

Evaluation of New Mixed Oxides for Use as Sulfur Tolerant Exhaust Gas Catalysts

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to

The Coordinating Research Council, Incorporated

from

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Progress Summary

The sulfur tolerance of CeO_2 and $\text{CeO}_2\text{-ZrO}_2$ (75% mole of CeO_2) toward CO oxidation has been investigated. The presence of SO_2 leads to loss of CO oxidation activity of both CeO_2 and $\text{CeO}_2\text{-ZrO}_2$. However, the deactivation of $\text{CeO}_2\text{-ZrO}_2$ is less severe. Surface characterization of the SO_2 treated oxides revealed that both materials had a lower surface area, presumably due to sulfation, than the samples that were not exposed to SO_2 . XRD results, in agreement with EDX sulfur measurements, indicate that the sulfation of both samples is probably limited to the surface. Morphological changes in CeO_2 resulted from increasing time and temperature of exposure to SO_2 , crystallite size growth were observed. The $\text{CeO}_2\text{-ZrO}_2$ was more resistant to the morphological changes under SO_2 containing medium and maintained its initial crystallite size at higher temperatures.

Introduction

Much attention has been focused recently on the redox behavior of CeO_2 under conditions relevant to the performance of the TWC. Studies have shown that CeO_2 possesses poor thermal stability under redox conditions at temperatures above 1000°C leading to a loss in its OSC.⁽¹⁾ Studies of CeO_2 sulfation in the presence and absence of a noble metal suggest that CeO_2 readily forms sulfate compounds. Both, surface and bulk-like sulfate species have been identified at temperatures above 400°C using IR and Raman spectroscopy.⁽²⁾ Moreover, sulfation is suggested to lead to a drastic change in the redox properties of CeO_2 .⁽³⁾ Research has focused on improving the stability of CeO_2 by incorporation of a second oxide, typically ZrO_2 , in the CeO_2 lattice. Recent work has shown that $\text{CeO}_2\text{-ZrO}_2$ mixed oxides, in general, have improved OSC and thermal stability than pure CeO_2 , although the properties of the mixed oxide materials depend strongly on the ZrO_2 concentration and the method of preparation.⁽⁴⁻⁶⁾ The effect of sulfur on the properties of these mixed oxide materials is not well understood.

In the present investigation, we have studied the effect of SO_2 on the physical properties and oxidation activity of CeO_2 and $\text{CeO}_2\text{-ZrO}_2$ (3:1) mixed oxide. The influence of sulfate formation on the availability of surface oxygen for the catalytic CO

oxidation is compared for the two materials. Further, the “SO₂-induced” destabilization of the crystal structure of both materials is investigated and correlated to the oxidation performance.

Experimental

Materials

Two catalysts, CeO₂ and CeO₂-ZrO₂, were used in this investigation. Both CeO₂ (> 99.9%) and CeO₂-ZrO₂ (with Ce to Zr atom ratio of 3:1) were provided by a commercial source. Both samples were aged by calcination in air at 550 °C for 11 h prior to use and are designated as “fresh” samples in the remainder of the paper. The 4% CO (Liquid Carbonic), 10% O₂ (Praxair), 104 ppm SO₂ (Matheson) in N₂ and N₂ (Praxair, > 99.999%) were used without further purification.

Characterization

The surface area and porosity of the catalyst samples were determined by N₂ physisorption according to the BET method using a volumetric sorption analyzer (model ASAP 2010, Micromeritics). X-ray diffraction (XRD) patterns of the samples were obtained with a Philips XPERT diffractometer using a standard Ni-filtered Cu K α radiation source operating at 40 kV and 30 mA. All measurements were made in the thin film mode with a scan rate of 0.08 2 θ °/s

Catalytic Experiments

The catalytic experiments were conducted at atmospheric pressure in a flow reaction system. The system was constructed of stainless steel tubing equipped with a 4 mm ID quartz U-tube reactor. The reactor contained a 10 mm ID section in which the catalyst was supported on a quartz frit. The reaction gases (CO, O₂, SO₂ and N₂) were mixed prior to the reactor zone and the desired flow rate of each gas was maintained within ± 1 cm³/min using mass flow controllers (Brooks model 5850E). An Omega CN 2011 programmable temperature controller was used to maintain the reaction temperature within ± 1 °C, measured by a K-type thermocouple placed inside a quartz thermocouple well (3 mm OD) in direct contact with the catalyst bed. The product stream was analyzed by a Nicolet 560 FT-IR equipped with a 2-meter length gas cell (Nicolet) maintained at 165°C by the means of a temperature controller (DigiSense). The gas phase CO and CO₂ concentrations were measured directly using the OMNIC software after initial calibration.

The catalytic CO oxidation with and without SO₂ in the reaction stream was investigated under three different sets of experimental conditions (Table 1). Prior to the CO oxidation reaction, the catalyst samples were pretreated under flowing 10% O₂ or a mixture of 40 ppm SO₂ and 6% O₂ (balance N₂, total flow rate = 30 cm³/min) by heating from 25°C to 600°C at the rate of 4.8°C/min and holding at 600°C for 2 h before cooling to 25°C in flowing N₂. For all experiments, 75 mg of catalyst was used and the standard reaction feed (for case 1 and 3) consisted of 1% CO and 2% O₂ in N₂ with a total flow rate of 112.5 cm³/min. For case 2 experiments, 20 ppm SO₂ was added to the feed stream

while the total flowrate was held constant. The reaction temperature was varied from 300°C to 600°C at 100°C intervals. After allowing 10 min to reach steady state, 3 effluent samples were analyzed at 17 min intervals at each temperature. The extent of reaction reversibility was checked for all runs after reaching 600°C, by decreasing the reaction temperature stepwise to 300°C and comparing the activity to the activity initially measured.

Table 1 Sample pretreatment and reaction conditions for CeO₂ and CeO₂-ZrO₂ samples.

| Sample Type | Pretreatment Conditions | Reaction Conditions |
|-------------|---|--|
| 1 | 10% O ₂ in N ₂ at 600°C | 1% CO + 2% O ₂ in N ₂ |
| 2 | 10% O ₂ in N ₂ at 600°C | 1% CO + 2% O ₂ + 20 ppm SO ₂ in N ₂ |
| 3 | 40 ppm SO ₂ + 6% O ₂ in N ₂ at 600°C | 1% CO + 2% O ₂ in N ₂ |

Results

The conversion of CO to CO₂ catalyzed by CeO₂ and CeO₂-ZrO₂ in the absence of SO₂ (Table 1, case 1) is shown in Figure 1. As seen in Figure 1A, for CeO₂, the CO conversion was 18% at 300°C, increased to ~ 100% at 500°C and remained a ~ 100% when the temperature was increased to 600°C. Furthermore, the CO oxidation behavior was fully reversible. The measured values of the conversion of CO as the temperature was decreased from 600°C back to 300°C were the same as those measured when the temperature was increased. The behavior of CeO₂-ZrO₂ was similar to CeO₂ under these conditions (Figure 1B). Conversion of CO reached 100 % at 500°C and was again fully reversible when the temperature was decreased from 600°C to 300°C.

Figure 2A shows the CO conversion catalyzed by CeO₂ in the presence of 20 ppm SO₂ (Table 1, case 2). The initial CO conversion at 300°C was 18% but at temperatures higher than 300°C, CO conversion was lower in comparison to the value measured for the CO+O₂ reaction in the absence of SO₂ (see Figure 1A). The CO conversion increased from 18% at 300°C to 85% at 500°C. However, when the temperature was further increased to 600°C the CO conversion dropped to ~ 50%. The catalyst deactivation was permanent, as the measured CO conversion values were lower when the reaction temperature was decreased than when the temperature was increased. At a final test temperature of 300°C the CO conversion was less than 10%.

The activity behavior of CeO₂-ZrO₂ under similar conditions was different than CeO₂. With the CeO₂-ZrO₂, the initial CO conversion increased from 18% at 300°C to 95% at 500°C. Increasing the temperature to 600°C did not result in a substantial decrease in activity as in the case of CeO₂. The initial CO conversion at 600°C was 95%

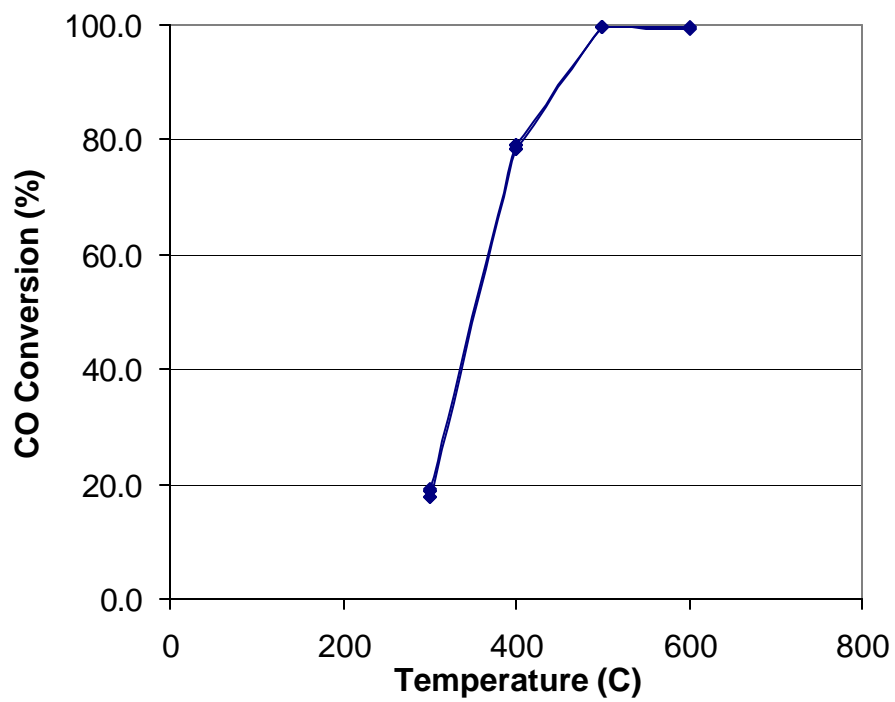


Figure 1A. CO conversion as a function of temperature for the reaction of 1% CO + 2% O₂ over CeO₂.

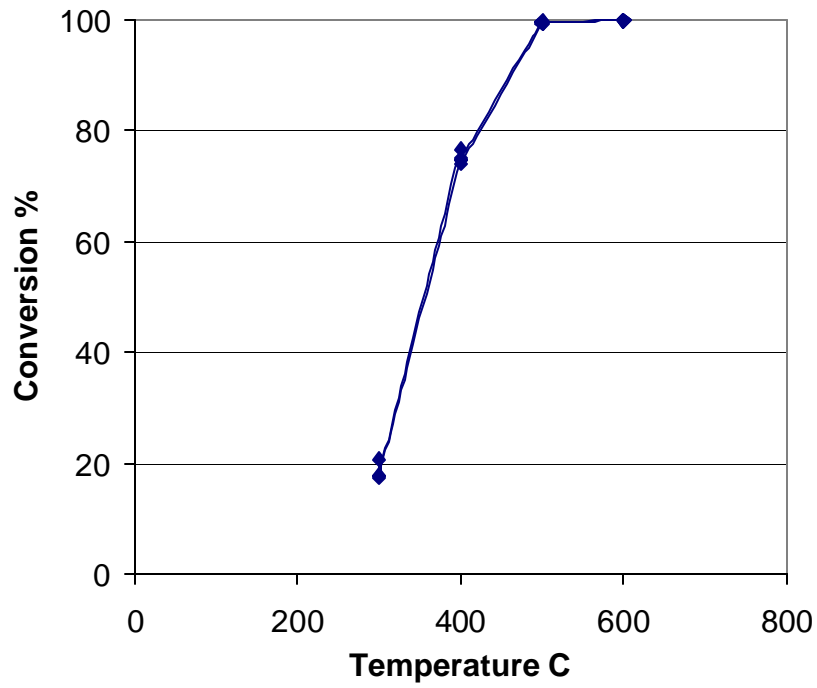


Figure 1B. CO conversion as a function of temperature for the reaction of 1% CO + 2% O₂ over CeO₂-ZrO₂.

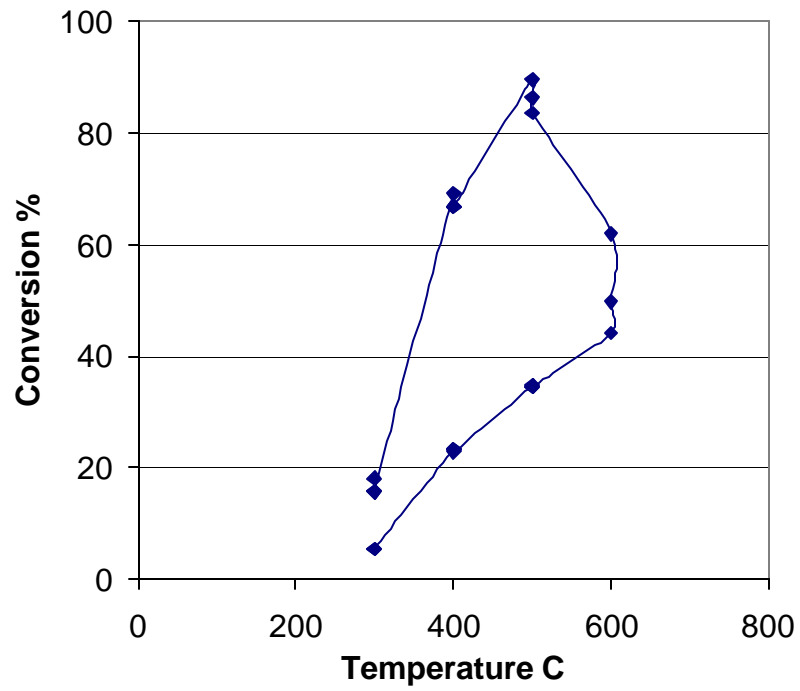


Figure 2A. CO conversion as a function of temperature for the reaction of 1% CO + 2% O₂ + 20 ppm SO₂ over CeO₂.

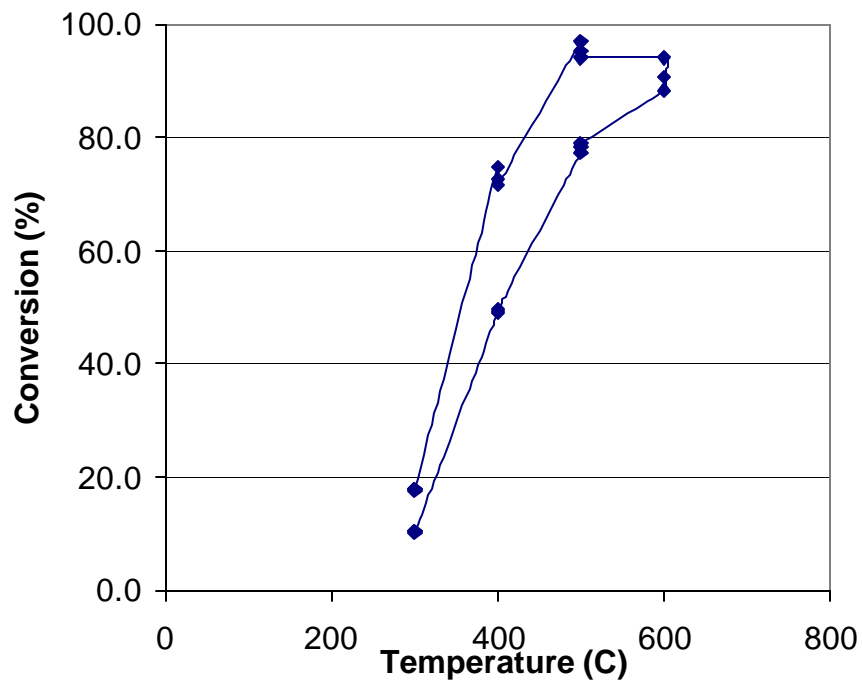


Figure 2B. CO conversion as a function of temperature for the reaction of 1% CO + 2% O₂ + 20 ppm SO₂ over CeO₂-ZrO₂.

and decreased to 88% in 40 min. Lowering the temperature revealed that the catalyst irreversibly deactivated; the CO conversion values were ~ 20% lower when the temperature was decreased as compared to when the temperature was increased. However, this decrease in activity was less than when the CeO₂ catalyst was used.

Further information on the SO₂ tolerance of CeO₂ and CeO₂-ZrO₂ was obtained by pre-sulfation of the samples as described in Table 1, case 3. Even without SO₂ in the reactant stream, the sulfated CeO₂ possessed very low activity for CO oxidation at all temperatures (Figure 3A). The CO conversion was negligible below 500°C and the maximum CO conversion reached at 600°C was only 6% (Figure 3A). The CO oxidation activity of CeO₂-ZrO₂ was also lower compared to the non pre-sulfated samples (Figure 3B). The initial CO conversion at 300°C for this sample was 3% and an increase in temperature to 600°C resulted in a maximum CO conversion of 48%. Thus, compared to the pre-sulfated CeO₂, the pre-sulfated CeO₂-ZrO₂ is approximately 8 times more active at 600°C.

The X-ray diffraction patterns for the CeO₂ catalyst samples after the different treatments are shown in Figure 4A. Fresh CeO₂ (curve a) displayed an XRD pattern that corresponded to the cubic fluorite structure of pure CeO₂ with characteristic intense peaks for the 111, 200, 220 and 311 faces. The XRD peaks were sufficiently broad that it was possible to use the Debye-Scherrer equation to calculate the average crystallite size (Table 2). The peak widths at half maxima for XRD lines at 29° and 48.5° (?) were used for the calculations. Fresh CeO₂ (curve a in Figure 4A) had an average crystallite size of 9.7 nm. There was no change in the XRD pattern of the sample (Table 1, case 1) after exposure to the CO+O₂ oxidation reaction up to 600°C (curve b in Figure 4a). However, exposure of the CeO₂ sample to CO+O₂+SO₂ reaction (Table 1, case 2) at 600°C (curve c, Figure 4A) resulted in a decrease in the X-ray line width for all the major lines, while the band position remained unchanged. The calculated crystallite size for this sample from XRD data was 23.3 nm. A similar narrowing of the XRD lines was observed (curve d, Figure 4A) for the CeO₂ sample after a sulfation pretreatment at 600°C (Table 1, case 3) resulting in a crystallite size of 26.7 nm.

The XRD patterns of the fresh and reaction-exposed CeO₂-ZrO₂ are shown in Figure 4B. The fresh CeO₂-ZrO₂ displayed a pattern similar to CeO₂ (curve a). No additional lines attributable to any phase of ZrO₂ were detected. However, the XRD lines displayed a greater degree of peak asymmetry as compared to pure CeO₂ (Figure 4A, curve a). Treatment of the CeO₂-ZrO₂ sample with CO+O₂ (Figure 4B, curve b) or CO+O₂+SO₂ (curve c) did not result in a change in the XRD pattern obtained as compared to the fresh CeO₂-ZrO₂. Similarly, pre-sulfation of the CeO₂-ZrO₂ at 600°C (curve d) resulted in no significant change in its XRD pattern. The crystallite sizes of the samples as calculated from the XRD data were in the range of 8.7-9.2 nm (Table 2).

The surface area, pore size, and pore volume, as measured by N₂ adsorption using the BET method are, shown in Table 2. The surface area of the fresh CeO₂ was 140.7 m²/g and the average pore diameter was 56 Å. Nitrogen adsorption carried out in the pressure range of 1e⁻⁵ – 0.1 P/P₀ indicated that all samples used for this study had negligible microporosity. The contribution of pores less than 20Å to the total pore

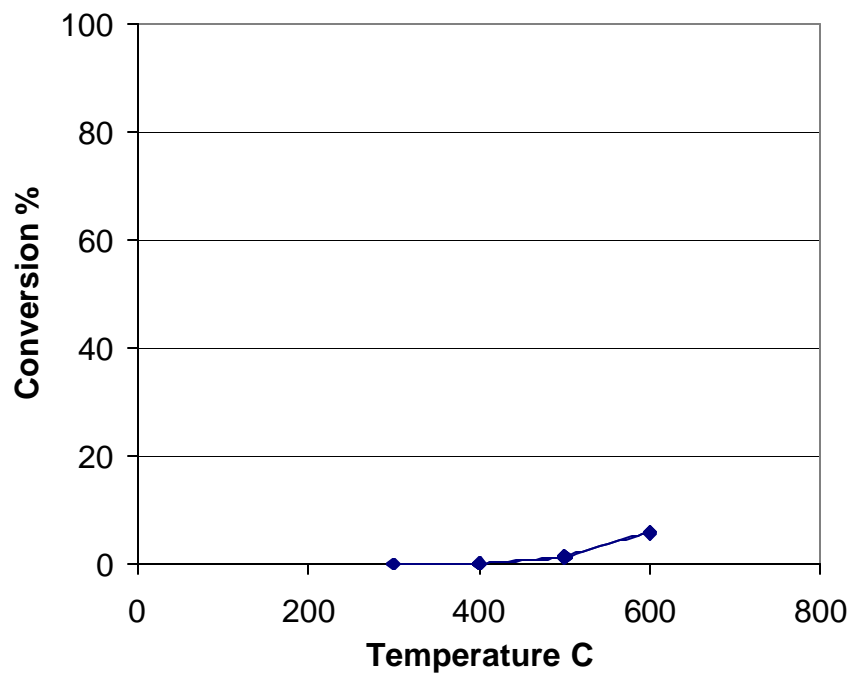


Figure 3A. CO conversion as a function of temperature for the reaction of 1% CO + 2% O₂ over CeO₂ (presulfated at 600°C for 2 h).

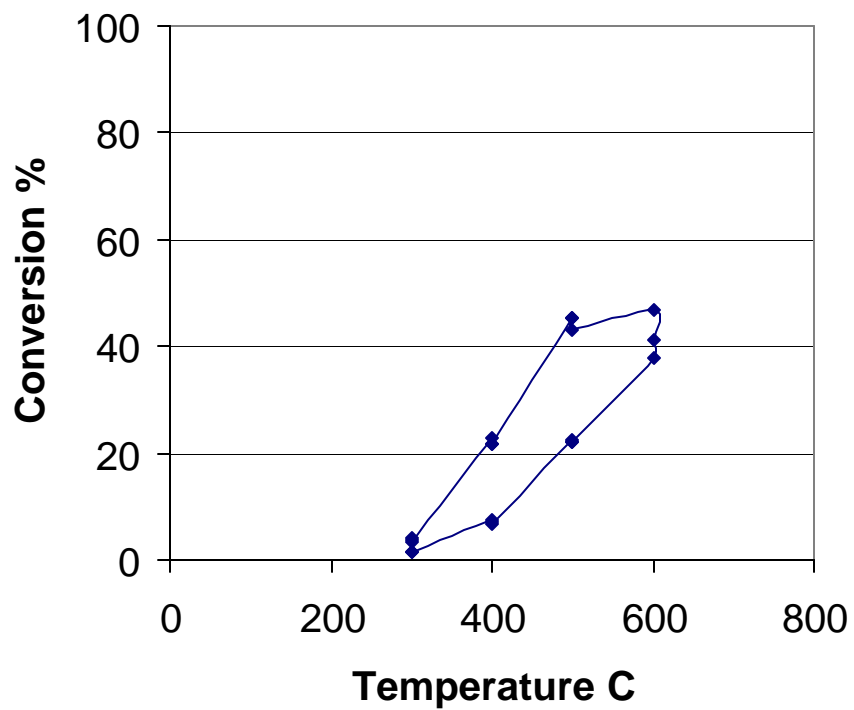


Figure 3B. CO conversion as a function of temperature for the reaction of 1% CO + 2% O₂ over CeO₂-ZrO₂ (pre-sulfated at 600°C for 2 h).

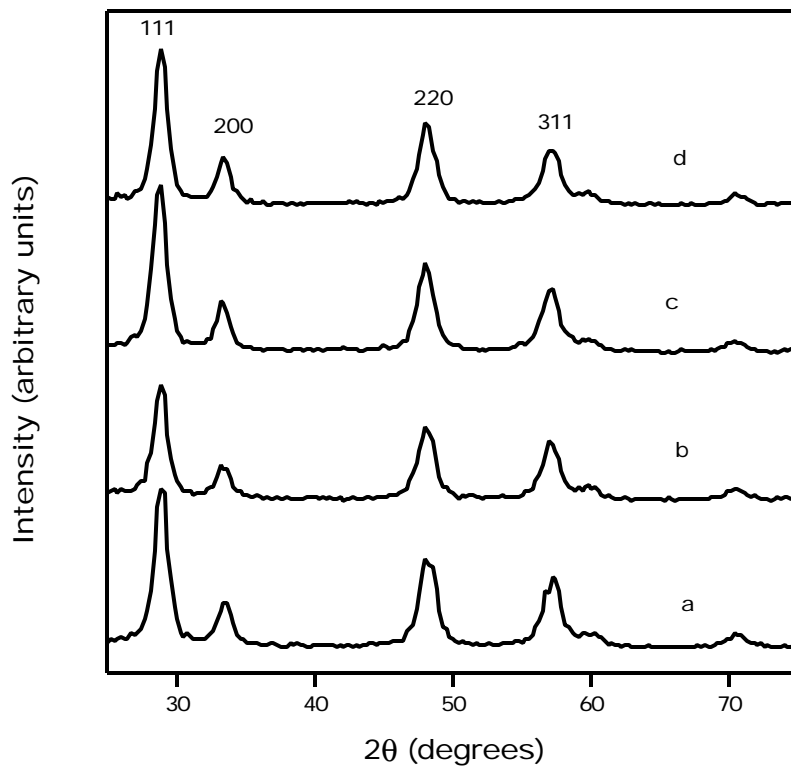


Figure 4A. XRD pattern of fresh CeO_2 (oxidized at 600°C) (a), and following $\text{CO} + \text{O}_2$ reaction up to 600°C (b), following $\text{CO} + \text{O}_2 + \text{SO}_2$ reaction up to 600°C (c) and following sulfation in 40 ppm $\text{SO}_2 + 6\% \text{O}_2$ at 600°C (d).

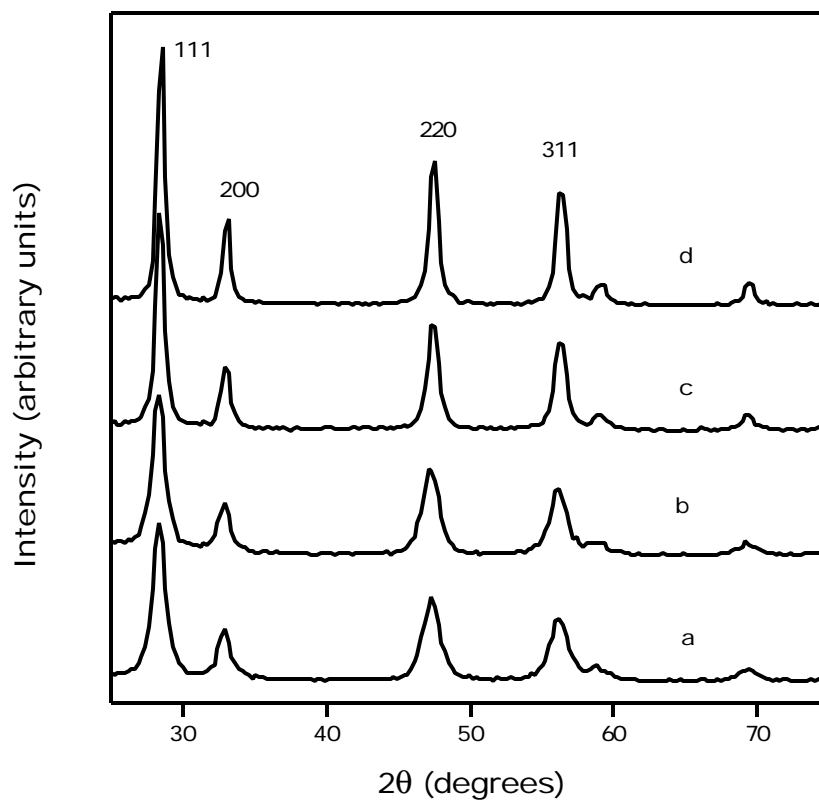


Figure 4B. XRD pattern of fresh CeO₂-ZrO₂ (oxidized at 600°C) (a), and following CO+O₂ reaction up to 600°C (b), following CO+O₂+SO₂ reaction up to 600°C (c) and following sulfation in 40 ppm SO₂+6% O₂ at 600°C (d).

Table 2. BET surface area, pore volume, pore diameter and crystallite size for CeO₂ and CeO₂-ZrO₂ samples.

| Sample | Pretreatment | BET Area m ² /g | Pore Volume* cc/g | Pore Diameter Å | Crystallite Size** nm |
|------------------------------------|---|-------------------------------|----------------------|-----------------------|-----------------------------|
| CeO ₂ | None | 140.7 | 0.198 | 56.2 | 9.7 |
| CeO ₂ | CO+O ₂ reaction | 138.1 | 0.193 | 56.2 | 10 |
| CeO ₂ | CO+O ₂ +SO ₂ reaction | 99.4 | 0.17 | 64.4 | 23.3 |
| CeO ₂ | Sulfation at 600°C | 75.8 | 0.194 | 102.2 | 26.7 |
| CeO ₂ -ZrO ₂ | None | 108.9 | 0.282 | 101.2 | 9.2 |
| CeO ₂ -ZrO ₂ | CO+O ₂ reaction | 101.9 | 0.262 | 102.8 | 8.7 |
| CeO ₂ -ZrO ₂ | CO+O ₂ +SO ₂ reaction | 83.7 | 0.118 | 113.8 | 8.8 |
| CeO ₂ -ZrO ₂ | Sulfation at 600°C | 89.6 | 0.261 | 116.4 | 9.1 |

* Macropore volume calculated from N₂ adsorption data.

**Average of line broadening data for the 111 and 220 XRD lines using the Scherrer equation.

volume was less than 1% for all samples. The reaction of only CO+O₂ at temperatures up to 600°C (Table 1, case 1) did not change the surface area or pore size of the material. Exposure of the CeO₂ to the CO oxidation reaction in the presence of SO₂ (Table 1, case 2) resulted in a decrease in its surface area by 30% and an increase in the average pore size from 56 Å to 68 Å. Pre-sulfation of the sample by using a SO₂+O₂ mixture at 600°C (Table 1, case 3) resulted in an even more severe effect on surface area and pore size.

The CeO₂-ZrO₂ showed similar to CeO₂ behavior following the CO+O₂ reaction at 600°C. Exposure to SO₂ also resulted in changes in its surface area and pore size. As seen in Table 2, the surface area of the CeO₂-ZrO₂ samples decreased by 46% and the pore size increased from 56 to 102 Å as a result of the CO+ O₂+ SO₂ reaction at 600°C. A similar effect was observed for CeO₂-ZrO₂ samples subjected to pre-sulfation at 600°C.

Scanning electron micrographs of the CeO₂ and CeO₂-ZrO₂ samples are shown in Figures 5 and 6. Figure 5A and B shows the morphological difference of the fresh CeO₂ and following sulfation at 600°C. It is evident from the micrograph that crystallite growth takes place confirming the XRD analysis. The crystallite sizes measured from the SEM micrographs were <10 nm for fresh CeO₂ and ~28 nm for sulfated CeO₂. These values agree well with the calculated XRD crystallite sizes (Table 2). The SEM micrographs of fresh and sulfated CeO₂-ZrO₂ are shown in Figure 6. Crystallite sizes for

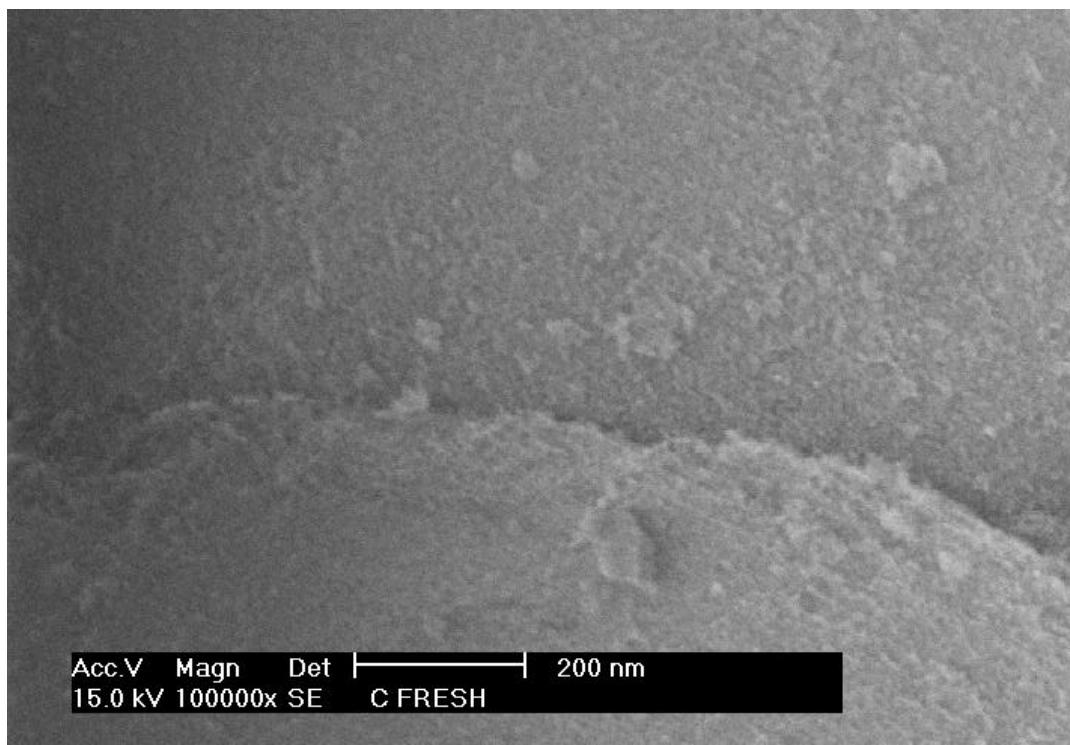


Figure 5A. Scanning electron micrograph showing surface details of a fresh CeO₂ catalyst sample.

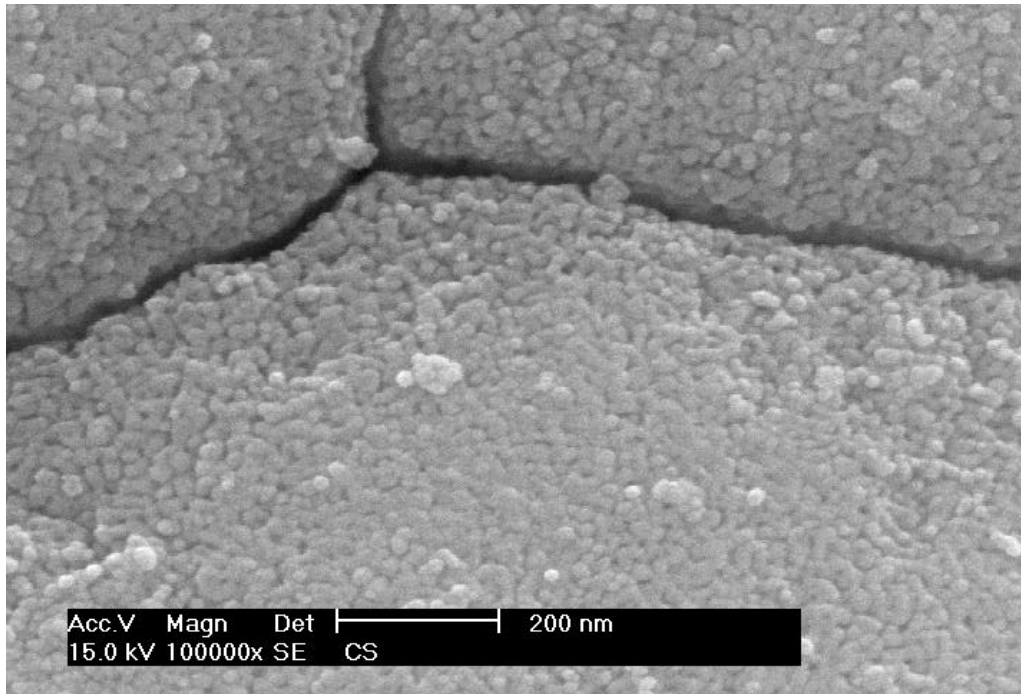


Figure 5B. Scanning electron micrograph showing surface features of a CeO₂ particle following treatment with a flowing mixture of 40 ppm SO₂ + 6% O₂ at 600°C for 2 h.

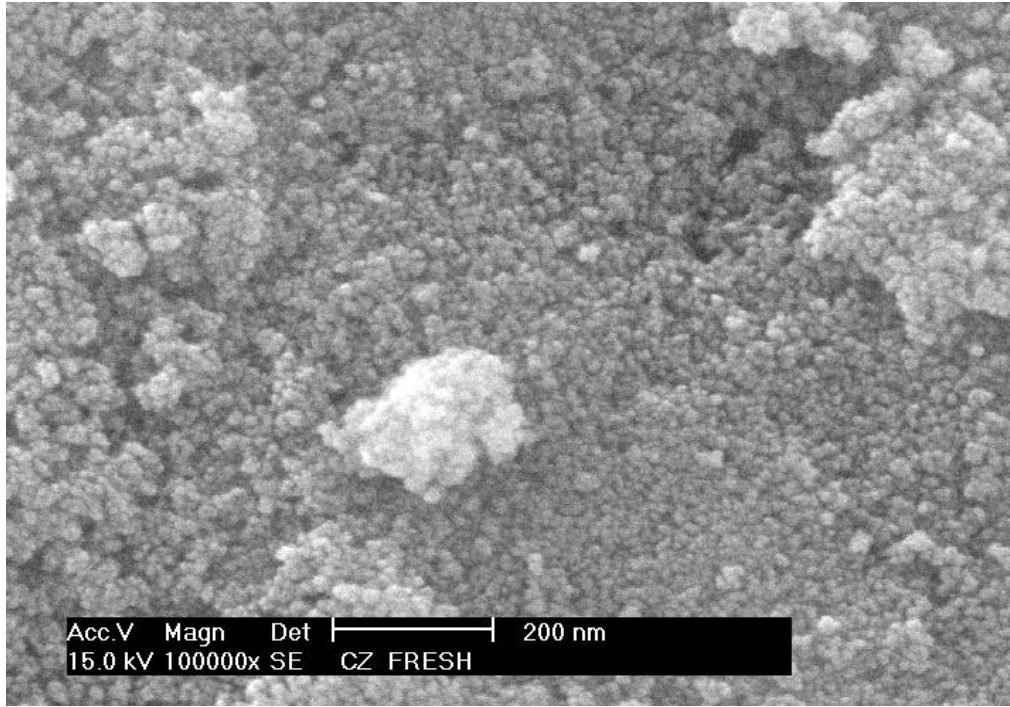


Figure 6A. Scanning electron micrograph showing surface details of a fresh CeO₂-ZrO₂ catalyst sample.

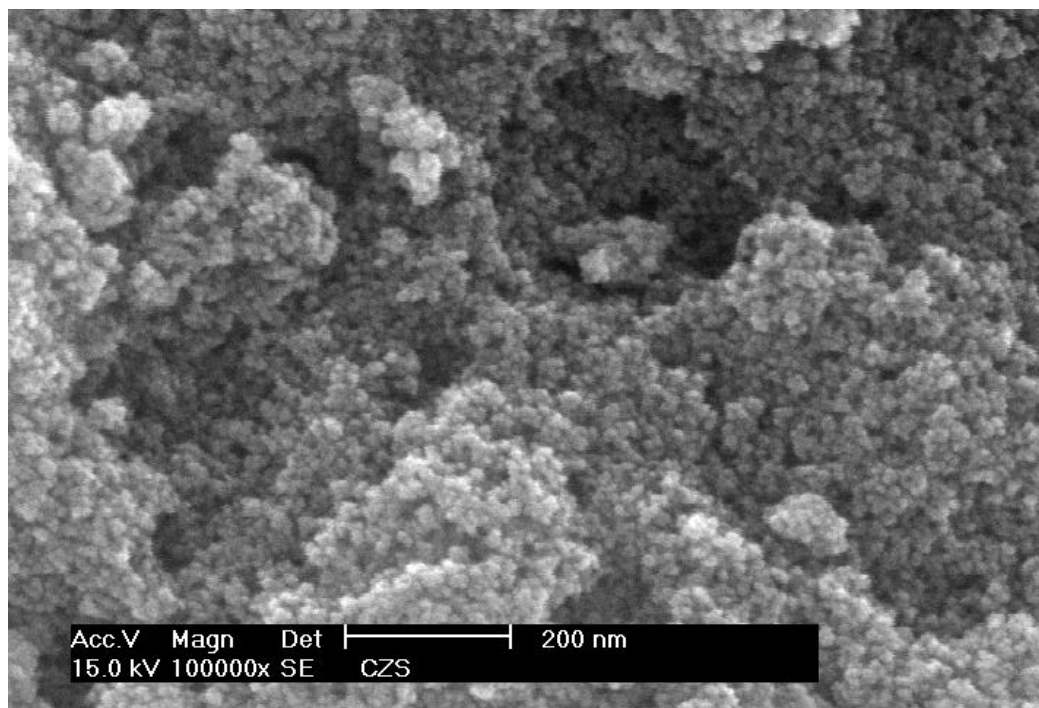


Figure 6B. Scanning electron micrograph showing surface features of a CeO₂-ZrO₂ particle following treatment with a flowing mixture of 40 ppm SO₂ + 6% O₂ at 600°C for 2 h.

Table 3. Sample compositions determined by EDX (atom percentage calculation excludes concentration of oxygen).

| Sample | Pretreatment | Atomic Percent | | |
|------------------------------------|---|----------------|------|-----|
| | | Ce | Zr | S |
| CeO ₂ | CO+O ₂ reaction | 100 | 0 | 0 |
| CeO ₂ | CO+O ₂ +SO ₂ reaction | 96.1 | 0 | 3.9 |
| CeO ₂ -ZrO ₂ | CO+O ₂ reaction | 76.4 | 23.6 | 0 |
| CeO ₂ -ZrO ₂ | CO+O ₂ +SO ₂ reaction | 72.2 | 21.9 | 5.9 |

particles in both Figure 6A and B were ~12 nm, again in agreement with the XRD data for CeO₂-ZrO₂.

Energy dispersive X-ray analysis (EDX) was employed to determine the sulfur content. Table 3 shows the relative atomic concentrations of Ce, Zr and S for the CeO₂ and CeO₂-ZrO₂ catalysts. The values shown in Table 3 were calculated using an EDAX software that averaged the signal from several thousand particles. After treatment with the sulfating gas mixture at 600°C for 2 h, both CeO₂ and CeO₂-ZrO₂ had sulfur concentrations less than 6% (note oxygen is not included in this estimate) suggesting that most of the sulfate species might be present on the surface. More importantly, the concentration of sulfur in both materials was comparable. Although there is no information regarding the stoichiometry of the sulfate species in the present case, it is reasonable to assume that the extent of sulfation in both materials was similar. Therefore, the sintering of CeO₂ particles on exposure to SO₂ cannot be explained by the extent of sulfation alone.

Summary of Results

The presence of SO₂ leads to loss of CO oxidation activity of CeO₂ and CeO₂-ZrO₂. The deactivation of CeO₂-ZrO₂ is less severe compared to that of CeO₂. Surface characterization of the SO₂ treated oxides revealed that both materials were susceptible to surface area loss, presumably due to sulfation. XRD results, in agreement with EDX sulfur measurements, indicate that the sulfation of both samples is probably limited to the surface. Morphological changes in CeO₂ with increasing time and temperature of exposure to SO₂ take place. They are manifested by crystallite size growth caused by grain sintering as shown by SEM. The CeO₂-ZrO₂ resisted morphological changes and maintained the crystallite size at high temperatures in the presence of SO₂. This “sulfur-resistance” of CeO₂-ZrO₂ is probably responsible for its higher CO oxidation activity compared to CeO₂.

Research Plans for the Year 3 of the Program

The investigation will be extended by studying the sulfur tolerance of the Pd/CeO₂ and Pd/CeO₂-ZrO₂ catalysts. Kinetics studies with reaction mixtures modeling real automotive exhausts will be coupled with Infrared and Raman spectroscopic investigations. In specific, we plan to

- Evaluate the sulfur tolerance of 1% Pd/CeO₂ and 1% Pd/CeO₂-ZrO₂ catalysts for TWC performance under lean, stoichiometric and cyclic conditions.
- Study CO adsorption on CeO₂ and Pd/CeO₂ by Infrared and Raman Spectroscopy for ascertaining the role of metal and oxide species in the redox behavior of CeO₂.
- Study in the collaboration with Prof. R. J. Gorte the transformation the surface species of sulfated ceria under conditions of OSC measurements by Raman spectroscopy to evaluate the impact of redox transitions of S atoms on measured OSC of the material.

References

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