

## Oxidation Entropies and Enthalpies for Ceria-based catalysts

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### Introduction

Ceria-based catalysts are important for providing oxygen-storage capacitance in automotive three-way catalysts [1,2] and are finding new applications as supports for water-gas-shift catalysts [3] and other reactions [4]. At least some of the crucial properties of ceria are related to the fact that Ce can exist as either  $Ce^{+3}$  or  $Ce^{+4}$ . The higher OSC of the mixed oxides has sometimes been attributed to the mixtures having higher surface areas following thermal treatments [5], but it seems clear that other factors also play a role [5,6]. However, while thermodynamic data for oxidation and reduction of bulk ceria are available, there is little analogous information on ceria-zirconia mixed oxides and ceria on various supports. Therefore, our laboratories have begun to investigate the equilibrium redox properties of ceria-based catalysts to quantify differences between ceria and ceria-based catalysts and to determine how compositions and structure affect these differences.

### Materials and Methods

Ceria-zirconia mixed oxides were prepared using the citric acid method. Stoichiometric amounts of  $Ce(NO_3)_3$  and  $ZrO(NO_3)_2 \cdot xH_2O$  were dissolved in distilled water and then mixed with aqueous citric acid ( $\geq 99.5\%$ , Aldrich) to produce a solution with a citric-acid:metal-ion ratio of 1:2. The solutions were stirred vigorously at room temperature for one hour and then the water was removed by evaporation. Finally, the resulting solids were heated in air at 723 K for 5 hours to produce the mixed oxides. The wet impregnation method is used to prepare ceria on different supports, and the resulting solids were also calcined at 723 K for 5 hours. The oxygen isotherms were measured in a flow reactor, using techniques that have been described elsewhere [7], and in a Coulometric titration setup [8].

Since the equilibrium  $P(O_2)$  are very low when the sample is partially reduced, the  $P(O_2)$  is defined by assuming equilibrium for  $H_2$  oxidation,  $H_2 + \frac{1}{2}O_2 = H_2O$ , in a gas-phase mixture with a fixed  $H_2O:H_2$  ratio, according to Equation 1).

$$P(O_2)^{1/2} = K_{equilib}^{-1} * P(H_2O)/P(H_2) \quad 1)$$

The equilibrium constant for oxidation of a metal oxide, such as  $CeO_{(2-x)}$ , is proportional to  $P(O_2)$ , so that this information provides the equilibrium constant and therefore the Gibbs Free Energy,  $\Delta G$ , for reaction at a particular value of  $x$ . Oxidation enthalpies,  $\Delta H$ , can be determined by measuring equilibrium isotherms at different temperatures, using Equation 2).

$$\Delta H = -R \delta \ln(P(O_2))/\delta(1/T) \quad 2)$$

### Results and Discussion

The isotherms for  $Sm_{0.2}Ce_{0.8}O_2$  showed that rare-earth dopants affect phase transition between 700 and 800°C, but do not improve the reducibility of ceria. Table 1 examined ceria supported on LDA (10%La<sub>2</sub>O<sub>3</sub>/alumina) following reduction in 90% H<sub>2</sub>-10%

H<sub>2</sub>O at 700°C. Preliminary data indicate  $-\Delta H \sim 600$  kJ/mol O<sub>2</sub> for Ceria/LDA, Compared to 760 kJ/mol for CeO<sub>2</sub>. The reduction of surface ceria is obviously different from the bulk ceria.

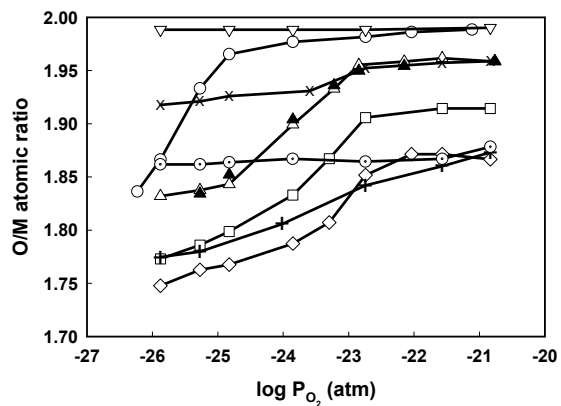
Fig. 1 shows isotherms at 973 K for ceria, zirconia, and a series of ceria-zirconia solid solutions having a wide range of compositions. Pure ZrO<sub>2</sub> showed minimal reduction in all cases, as expected. The isotherm for pure ceria also agreed well with published data [9] and was found to be independent of sample surface area for BET areas between 2 and 35 m<sup>2</sup>/g. It is worth noting again that ceria is almost completely oxidized (O:M = 1.98, M = Ce + Zr) at a  $P(O_2)$  of 10-23 atm, the oxygen fugacity that is reached with a gas mixture consisting of 8% H<sub>2</sub>O and 92% H<sub>2</sub>. The data in Fig. 3 show that the properties of the solid solutions cannot be described as physical mixtures of ceria and zirconia. Each of the solid solutions undergoes reduction at much higher values of  $P(O_2)$  than is observed for pure CeO<sub>2</sub> or ZrO<sub>2</sub>. For example, even the Ce<sub>0.92</sub>Zr<sub>0.08</sub>O<sub>2</sub> sample is significantly more reduced than CeO<sub>2</sub> at all  $P(O_2)$  between 10<sup>-21</sup> and 10<sup>-26</sup> atm. Calcining the Ce<sub>0.92</sub>Zr<sub>0.08</sub>O<sub>2</sub> sample to 1323 K had no effect on the oxygen isotherm, showing that the differences are not simply related to the surface areas.

With CeO<sub>2</sub>, Ce<sub>0.92</sub>Zr<sub>0.08</sub>O<sub>2</sub>, and Ce<sub>0.14</sub>Zr<sub>0.86</sub>O<sub>2</sub>, the samples remained single-phase after calcination at 1323 K and thermodynamic redox properties remained unchanged. By contrast, Ce<sub>0.59</sub>Zr<sub>0.41</sub>O<sub>2</sub> formed two mixed-oxide phases following 1323-K calcination and the isotherm changed to what would be expected for a physical mixture of the two phases that were formed.

While the oxidation enthalpy for CeO<sub>2</sub> was between -750 and -800 kJ/mol O<sub>2</sub>, the oxidation enthalpies on each of the mixed oxides was between -500 and -550 kJ/mol O<sub>2</sub> and almost independent of the extent of reduction. The shapes of the isotherms for the mixed oxides were primarily affected by the oxidation entropies, which depended strongly on the sample and the extent of reduction. The oxidation enthalpies and entropies for the solid solutions could be explained by viewing oxidation and reduction as a strictly local phenomenon. Each metal cation in the fluorite lattice has 12 nearest neighbors and each oxygen anion is in contact with 4 metal cations. If one assumes that the energetics of oxidation are strictly local, that the energy to remove an oxygen ion depends only on the four metal cations that are in direct contact, the energy associated with adding an oxygen to a local structure with two Ce<sup>+3</sup> cations and two Zr<sup>+4</sup> cations should be similar to the energy for oxidation of the pyrochlore, independent of the bulk composition. This is what we observed. For oxidation of Ce<sub>0.81</sub>Zr<sub>0.19</sub>O<sub>1.9</sub> to Ce<sub>0.81</sub>Zr<sub>0.19</sub>O<sub>2</sub>, the entropy change is large because, on average, each Zr<sup>+4</sup> cation can be thought of as pairing with one or more other Zr<sup>+4</sup> cations and each pair of Zr<sup>+4</sup> cations can interact with a number of Ce<sup>+3</sup> cations in its vicinity. A large number of such possible combinations results in a high entropy change. Once each pair of Zr<sup>+4</sup> cations is part of a (Zr<sup>+4</sup>-Ce<sup>+3</sup>)<sub>2</sub> cluster, we suggest that the number of ways in which these Zr<sup>+4</sup> cations can be used in forming a second cluster are limited, at least if there is a repulsion between oxygen vacancies; hence, the number of oxygens available for removal decreases at a stoichiometry corresponding to all of the Zr<sup>+4</sup> being part of a reduced cluster. Similarly for Ce<sub>0.14</sub>Zr<sub>0.86</sub>O<sub>2</sub>, the entropies are near zero because only specific O<sup>-2</sup> anions with two Ce<sup>+4</sup> ions can be removed from the lattice.

**Table 1.** ceria supported on LDA (10%La<sub>2</sub>O<sub>3</sub>/alumina) following reduction in 90% H<sub>2</sub>-10% H<sub>2</sub>O at 700°C

	LDA	15 wt% ceria	30 wt% ceria	50 wt% ceria
SA (m <sup>2</sup> /g)	114	94	68	63
O:M Ratio	-	1.55	1.75	1.95



**Figure 1.** Oxygen to total metal (Ce+Zr) ratios for the Ce<sub>y</sub>Zr<sub>1-y</sub>O<sub>2-x</sub> samples, following calcination at 973 K, as a function of P(O<sub>2</sub>). The y values in the samples are as follows: (○) y=1, (Δ) y=0.92, (◻) y=0.81, (◇) y=0.59, (+) y=0.5, (Θ) y=0.25, (x) y=0.14, and (□) y=1.0. The closed symbols for y=0.08 (▲) were obtained from the sample calcined at 1323 K for 4 h.

#### References

- [1] M. Ozawa, M. Kimura, A. Isogai, *Journal of Alloys and Compounds* 193 (1993) 73.
- [2] H. Shinjoh, *Journal of Alloys and Compounds* 408-412 (2006) 1061.
- [3] G. Jacobs, P.A. Patterson, U.M. Graham, D.E. Sparks, B.H. Davis, *Applied Catalysis a-General* 269 (2004) 63.
- [4] A. Bueno-Lopez, K. Krishna, M. Makkee, J.A. Moulijn, *Journal of Catalysis* 230 (2005) 237.
- [5] C. de Leitenburg, A. Trovarelli, J. Llorca, F. Cavani, G. Bini, *Applied Catalysis A: General* 139 (1996) 161.
- [6] T. Masui, T. Ozaki, K.-i. Machida, G.-y. Adachi, *Journal of Alloys and Compounds* 303-304 (2000) 49.
- [7] T. Kim, J.M. Vohs, R.J. Gorte, *Industrial & Engineering Chemistry Research* 45 (2006) 5561.
- [8] P.R. Shah, T. Kim, G. Zhou, P. Fornasiero, R.J. Gorte, *Chemistry of Materials* 18 (2006) 5363.
- [9] D.J.M. Bevan, J. Kordis, *Journal of Inorganic & Nuclear Chemistry* 26 (1964) 1509.