetric peak, centered at 29.3 degrees 2θ, commonly associated with the formation of a solid solution. It should be noted, however, that Egami and coworkers have demonstrated that XRD data cannot distinguish between true solid solutions of ceria and zirconia and mixed oxides with small ceria and zirconia domains [18], so that even the data in Fig. 1 e) do not necessarily prove that the $Ce_{0.5}Zr_{0.5}O_2$(C) sample is a indeed true solid solution.

The temperature-programmed-desorption (TPD) and pulse-reactor measurements were performed in the same system that has been described in earlier papers [10,17]. The system is essentially a tubular reactor in which the feed to the reactor can be switched using solenoid valves controlled by a computer. The effluent from the reactor can be monitored continuously using a quadrupole mass spectrometer. In most TPD and pulse-reactor measurements, 100 mg of sample were placed in the ¼-inch, quartz, tubular reactor, held at atmospheric pressure. In TPD experiments, the composition of the gas fed to the reactor, which could be varied from pure He to He mixed with 5% O_2, 7% H_2, or 5% CO, was kept constant while the temperature of the sample was ramped at 10 K/min. (While TPD in an oxidizing or reducing environment is usually referred to as temperature-programmed oxidation or reduction, all of these experiments will be referred to as TPD in this manuscript.) In the pulse-reactor measurements, the sample temperature was fixed and the composition of the feed was varied in steps. In all cases, the total flow rate of gas fed to the reactor was maintained at 80 ml/min. The mass spectrometer signal was calibrated with known gas concentrations, enabling us to calculate the absolute quantities corresponding to the TPD and pulse-reactor signals.

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 the pulse-reactor measurements, using the same catalysts.

For each of the characterization techniques, it was essential to know the amounts of sulfur on the samples. In the case of Pd/ceria, this information can be obtained by TPD measurements [11]. Cerium sulfates decompose over a narrow range of temperatures, with the evolution of SO_2 and O_2. The amounts of SO_2 that form can be easily quantified, and experiments on bulk $Ce(SO_4)_2$ gave good agreement between the TPD results and the known sulfur content [11]. Because it was not possible to determine sulfur loadings on the zirconia-containing samples using TPD, the sulfur loadings on Pd/ZrO_2 and Pd/$Ce_{0.5}Zr_{0.5}O_2$(N) were determined by gravimetric methods. In this case, the sample weights, before and after treating in flowing SO_2, were measured using a Cahn 2000 microbalance. The weights were determined in vacuum (~10^{-7} torr) after heating to 423 K to remove weakly adsorbed species. After exposure to 1% SO_2 in 50% O_2 for 30 min at 673 K, the weight change on the Pd/ZrO_2 sample was 10.2 mg/g. Assuming that the weight change is due to the replacement of O^{2-} with $(SO_4)^{2-}$, the sulfate coverage was calculated to be 160 μmol/g, or approximately 1.2 sulfates/nm^2 based on the surface area. This value is somewhat less than one would expect for a zirconia surface covered by monolayer of sulfate. After the same exposure of SO_2 to the Pd/$Ce_{0.5}Zr_{0.5}O_2$(N) sample, the weight change was 59.5 mg/g, corresponding to a sulfate coverage of 950 μmol/g. Finally, the sulfate coverage on Pd/CeO_2 exposed to SO_2 for 30 min was 1,600 μmol/g, a value less than that corresponding to bulk $Ce(SO_4)_2$, 6,000 μmol/g, but certainly much larger than could be expected for a monolayer.

Results

FTIR Measurements

Fig. 2 shows a comparison of FTIR spectra measured on the Pd/CeO_2 and Pd/ZrO_2 samples following exposure to 1% SO_2 in 50% O_2 for 20 min at various temperatures. On Pd/CeO_2, exposure to SO_2 at 373 K gives rise primarily to bands at 980 cm^{-1} and 1220 cm^{-1}, which have been interpreted as being due to surface sulfites and hydrogen sulfites [12,20-23]. It is noteworthy that the feature at 980 cm^{-1} is close to that expected for the symmetric stretch of the SO_2 anion, 990 cm^{-1} [23]. A very small feature at 1345 cm^{-1} is likely due to the formation of small amounts of sulfate. For exposure at 473 K, the main feature is at 1370 cm^{-1} and this has been interpreted as being due a surface sulfate [20-22]. Finally, exposure at 673 K results in a broad band centered at 1160 cm^{-1}, which is reported to be due to sulfates in the bulk [20]. While we regard the FTIR assignments as somewhat ambiguous (For example, molecular sulfates, both bridging and chelating, are reported to exhibit maximum frequencies in the range from 1200 to 1240 cm^{-1} [24].), these assignments are in essential agreement with previous TPD results from our laboratory [11]. In our earlier study, the desorption curves were consistent with the presence of molecular SO_2 on the sample when ceria was exposed to SO_2 below 473 K. For exposures above 473 K, the TPD results clearly indicated decomposition of a cerium sulfate, with only the amounts of sulfate increasing with increasing temperature for fixed exposure times. At 673 K, prolonged exposures were sufficient to form bulk $Ce(SO_4)_2$.

The data for Pd/ZrO_2 are similar at the lower temperatures, but differences are evident following exposures above 473 K. At 298 K, molecularly adsorbed SO_2 is again the primary product, as indicated by the peaks at 980 and 1240 cm^{-1}. The IR spectra taken at 373 and 473 K change slightly in that some surface sulfate appears to have formed, as indicated by the peak at 1350 cm^{-1}. However, unlike with Pd/CeO_2, the feature at 980 cm^{-1} due to molecular SO_2 remains on Pd/ZrO_2 after heating to 473 K, implying that higher temperatures are required to form the sulfate on Pd/ZrO_2. At 673 K, the surface-sulfate band at 1370 cm^{-1} is much more intense and this remains the main feature in the spectrum at 723 K, with only a relatively small peaks forming near 1160 cm^{-1}, the region of the spectrum that has been associated with bulk sulfates.

TPD and Pulse Experiment Results

Fig. 3 shows TPD curves performed using pure He as the carrier for 1 wt% Pd on CeO_2, $Ce_{0.5}Zr_{0.5}O_2$, $Ce_{0.25}Zr_{0.75}O_2$, and ZrO_2, after exposure to 1% SO_2 in 50% O_2 at 673 K for 30 min, monitoring the SO_2 (m/e = 64) and the O_2 (m/e = 32) signals. Results for the $Ce_xZr_{(1-x)}O_2$(N) and $Ce_xZr_{(1-x)}O_2$(C) were essentially indistinguishable. As in previous work on Pd/ceria [11], O_2 desorbed simultaneously with the SO_2 in a ratio of 1:2 in a narrow feature between 900 and 1050 K, showing that SO_2 formation is associated with sulfate decomposition. In Fig. 3a), the amount of SO_2 removed from Pd/CeO_2 after the fixed exposure of this study was approximately 1,600 μmol/g, a substantial fraction of the amount of SO_2 that could be formed by decomposition of bulk $Ce(SO_4)_2$, 6,000 μmol/g. The large amount of sulfate present on the Pd-CeO_2 sample after exposure to SO_2 at 673 K also agrees with the IR results that suggest formation of the bulk sulfates.

By comparison, the results for Pd/ZrO_2, Fig. 3d), show negligible amounts of SO_2 desorbing from the sample below 1100 K. As discussed in the Experimental section, gravimetric measurements on a sample exposed to SO_2 in exactly the same manner indicated a surface coverage of 160 μmol/g, a value that is 10% of that formed on CeO_2 but one that should be easily detected in our experiments if sulfate decomposition occurred at the same temperature on the two oxides. While temperature limitations for the reactor and desorption from the walls of the reactor made quantification of SO_2 desorption difficult above 1100 K, there appears to be increased desorption of SO_2 at these temperatures on the zirconia-containing materials compared to what is observed with pure CeO_2, suggesting that the zirconia sulfate decomposes at a higher temperature. The effect of conjugate oxide on sulfate decomposition has been observed previously in that sulfates formed on ceria under reducing conditions, and likely associated with Ce^{+3}, decomposed between 1050 and 1200 K, a temperature approximately 100 K higher than on CeO_2 [11].

The TPD curves in Fig. 3b) and 3c) were obtained on the $Pd/Ce_{0.5}Zr_{0.5}O_2$(N) and $Pd/Ce_{0.25}Zr_{0.75}O_2$(N) samples. The main feature in both curves is the evolution of SO_2 between 900 and 1050 K that we observed on CeO_2, although there is again increased desorption above 1100 K as well. Indeed, the TPD curves on the mixed-oxide samples have the appearance one would expect for a physical mixture of the Pd/CeO_2 and Pd/ZrO_2 samples. The feature between 900 and 1050 K has an identical appearance to that observed in pure CeO_2, suggesting that similar cerium sulfates are formed on the mixed oxides as on pure CeO_2. The amounts of SO_2 formed in TPD between 900 and 1050 K on the mixed-oxide supports were 870 μmol/g on $Pd/Ce_{0.5}Zr_{0.5}O_2$(N) and 310 μmol/g on $Pd/Ce_{0.25}Zr_{0.75}O_2$(N). Notice that the sulfate coverage determined from TPD on the $Pd/Ce_{0.5}Zr_{0.5}O_2$(N) sample is in good agreement with the value obtained from the gravimetric analysis, 950 μmol/g. The coverage determined from gravimetric analysis includes sulfates formed on the zirconia and should be somewhat larger.

In Fig. 4, we have plotted the amount of SO_2 removed in TPD between 900 and 1050 K from each sample. For the mixed oxides, we include data for the samples prepared by simple decomposition of the nitrate salts and for the samples prepared using citric acid. Assuming that SO_2 desorbing in this temperature interval is associated with ceria, the result indicates an almost linear relationship between the amount of $Ce(SO_4)_2$ that forms in each sample and the Ce content of the sample. Because the exposure used in the measurements in Fig. 4 was insufficient to completely sulfate pure CeO_2, the linearity of Fig. 4 implies that the reaction probability for forming cerium sulfates is independent of the ZrO_2 content. Together with the constant decomposition temperature of the sulfate, it appears that propensity of ceria to form sulfates is essentially unaffected by the presence of zirconia in the mixed oxides that were studied here.

We also examined the decomposition of the sulfates under reducing conditions. The TPD curves in Fig. 5 were obtained on the Pd/CeO_2, Pd/$Ce_{0.5}Zr_{0.5}O_2$(N), and Pd/ZrO_2 samples using a He carrier with 7% H_2. The samples were again exposed to 1% SO_2 in 50% O_2 at 673 K for 30 min. The results for Pd/CeO_2 and Pd/$Ce_{0.5}Zr_{0.5}O_2$(N), Figs. 5a) and b), are similar to what we had reported previously for Pd/CeO_2 [11], although there may be a slight upward shift in the peak temperature on the mixed oxide. However, on both samples, we observe the formation of H_2S (m/e = 34) between 700 and 800 K, a much lower temperature than that at which ceria sulfate decomposes. As reported previously, only fraction of the sulfur in the Pd/CeO_2 sample left as H_2S, with the rest remaining in the sample as Ce_2O_2S. This was also true of Pd/$Ce_{0.5}Zr_{0.5}O_2$(N). In contrast, the results for Pd/ZrO_2, shown in Fig. 5c), demonstrate that H_2S is formed over a wide range of temperatures, also generally at a much higher temperatures, between 800 and 1200 K. Because it was difficult to accurately quantify the amount of H_2S that formed on Pd/ZrO_2, we are uncertain whether some of the sulfur remained in the sample as ZrOS.

Fig. 6 shows the analogous TPD results for Pd/CeO_2, Pd/$Ce_{0.5}Zr_{0.5}O_2$(N), and Pd/ZrO_2 using 5% CO in He as the reductant. Again, each of the samples was exposed to 1% SO_2 in 50% O_2 for 30 min at 673 K. The only product observed in more than trace amounts on each of the samples was CO_2 (m/e = 44); but this time the oxidation product, CO_2, formed at approximately the same temperature, 750 K, on all three samples. The amounts of CO_2 that formed on Pd/CeO_2, Pd/$Ce_{0.5}Zr_{0.5}O_2$(N), and Pd/ZrO_2 were approximately 4,200, 2,800, and 800 μmol/g, respectively. Since a maximum of 100 μmol/g could be formed by reduction of PdO on each catalyst, the majority of the CO_2 must be formed by reduction of the supports. For Pd/CeO_2, previous work showed that most of the oxygen comes from reduction of the sulfate to form Ce_2O_2S [11]. We suggest that a similar reduction of the sulfate must be occurring with Pd/ZrO_2 and this reduction must occur at approximately the same temperature.

To confirm that the reduction observed in Fig. 6c) is associated with sulfates and that the reduction of the sulfate is reversible, we performed the CO-O_2 pulse measurements on the Pd/ZrO_2, before and after exposure to SO_2, with the results at 873 K shown in Fig. 7. A temperature of 873 K was chosen here because it is above the reduction peak in Fig. 6. In performing the pulse experiments, the initially oxidized samples were first exposed to two CO (m/e = 28) pulses at approximately 500 and 1100 s. Sample reduction was characterized by the amount of CO_2 (m/e = 44) that formed in the first pulse, while the second CO pulse demonstrated the samples had been completely reduced. The reduced samples were then re-oxidized by two O_2 (m/e = 32) pulses at ~1900 and 2500 s, after which they were again reduced by a CO pulse at ~3200 s.

For unpoisoned Pd/ZrO_2, the amount of CO_2 that formed during the CO pulses at 500 and 3200 s was approximately 160 to 200 μmol/g. Reduction of PdO would provide less than 100 μmol/g for a 1-wt% catalyst, and the Bouduard reaction can be ruled out as a source of CO_2 since no CO_2 is formed during the O_2 pulses. Therefore, the data imply that some zirconia has been reversibly reduced by the CO pulses, in agreement with a previous report from the literature [10]. The results for SO_2-poisoned Pd/ZrO_2 are qualitatively similar; but much more oxygen is removed from the sample, ~710 μmol/g, a value close to the amount of CO_2 formed in the TPD experiment in Fig. 6c). The reduction of the poisoned sample was reversible, as demonstrated by the fact that the amount of CO_2 formed in the last CO pulse was the same as the amount formed in the first CO pulse. Finally, it is noteworthy that reduction of 160 μmol/g of SO_4^{2-} to S^{2-} would provide 640 μmol/g of oxygen.

The effect of oxidation and reduction on Pd/ZrO_2 that had been exposed to 1% SO_2 in excess O_2 for at 673 K for 10 min was also examined by FTIR, with the results shown in Fig. 8. The spectrum in Fig. 8a) was obtained after reducing the poisoned sample in 40 Torr CO for 10 min at temperatures approaching 873 K. (Because it was difficult to heat the sample to such high temperatures in the IR cell, the actual reduction temperature was likely somewhat lower.) Two bands are observed in the region expected for υ(S=O) stretches at 1370 and 1250 cm^{-1}, and we interpret these as being due to unreduced sulfate on the zirconia surface. After oxidation in O_2 for 10 min near 873 K, the spectrum of the sample changes to that shown in Fig. 8b), which is essentially identical to the spectrum at 673 K shown in Fig. 2b). The spectrum of the oxidized sample shows an increased intensity for the 1370-cm^{-1} peak and a decreased intensity for the 1250-cm^{-1} peak. After reduction again in CO at 873 K for 10 min, the spectrum, Fig. 8c), reverts to its original appearance following the initial reduction. The data in Fig. 8 clearly shows the reversibility of the oxidation and reduction of the sulfate. If the assignment for the 1370-cm^{-1} peak being due to surface sulfates is correct, the spectra would indicate a decrease in the coverage of these species. The increased intensity for the 1250-cm^{-1} peak could be due to bulk sulfates being easier to observe with the decreased surface-sulfate loading.

Discussion

Clearly, sulfates can be formed on ceria, on zirconia, and on ceria-zirconia mixed oxides. Based on the observations of the present study, only surface sulfates are formed on zirconia by exposure to SO_2 under oxidizing conditions at 673 K, while bulk sulfates form readily on ceria and ceria-zirconia mixed oxides. Sulfates on zirconia decomposed at higher temperatures than sulfates formed on ceria, but the temperature at which reduction occurs for sulfates on ceria and zirconia during exposure to CO is very similar.

One surprise from the present study is that the mixed oxides showed very similar results to what one would expect for a physical mixture of pure ceria and zirconia. The amounts of sulfate that formed on the mixed oxides following a fixed exposure to SO_2 and O_2 varied linearly with the Ce content; the TPD curves on the mixed oxides showed features that could be associated with pure ceria and pure zirconia. These observations suggest that the sulfate ions are associated with a single metal cation or very small clusters of adjacent cations. Furthermore, the environment surrounding that cation does not appear to affect the chemistry that we observe for the sulfate, consistent with our earlier findings with ceria [10,11]. For example, with pure ceria, both surface and bulk sulfates decomposed to SO_2 and O_2 in the same narrow temperature range. Also, when sulfates were formed under somewhat reducing conditions on ceria, we observed two well-defined decomposition features which were interpreted as being due to Ce^{+4} and Ce^{+3}. If the sulfate decomposition were associated with an average, bulk oxidation state, the decomposition temperature would likely have varied between the two extremes, rather than decomposing in two separate features.

We suggest that there are several ways to reconcile our results with those of Liu, et al, who reported an increased stability of sulfate groups on ceria upon formation of solid solutions with zirconia [15]. First, the low desorption temperatures observed in that study, which cannot be explained by the fact that they performed their desorption measurements at lower pressures [26], might indicate that the species formed on the single crystals were not true sulfates. Decomposition of a sulfate should give rise to desorption of SO_2 and O_2 in a 2:1 ratio, which was not established. Alternatively, there is precedence for the chemistry of the single crystals being much different from that of low-temperature powders [2,28].

Sulfates on both ceria and zirconia are reduced in a similar temperature range when exposed to CO, approximately 800 K. This relatively low reduction temperature helps to explain some of the chemistry associated with sulfated zirconias used as acid catalysts. In that case, too, reduction of the sulfate has been reported. For example, a TPD study of benzene on sulfated zirconia showed the formation of CO_2 at a similar temperature to that observed here [25]. It has been shown that reduction of $Ce(SO_4)_2$ results in the formation of Ce_2O_2S [26]. By analogy, reduction of $ZrO(SO_4)$ must result in ZrOS [27].

Judging by the temperature at which H_2S is formed, reduction of the sulfates in H_2 seems to occur at the same temperatures at which reduction occurs with CO. (While it should be possible to monitor this reduction by H_2O formation, this was not possible in our system.) On the ceria-containing materials, rapid H_2S formation at 750 K must be caused by reaction of H_2 with excess sulfur on the surface. The high sulfate coverages on ceria, along with the change in the stoichiometric Ce:S ratio going from $Ce(SO_4)_2$ to Ce_2O_2S, will result in significant amounts of free sulfur available for reaction with H_2. In the case of zirconia, the sulfate coverages were much lower, even though the sulfates appear to remain at the surface. The formation of H_2S may occur over a wider temperature range if it involves reaction with ZrOS.

As discussed in an earlier study, the oxidation and reduction of sulfate species on ceria and ceria-zirconia mixed oxides leads to an increase in the apparent "oxygen storage capacity" of sulfur- poisoned samples when this property is measured using CO-O_2 pulse data [9]. Since it is well known that sulfur poisoning decreases the true OSC of operating catalysts [10,11], the values determined from pulse studies and from temperature-programmed reduction measurements are likely not very meaningful for understanding OSC. Obviously, developing simple methods for measuring OSC remains an interesting and important challenge.

Conclusion

Exposure of supported Pd catalysts prepared from ceria, zirconia, and ceria-zirconia mixed oxides to SO_2 under oxidizing conditions at above 473 K results in the formation of sulfates. Sulfates on zirconia are distinguishable from those on ceria in that only surface sulfates are formed on zirconia The decomposition temperature for sulfate occurs at a higher temperature than that for cerium sulfate, but both sulfates are reduced by CO above 750 K. Most significantly, the ceria-zirconia mixed oxides exhibit SO_2 adsorption properties similar to what would be expected for a physical mixture of ceria and zirconia, implying that the sulfates are likely associated with a single metal cation. Both sulfates can also be reversibly oxidized and reduced using CO and O_2 pulses, with oxysulfides being the likely product following reduction.

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Table 1

BET surface areas of the samples used in this study.

		CeO_2	$Ce_{0.75}Zr_{0.25}O_2$	$Ce_{0.5}Zr_{0.5}O_2$	$Ce_{0.25}Zr_{0.75}O_2$	ZrO_2
S.A.(m^2/g)	normal	80	42	45	56	82
	citric acid		98	84	110	

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Captions:

Fig.1 X-ray diffraction patterns for a) CeO_2, b) ZrO_2, c) a physical mixture of CeO_2 and ZrO_2, d)$Ce_{0.5}Zr_{0.5}O_2$(N), and e) $Ce_{0.5}Zr_{0.5}O_2$(C). All samples were calcined in air at 873 K.

Fig.2 DRIFTS spectra obtained for the following conditions:
i) a) A Pd/CeO_2 catalyst calcined at 773 K. The remaining spectra were obtained after exposure to 1% SO_2 and 50% O_2 for 20 min at b) 373 K, c) 473 K, and d) 673 K.
ii) a) A Pd/ZrO_2 catalyst calcined at 773 K. The remaining spectra were obtained after exposure to 1% SO_2 and 50% O_2 for 20 min at b) 298 K, c) 373 K, d) 473 K, e) 673 K, and f) 723 K.

Fig.3 TPD results using pure He as carrier gas for a series of SO_2 poisoned catalysts: a) Pd/CeO_2; b) Pd/$Ce_{0.5}Zr_{0.5}O_2$(N), c) Pd/$Ce_{0.25}Zr_{0.75}O_2$(N), and d) Pd/ZrO_2. All catalysts were poisoned by 1% SO_2 in 50% O_2 at 673 K for 30 min.

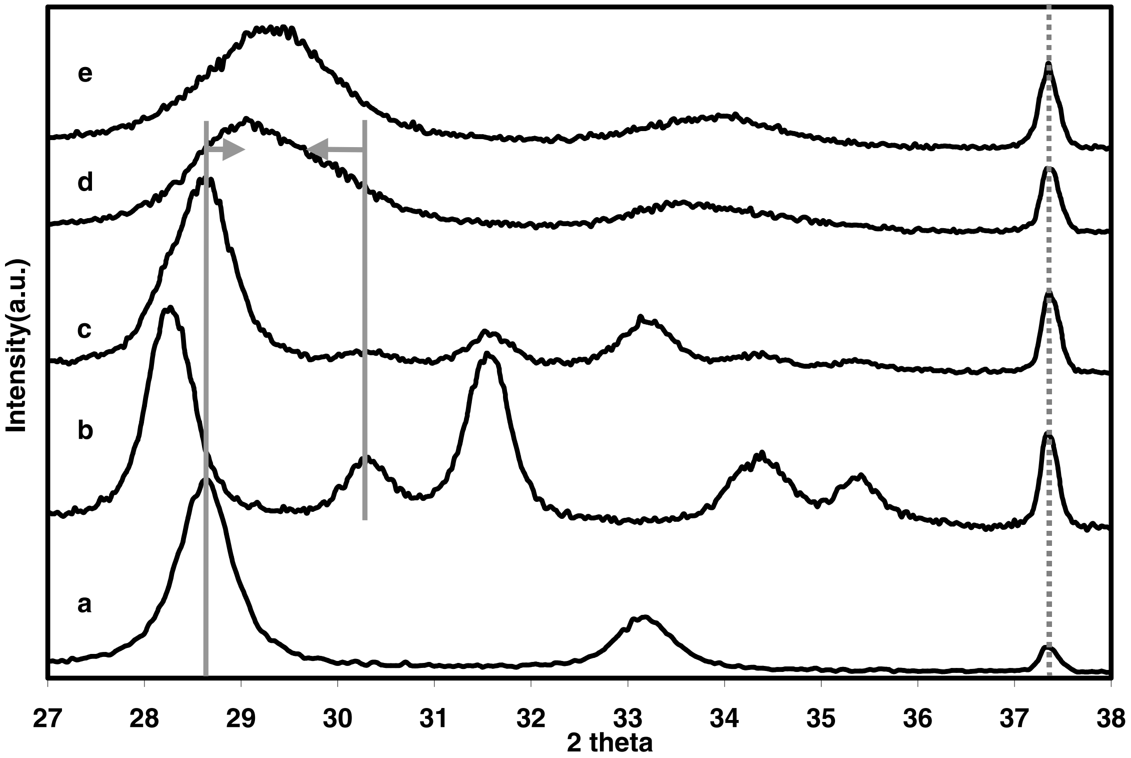
Fig.4 A plot of the amount of SO_2 formed in TPD between 900K and 1050 K as a function of Ce content of the sample. Hollow diamonds show data from $Ce_xZr_{(1-x)}O_2$(C); solid diamond are data from $Ce_xZr_{(1-x)}O_2$(N).

Fig.5 TPD results obtained using a 7% H_2 in He for SO_2-poisoned catalysts: a) Pd/CeO_2, b) Pd/$Ce_{0.5}Zr_{0.5}O_2$(N), and c) Pd/ZrO_2.

Fig.6 TPD results using a 5% CO in He SO_2-poisoned catalysts: a) Pd/CeO_2, b) Pd/$Ce_{0.5}Zr_{0.5}O_2$(N), and c) Pd/ZrO_2. The amounts of CO_2 in these experiments were: a) 4200 μmol/g, b) 2800 μmol/g, and c) 800 μmol/g respectively.

Fig.7 CO-O_2 pulse experiments for Pd/ZrO_2 operated at 873 K, before and after poisoning in 1% SO_2 and 50% O_2 at 673 K for 30 min. The amounts of CO_2 formed during the CO pulses are approximately 160 μmol/g for fresh catalyst and 710 μmol/g for poisoned catalyst.

Fig.8 FTIR spectra of the Pd/ZrO_2 sample poisoned in 1% SO_2 and 50% O_2 at 673 K for 10 min, obtained after the following pretreatments:
a) heated to 873 K in 40 torr CO for 10 min;
b) heated in O_2 at 873 K for 10 min;
c) heated to 873 K in 40 torr CO for 10 min.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d
c
b
a
Intensity(a.u.)
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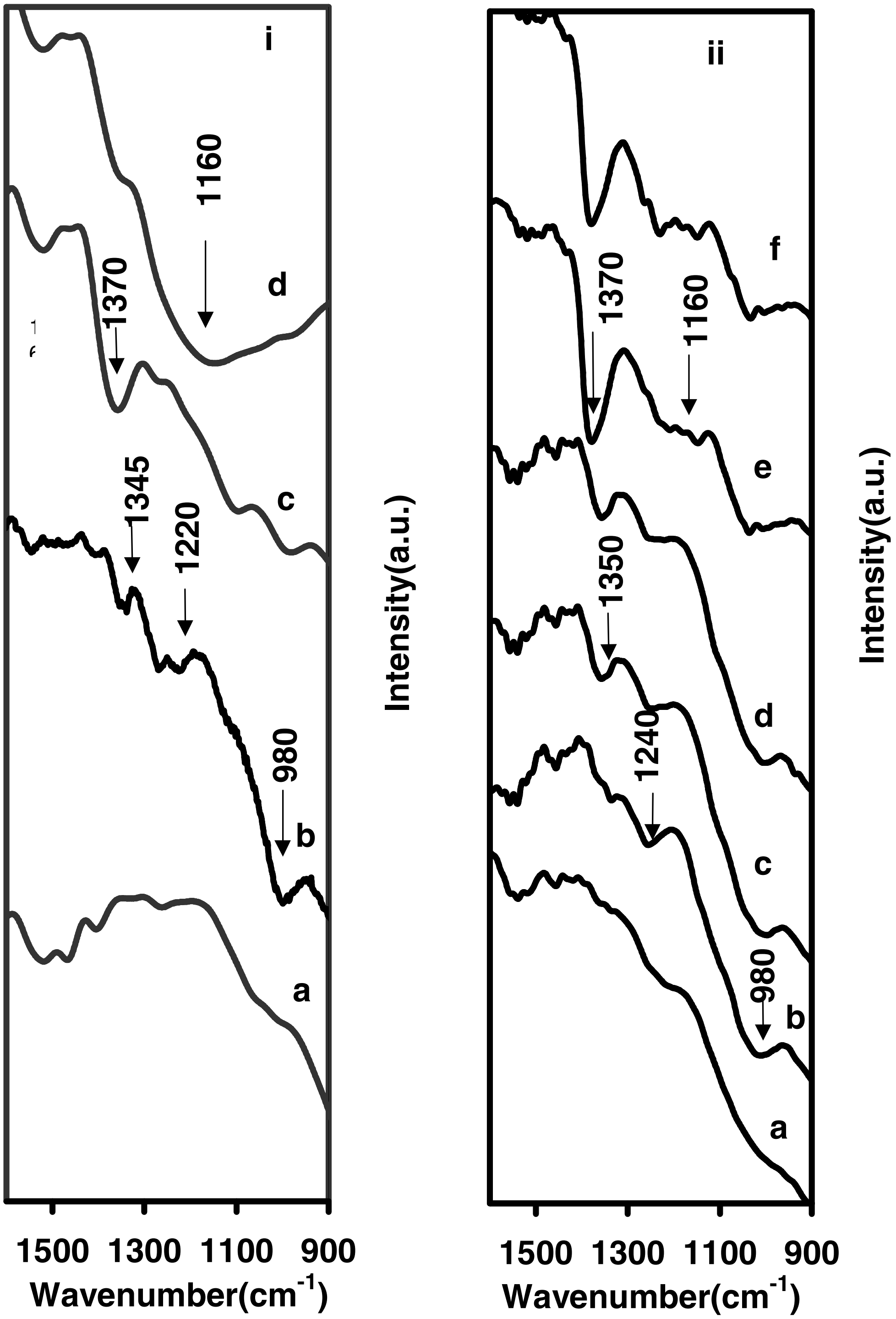
28
29
30
31
32
33
34
35
36
37
38
2 theta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1370
d
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1220
980
b
a
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Wavenumber(cm-1)
Intensity(a.u.)
ii
f
1370
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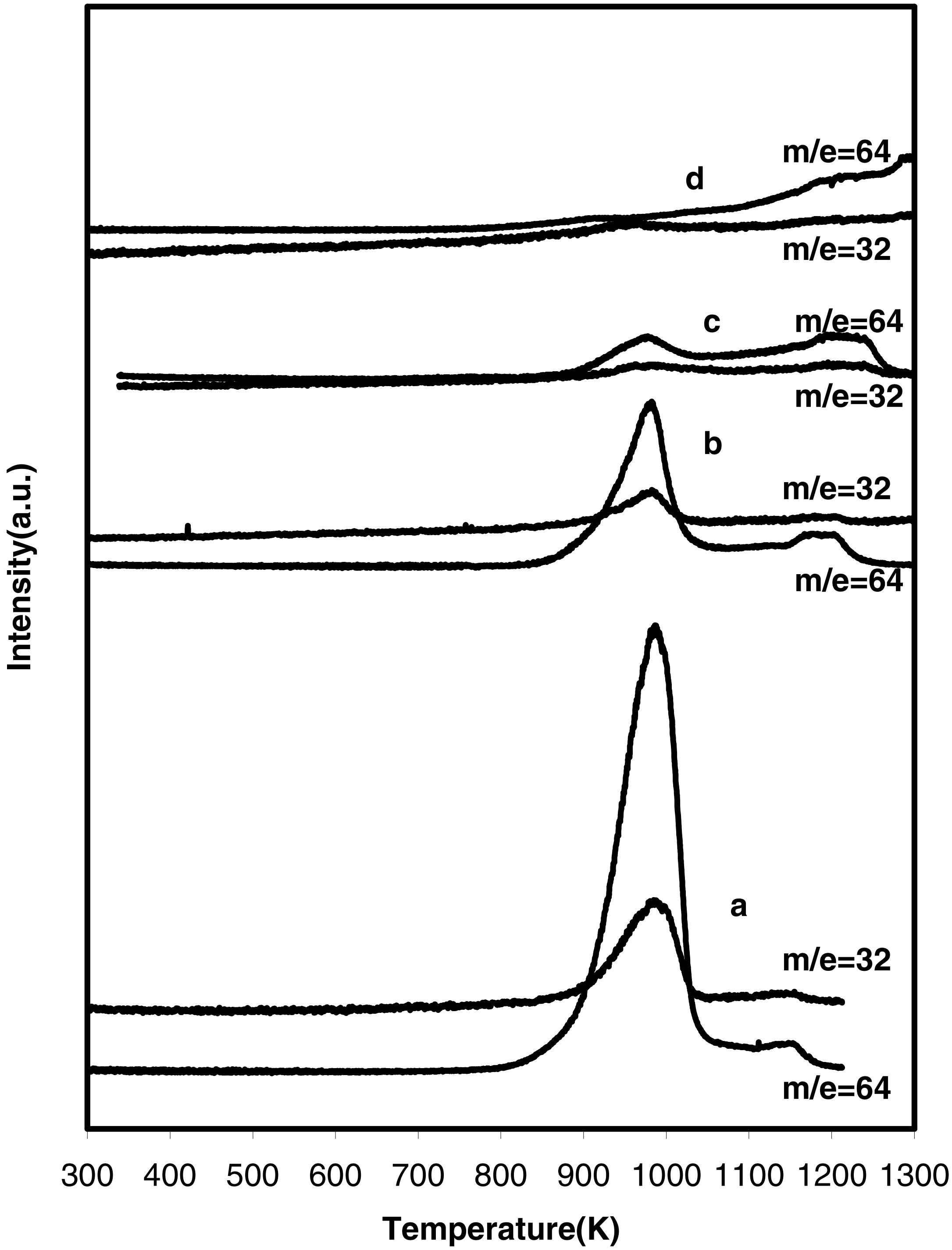
e
1350
d
1240
c
980
b
a
1500 1300 1100 900
Wavenumber(cm-1)
Intensity(a.u.)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Temperature(K)
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1200
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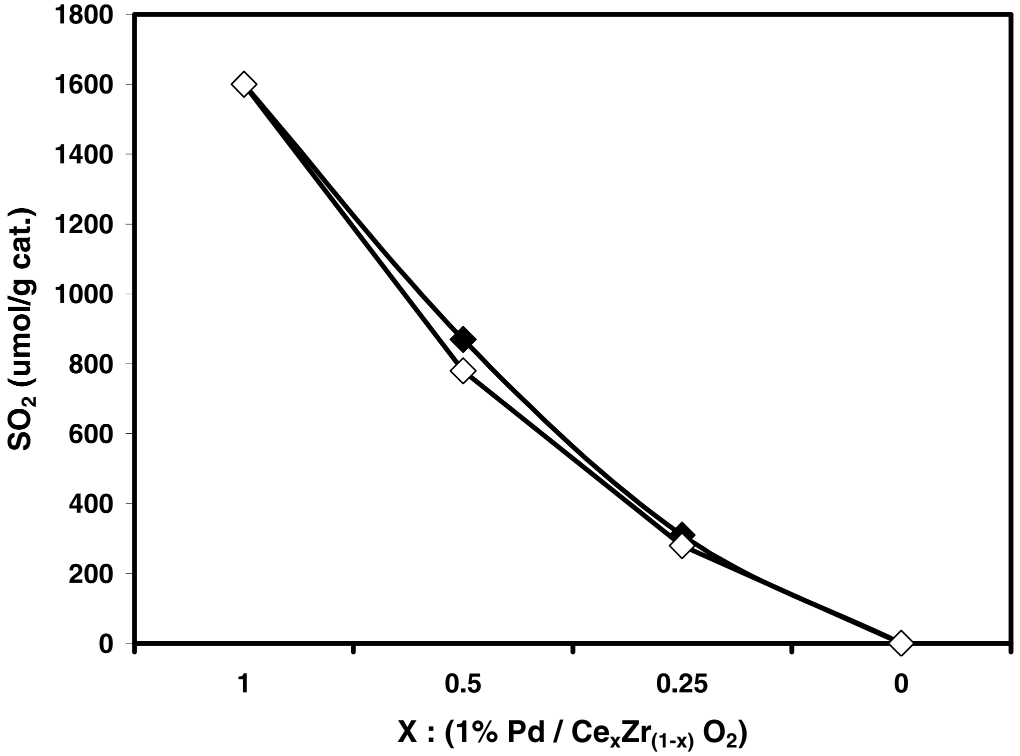
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1600
1400
1200
1000
800
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SO2 (umol/g cat.)
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0.25
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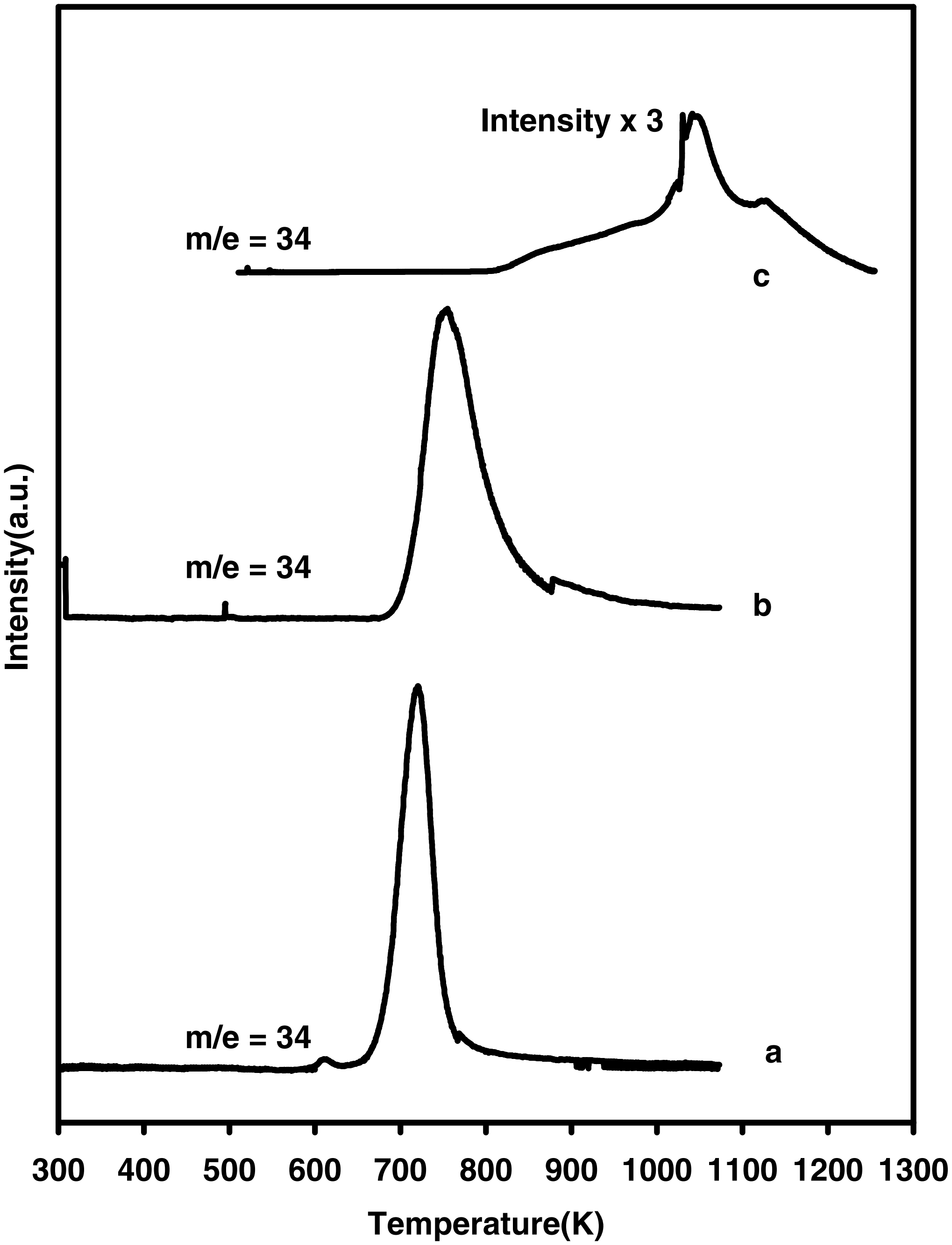
X : (1% Pd / CexZr(1-x) O2)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b
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Intensity(a.u.)
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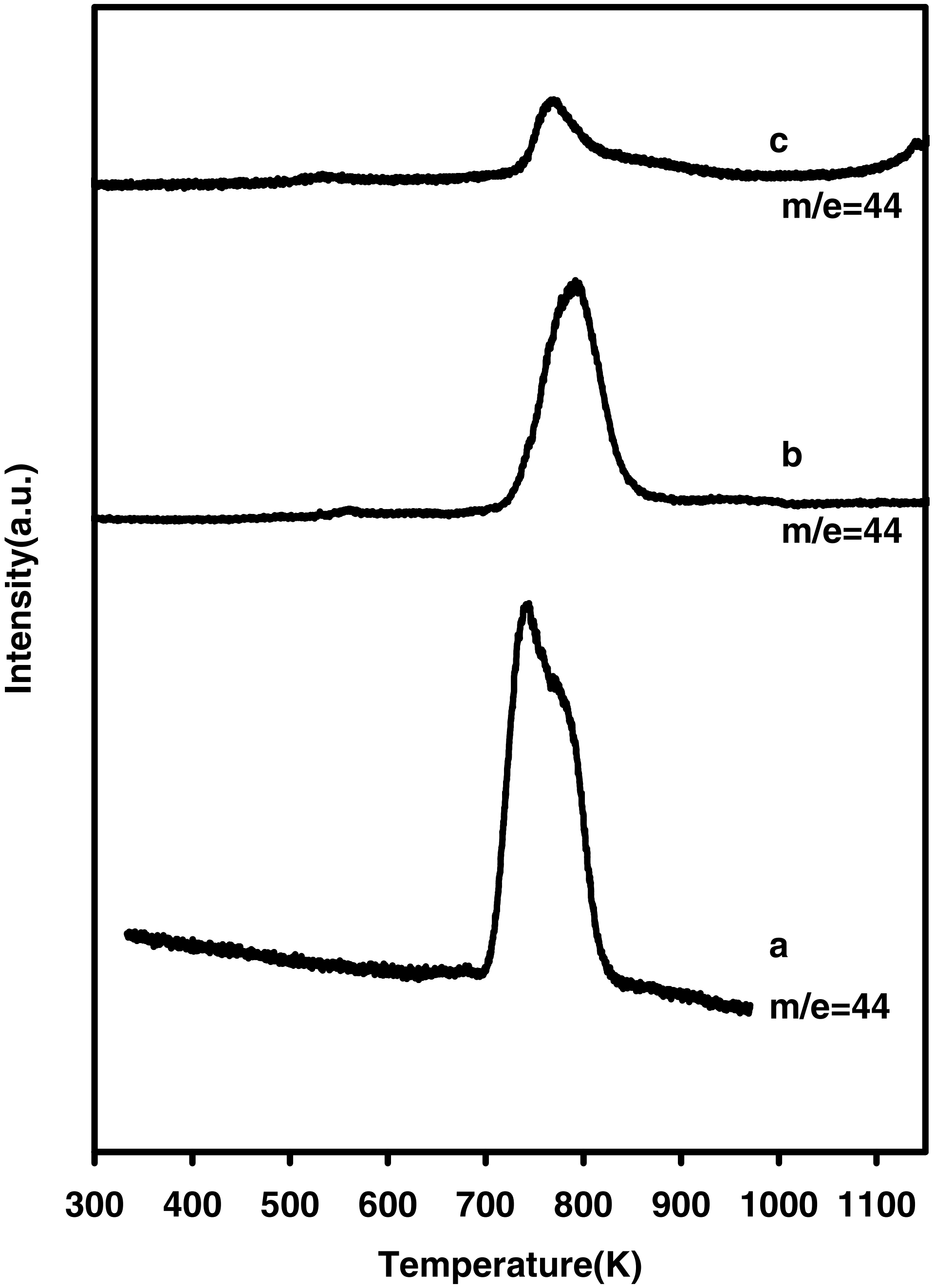
1100
1200
1300
Temperature(K)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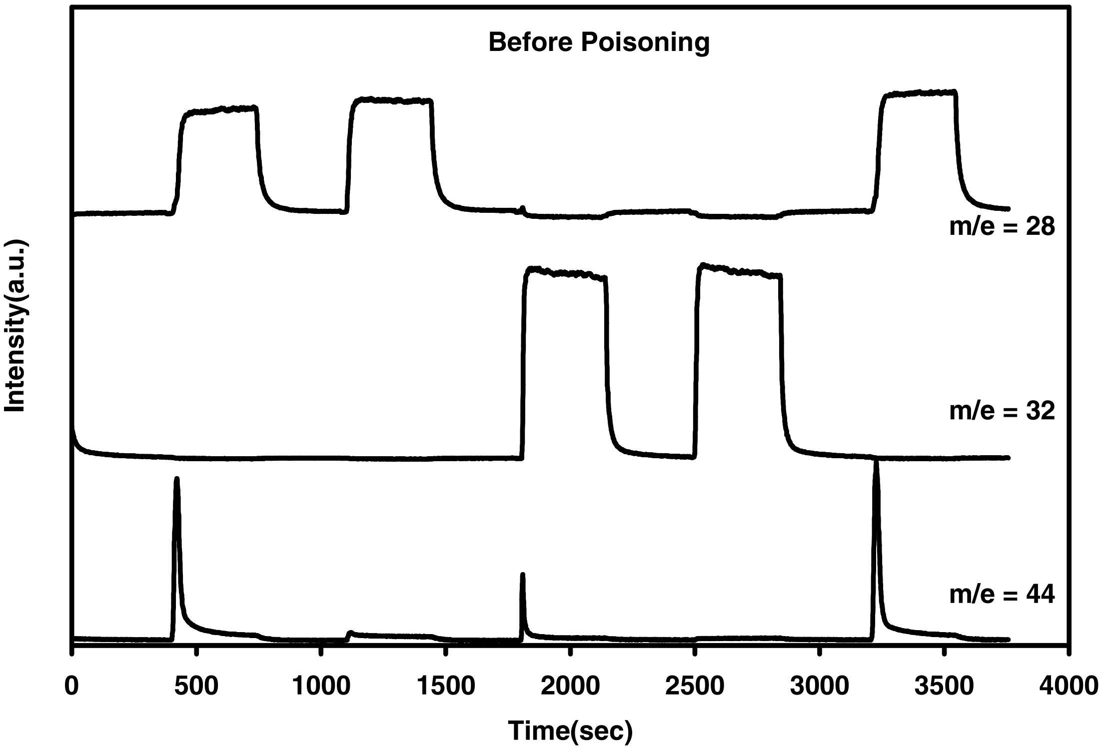
Temperature(K)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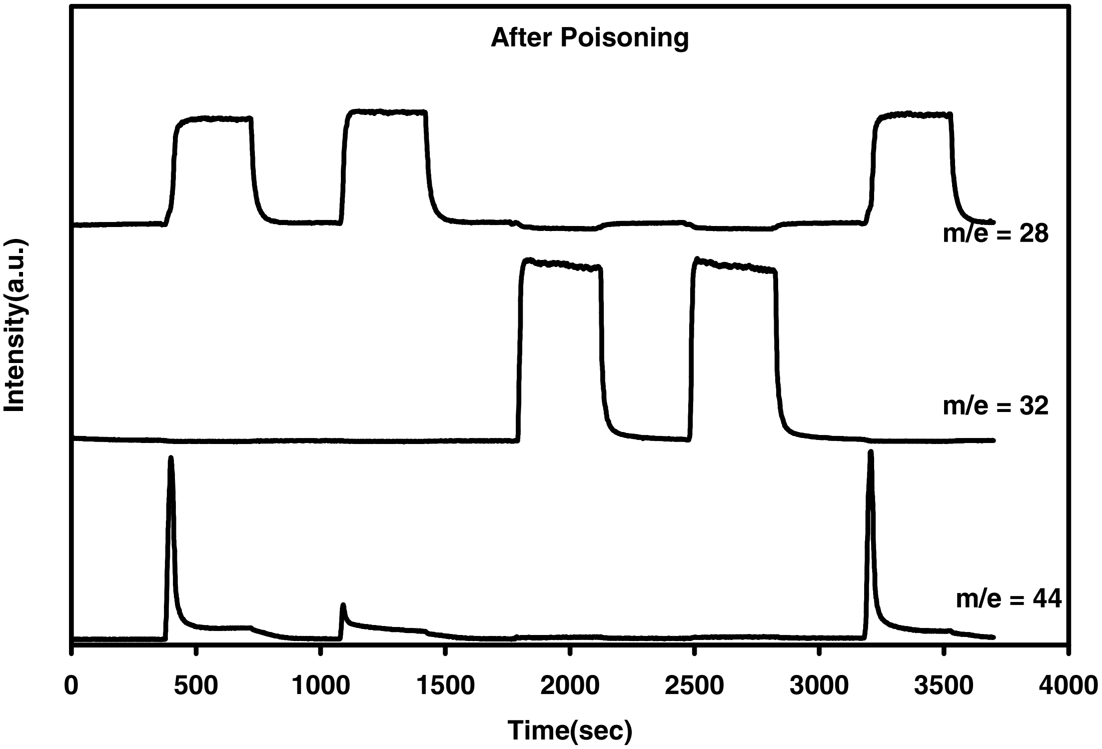
1500
2000
2500
3000
3500
4000
Time(sec)


After Poisoning
Intensity(a.u.)
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m/e = 32
m/e = 44
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500
1000
1500
2000
2500
3000
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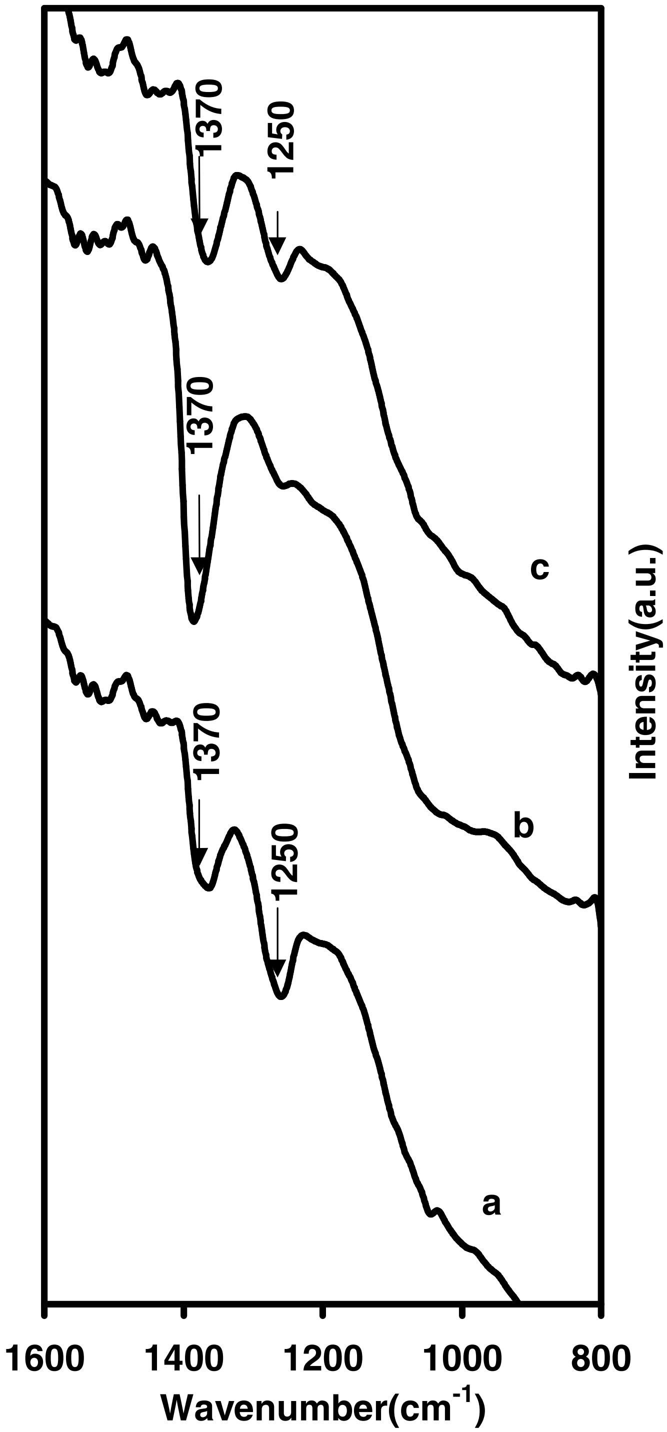
4000
Time(sec)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1250
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c
b
a
Intensity(a.u.)
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1400
1200
1000
800
Wavenumber(cm^{-1})