Evidence of Entropy Effects in the Reduction of Ceria-Zirconia Solid Solutions

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Introduction

Ceria-zirconia solutions are widely used for oxygen-storage capacitance (OSC) in automobiles [1], and ceria-based catalysts are finding new catalytic applications as supports [2,3]. The role of ceria in each of these applications almost certainly involves oxidation and reduction of ceria. However, while thermodynamic data for oxidation and reduction of bulk ceria are available [4], there is little analogous information on ceria-zirconia mixed oxides, even though these materials are well known to be more easily reduced than pure ceria. Hence, in our laboratory flow system experiments [5] and coulometric titration [6] have been used to determine the thermodynamics of oxidation of ceria-zirconia solid solutions.

Materials and Methods

Ceria-zirconia solid solutions of various compositions were prepared by the citric acid method [7]. X-ray diffraction was used to characterize the samples. Flow system experiments and coulometric titration experiments were used to obtain equilibrium oxygen fugacity ($P(O_2)$) as a function of temperature and stoichiometry of the samples. This data was used to calculate the thermodynamic properties for oxidation of the ceria-zirconia solid solutions, using the following equations:

$$n\ Ce_yZr_{1-y}O_{2-x} + O_2 \rightleftarrows n\ Ce_yZr_{1-y}O_{2-x+2/n}$$

$$K = \frac{1}{P(O_2)_{eq}} \qquad \Delta G^o = -RT\ln K$$

$$\Delta H^o = R\frac{\partial \ln P(O_2)_{eq}}{\partial(1/T)} = -RT^2\frac{\partial(\Delta G^o/RT)}{\partial T} \qquad \Delta S^o = \frac{\Delta H^o - \Delta G^o}{T}$$

Results and Discussion

It was found that the differential oxidation enthalpy for both $Ce_{0.81}Zr_{0.19}O_2$ and $Ce_{0.25}Zr_{0.75}O_2$ was similar, between -500 and -550 kJ/mol O_2, and independent of the extent of reduction [6]. It was lower than the oxidation enthalpy of ceria of around -780 kJ/mol O_2, which can probably explain the ease of reduction of ceria-zirconia mixed oxides. Furthermore, there was a step change in -ΔS of reduction for $Ce_{0.81}Zr_{0.19}O_2$, from ~250 J/mol·K to less than 100 J/mol·K, after removal of approximately one oxygen for every two Zr^{+4}. To explain this thermodynamic data a model was presented (fig. 1) which views the reduction of ceria-zirconia as removal of oxygen to form "pyrochlore-like" structures, with some of the changes in reducibility associated with the number of sites from which oxygen can be removed.

Significance

This work gives insight into thermodynamic and redox properties of ceria-zirconia solid solutions.

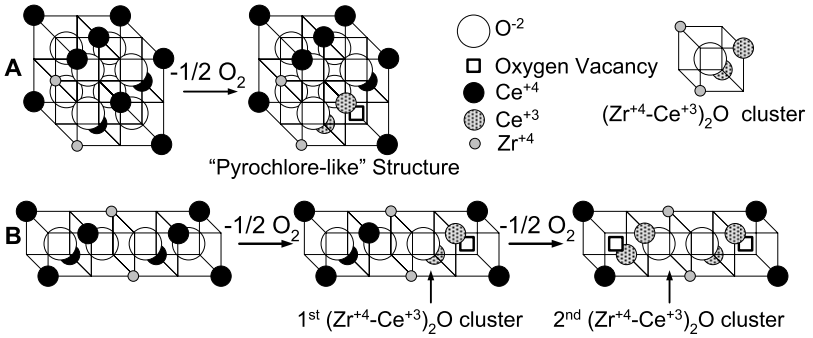

Figure 1. Schematic diagram of the proposed pyrochlore-like cluster. A. Formation of the "Pyrochlore-Like" Structure. B. The two step-reduction of $Ce_{0.81}Zr_{0.19}O_2$ (only a part of the lattice structure is shown).

References

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