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Reducibility of Cerium-based Mixed Metal Oxide Supports

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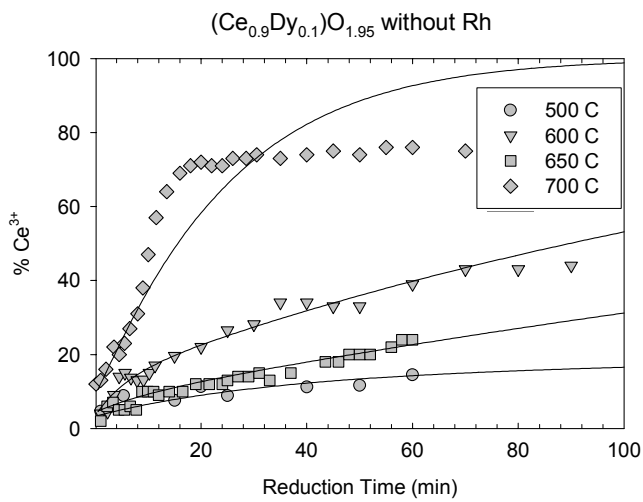
Beamline: X23B

Introduction: Cerium oxide has been widely studied and applied in catalytic materials to promote oxidation and reduction reactions, especially in noble metal catalysts[1]. In three way automotive catalysts, cerium is frequently doped with Zr to improve the oxygen storage capacity[2]. It has been proposed that a distortion of the oxygen bonding environment within the mixed Ce-Zr fluorite lattice is responsible for enhanced oxygen mobility[3], but oxygen vacancy concentrations may contribute. To further investigate the effect of oxygen vacancies, we have doped ceria with Dy and Gd. The addition of cations which are present only in a tri-valent state forces oxygen vacancies in proportion to the doping concentration. Doping with Dy^{3+} introduces oxygen vacancies with effectively zero change in lattice constant. Gd^{3+}, commonly used in fuel cell materials to enhance ionic mobility, introduces a small increase in lattice constant.

Methods and Materials: The mixed oxides were prepared by several methods [4,5]. Mixing concentrations of up to 50% of the dopant were used. After synthesis, samples were typically calcined to 500 C for a 2-3 hours before use in reductions studies. XRD confirms the presence of a single fluorite phase in the mixed oxides. SEM / EDX scans across particles of selected samples showed the presence of both components confirming that selective precipitation of cerium oxide is not occurring. BET surface areas were obtained for each sample and yielded surface areas of 40 to 50 m^2/g with relatively small pore volumes. Additional long treatment in hydrogen was found to gradually decrease the surface area indicative of slow densification of the particles. Rietveld analysis of the XRD patterns yielded particle sizes of 12 to 13 nm. A portion of each sample was impregnated with Rh nitrate and calcined to 400 C.

The kinetics of reduction were studied using *in situ* isothermal XANES measurements at the Ce L_{III} edge. A flow cell was used to alternate between oxidizing (5% air in He) and reducing (4%H_2 in He) conditions. The extent of reduction was obtained from quanitifiable changes in the Ce edge shape. A XANES spectrum could be recorded at one minute intervals.

Results: XANES results are shown in the Figure for a typical isothermal reduction of $Ce_{0.9}Dy_{0.1}O_{1.95}$. The rate of reduction vs time in general can not be described by a single first order rate of reduction of surface sites. At temperatures below 600 C, good fits are obtained to a model which includes three parameters: the dispersion of the particles, the rate of reduction of surface cerium atoms and the rate of transfer of surface Ce3+ into the bulk. However, this model does not fit the data at 700 C and above where deep reduction occurs. Following such deep reduction, the reduction behavior appears to be altered and subsequent oxidations and reductions are more sluggish.



Addition of Rh to the oxides greatly enhances the rate of reduction. Based upon the dispersion deduced from surface area measurements the reduction must include substantial reduction of the bulk. The effects of addition of Dy and Gd are subtle, but there is a slight enhancement of the reduction rates resulting from the doping. The enhancement seems larger for Gd than Dy and increases as Gd concentration increases from 10 to 20%.

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