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## Application Ce L<sub>1</sub> HERFD XAS to determine the atomic structure of CeO<sub>2</sub> based nano-catalysts under working conditions

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**Abstract.** Ce L<sub>1</sub>-edge high-energy-resolution fluorescence detected (HERFD) X-ray absorption spectroscopy (XAS) was applied to unravel the electronic structure of Pt-promoted CeO<sub>2</sub> nanoparticles under different redox conditions. The Ce L<sub>γ</sub><sub>3</sub> emission line was chosen for partial fluorescence yield detection to improve the XAS spectral resolution. Oxygen vacancies were formed on the surface of ceria nanoparticles upon reducing in 5% CO in He. Theoretical Ce L<sub>1</sub>-edge simulations showed good agreement with the experimental data.

### 1. Introduction

Cerium dioxide is a unique material that can reversibly store oxygen in its structure and provide it for catalytic reactions under reducing conditions. The catalytic properties of CeO<sub>2</sub>-based materials are strongly related to the surface morphology and the presence of Ce-substituting dopants [1,2]. Nano-sized CeO<sub>2</sub> is of special interest because of the large surface area and the high concentration of unsaturated bonds. However its relation between structure of Ce on the atomic scale and reactivity still remains unclear. Here, we report the oxidation state and local environment of Ce atoms in CeO<sub>2</sub> nanoparticles measured under different redox conditions (in CO and O<sub>2</sub> atmospheres) using *in situ* Ce L<sub>1</sub> HERFD XAS and compare these to the theoretical simulations. We chose the Ce L<sub>1</sub> edge instead of the more commonly investigated Ce L<sub>3</sub> edge because it is not affected by multi-electronic transitions and thus can be simulated within the conventional one-electron transition approximation. To improve the energy resolution, we measured HERFD XAS [3,4].

### 2. Methods

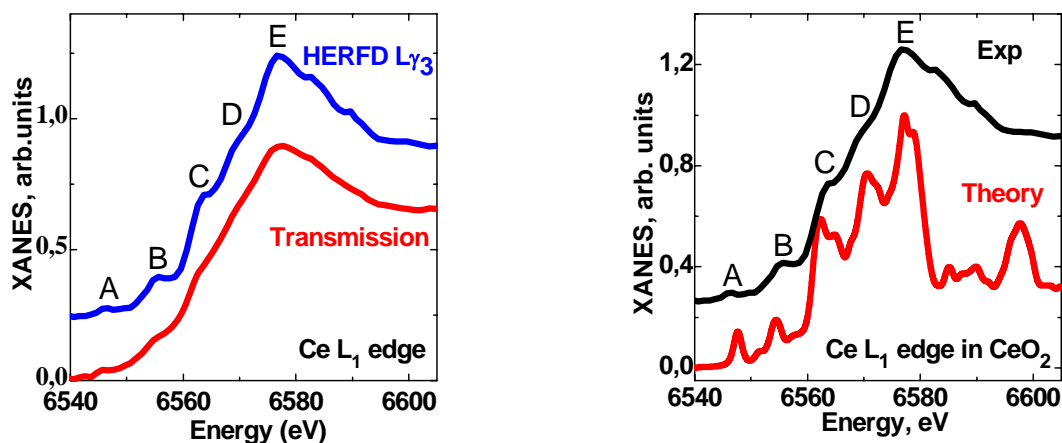
The polyhedral CeO<sub>2</sub> nanoparticles (NPs) of averaged size of 9 nm were prepared by a hydrothermal method that is described in [5]. Platinum nanoparticles (1.5 wt%) with the size varying between 1 and 2 nm were deposited using incipient wetness impregnation method using platinum nitrite solution, calcined in air at 400°C and reduced in 5% H<sub>2</sub> at 350°C.

Transmission XAS experiments were performed at a laboratory Rigaku R-XAS absorption spectrometer at Southern Federal University using a Ge 311 monochromator. Ce L<sub>1</sub> HERFD XAS measurements were also performed at the SuperXAS beamline (Swiss Light Source, PSI, Switzerland) using a double-crystal Si (111) incident beam monochromator and multi-crystal Johann-type emission spectrometer [6]. The spectrometer was equipped with three Si(111) crystals with a bending radius of 1000 mm, and which operated at the 333 reflection tuned to the maximum of the Ce L<sub>γ</sub><sub>3</sub> emission line (N<sub>3</sub> to L<sub>1</sub> transition).

Ce  $L_1$ -edge spectra were simulated using the full-potential linear augmented plane-wave approximation (FLAPW) implemented in the Wien2k program package [7]. The generalized gradient approximation in the scheme of Perdew–Burke–Ernzerhof (GGA-PBE) [8] was used for the treatment of exchange–correlation effects. The structures of  $CeO_2$  and oxygen deficient  $Ce_7O_{12}$  phases were used for simulations.

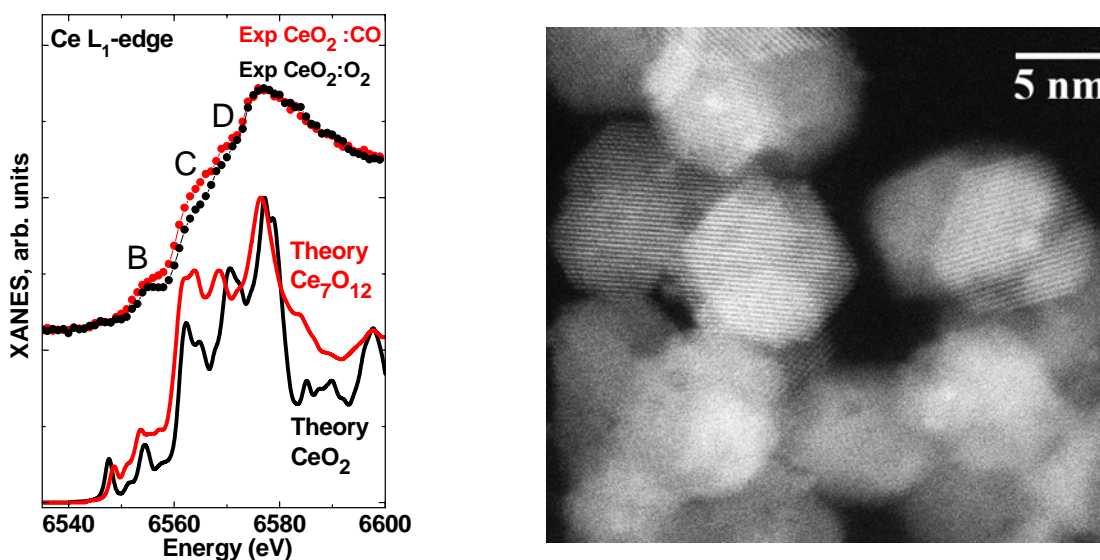
### 3. Results and discussion

The natural width of Ce  $L_1$  and  $N_3$  levels are 4.2 and 1.6 eV respectively [9,10]. Therefore, HERFD XAS at the Ce  $L\gamma_3$  ( $L_1-N_3$ ) emission line results in a better energy resolution compared to measuring XAS in transmission mode. The estimated total HERFD broadening [11], assuming a crystal analyzer resolution 2 eV and monochromator resolution 0.6 eV, is 2.7 eV at Ce  $L\gamma_3$ . Figure 1 (left panel) compares Ce  $L_1$  HERFD with transmission XAS. Features B and C become sharper using  $L\gamma_3$  fluorescence detection. Since Ce  $L_1$  HERFD XAS spectra are rich in features they provide enhanced sensitivity to the local atomic and electronic structure of Ce atoms in the presence of oxygen vacancies. The right panel shows the simulated Ce  $L_1$  spectrum in  $CeO_2$  using the FLAPW approximation. The simulations were performed both in the ground state and by constructing a supercell and a core hole on Ce 2s level. The ground state approximation reproduced well the experimental data; introducing a core hole did not change the calculated spectrum significantly.



**Figure 1.** (Left) Ce  $L_1$  XAS of bulk  $CeO_2$  detected using transmission mode (red curve), HERFD using Ce  $L\gamma_3$  emission line (blue curve). (Right) Comparison of experimental (black curve) and simulated (red curve) spectra of  $CeO_2$ .

Figure 2 shows the effect of oxygen vacancies formation on the Ce  $L_1$  HERFD XAS spectra of Pt- $CeO_2$  nano-catalysts during interaction with CO at 150°C. During this process both the oxidation state and the local atomic structure of Ce atoms changed. A  $Ce_7O_{12}$  structure [12] was used as model a  $CeO_2$  structure with high concentration of oxygen vacancies. Two non-equivalent crystallographic positions of Ce in  $Ce_7O_{12}$  can be considered as Ce atoms with respectively one and two oxygen vacancies in the first coordination sphere. The experimentally observed variations of the spectral shape, mainly visible in peak C, were reproduced. The feature at the lower energy is reminiscent of reduced cerium.



**Figure 2.** (Left): Experimental Ce L<sub>1</sub> HERFD XAS spectra of 1.5%Pt/CeO<sub>2</sub> polyhedral nanoparticles under 4% O<sub>2</sub> (black circles) respectively 5% CO at 150°C (red circles). Bottom: calculated X-ray XAS spectra of CeO<sub>2</sub> (black line) respectively Ce<sub>7</sub>O<sub>12</sub> (red line). (Right) STEM image of 1.5%Pt-CeO<sub>2</sub> catalyst.

#### 4. Conclusions

Ce L<sub>1</sub> HERFD XAS enables distinguishing the oxidation state of cerium. The Ce local atomic structure in well-defined 1.5%Pt-CeO<sub>2</sub> ceria catalysts was determined under different redox conditions. A clear change in the Ce L<sub>1</sub> near-edge was observed while cycling the atmosphere between 4% O<sub>2</sub> and 5% CO. Unlike the Ce L<sub>3</sub> edge, the L<sub>1</sub> HERFD XAS can be easily reproduced using readily available theoretical codes within the one-electron approximation. The spectral features observed experimentally were successfully compared to theoretical simulations of stoichiometric CeO<sub>2</sub> and an oxygen-deficient Ce<sub>7</sub>O<sub>12</sub> structure. Ce L<sub>1</sub> HERFD XAS provides a unique opportunity to determine the structure of oxygen deficient ceria.

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#### References

- [1] Trovarelli A 2002 *Catalysis by ceria and related materials* ed G J Hutchings, Catalytic Science Series, Imperial College Press: London.
- [2] Si R and Flytzani-Stephanopoulos M, 2008 *Angew. Chem. Int. Ed.* **47** 2884.
- [3] Hämäläinen K, Siddons D P, Hastings J B, Berman L E 1991 *Phys. Rev. Lett.* **67** 2850.
- [4] Safonova O V, Tromp M, van Bokhoven J A, de Groot F M F, Evans F, Glatzel P 2006 *J. Phys. Chem. B.* **110** 16162-16164
- [5] Paun C, Safonova O V, Szlachetko J, Abdala P, Nachtegaal M, Sa J, Kleymenov E, Cervellino A, Krumeich F, van Bokhoven J A 2012 *J. Phys. Chem. C* **116** 7312-7317

- [6] Kleymenov E, van Bokhoven JA, David C, Glatzel P, Janousch M, Alonso-Mori R, Studer M, Willmann M, Bergamaschi A, Henrich B, Nachtegaal M 2011 *Rev. Sci. Instrum.* **82** 065107.
- [7] Schwarz K and Blaha P 2003 *Comput. Mater. Sci.* **28** 259.
- [8] Perdew J P, Burke S, Ernzerhof M 1996 *Phys. Rev. Lett.* **77** 3865.
- [9] Fuggle J C and Inglesfield J E 1992 *Topics in Applied Physics* Vol. **69** ("Unoccupied Electronic States") edited by J.C. Fuggle, J.E. Inglesfield (Springer, Berlin, 1992)
- [10] Campbell J L, Rapp T 2001 *Atomic Data and Nuclear Data Tables* **77** 1.
- [11] Glatzel P, Weng T, Kvashnina K, Swarbrick J, Sikora M, Gallo E, Smolentsev N, Kvashnin Y, Kavcic M, Alonso Mori R 2012 *Journal Electronic Spectroscopy and Related Phenomena*, submitted.
- [12] Kuemmerle E A, Heger G 1999 *Journal of Solid State Chemistry* **147** 485.