

## Quantitative Determination of Ce Oxidation State by Ce L<sub>3</sub>-edge XANES

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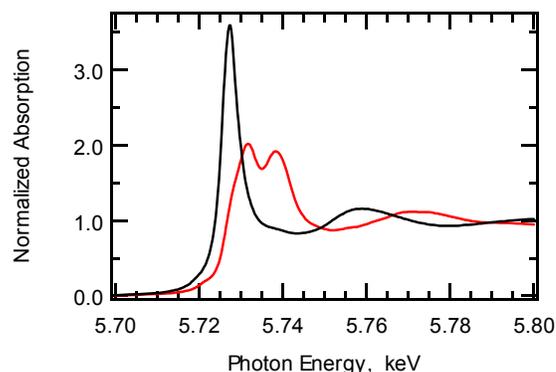
Beamline(s): X19A, X18B

**Introduction:** The ability of cerium oxide to enhance the activity of mixed metal oxides in oxidation catalysis, e.g. CO conversion in automotive catalysts, is well known. This enhancement has been ascribed to the oxygen exchange capability of cerium oxide, which can be thought of as acting as an oxygen buffer. The ability to store and exchange oxygen is related to the cerium oxidation state, i.e. the beneficial activity depends on the activity of the redox couple Ce<sup>4+</sup>-Ce<sup>3+</sup> and its ability to change from Ce<sup>4+</sup> (CeO<sub>2</sub>) under oxidizing conditions to Ce<sup>3+</sup> (Ce<sub>2</sub>O<sub>3</sub>) under net reducing conditions, and vice versa. Thus, having knowledge of the Ce oxidation state is paramount to understanding the relative ability of the Ce to undergo the redox chemistry. Ce L<sub>3</sub>-edge XANES has been shown to be an excellent tool for determining the Ce<sup>3+</sup>/Ce<sup>4+</sup> concentration in cerium oxide catalysts, and we have taken advantage of this to determine this information in a series of cerium oxide based catalysts.

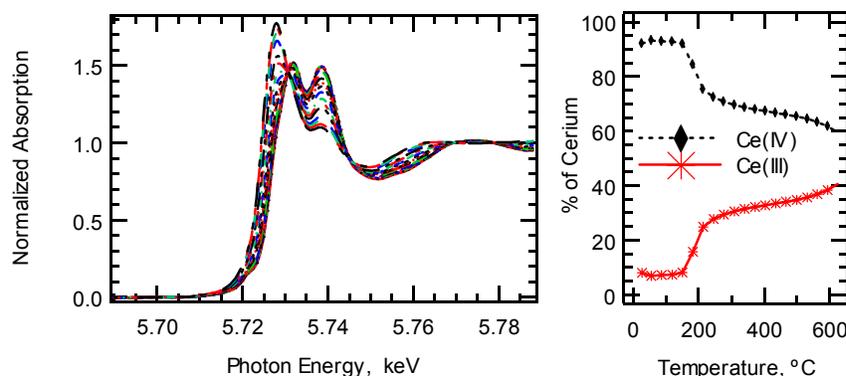
**Methods and Materials:** Ce(IV) oxide and Ce(III) sulfate were used as reference compounds for Ce<sup>4+</sup> and Ce<sup>3+</sup>, respectively. Data were collected in transmission from powders on tape. The data from the catalysts was also obtained in transmission, from samples of optimum thickness. These powders were pressed into wafers and held in a quartz tube reactor where they could be heated in the presence of a flow of hydrogen. Data were collected as a function of temperature.

**Results:** Figure 1 shows the Ce L<sub>3</sub>-edge XANES of CeO<sub>2</sub> and Ce<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>. The Ce(III) spectrum shows only a single white line and that of Ce(IV) oxide a doublet. These data are in excellent agreement with those in the literature. The left hand panel of Figure 2 shows a series of temperature programmed XANES, collected from one of the samples as the temperature was continuously raised from room temperature to 700°C in a flow of H<sub>2</sub>. As can be seen the spectrum gradually changes from one of Ce<sup>4+</sup> to one of Ce<sup>3+</sup>. Using a least squares fitting of these spectra with the reference spectra one can determine the amount of Ce<sup>4+</sup>/Ce<sup>3+</sup> at any given temperature, and this is shown in the right hand panel of Figure 2.

**Conclusions:** Ce L<sub>3</sub>-edge XANES can be used to quantitatively determine the amount of Ce in mixed cerium oxide catalysts.



**Figure 1.** Ce L<sub>3</sub>-edge XANES of Ce(III) sulfate and Ce(IV) oxide.



**Figure 2.** Left: TP-XANES during reduction of cerium oxide-based sample in a flow of H<sub>2</sub>. Right: Amount of Ce(IV) and Ce(III) at any given temperature