

XANES study on the valence transitions in cerium oxide nanoparticles

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The aim of this work is the determination of Ce environment and valence state in Cerium oxide nanoparticles prepared by the microemulsion method. X-ray absorption near-edge structure measurements at Ce L₃ edge were performed on the nanoparticles as a function of annealing temperature, ranging from 298K to 873K under air condition. The experimental results support the conclusion that Ce ion, in the investigated systems, is in trivalence state when the annealing temperature is below 473K. As the temperature increases up to 623K, the XANES spectrum shows the coexistence of Ce³⁺ and Ce⁴⁺ states. When the temperature is higher than 623K, the spectra become identical to that of CeO₂ with a distinct double-peak structure, corresponding to the Ce⁴⁺ state.

Keywords: Cerium Oxide nanoparticles, valence transitions, XANES.

1. Introduction

The study of the physical properties of cerium oxide nanocrystals has become an active area of research in recent years. Such research has been primarily motivated by catalytic applications, such as oxidation of organic materials and reduction of heavy metal ions in industrial waste streams (Luca *et al.*, 1998). The electronic structure of nanocrystalline materials is of fundamental importance to the understanding of their properties. As we know, the preparation of cerium oxide nanocrystals require a heat-treatment, therefore, it is necessary to investigate the structural and electronic properties of the cerium oxide nanoparticles during the heat-treatment procedure. X-ray absorption near edge structure (XANES) spectroscopy, an unique element-specific technique sensitive to the local structure, can provide insight into local environment as well as electronic structures of materials. In particular, XANES studies at the rare-earth (RE) L₃ thresholds play an essential role due to simplicity and universal applicability (Borgna *et al.*, 1998, Chang *et al.*, 2000). In this paper, the cerium oxide nanoparticles are prepared by the microemulsion method and the cerium oxide nanocrystals are obtained by increasing the calcination temperature. The XANES spectra are used to investigate the electronic properties of these nanoparticles at different annealing temperature.

2. Experimental

CeO_{2-x} colloid was prepared in "microreactors" of reverse micelles and microemulsions, formed from cetyltrimethyl ammonium bromide (CTAB), butanol and Ce(NO₃)₃·6H₂O in cyclohexane (Bin *et al.*, 1999). The nanometre CeO_{2-x} (0 < x < 2) powder was obtained from the colloid solution by rotatory evaporation, and then was annealed at 473K, 623K, 773K, 873K for 2h under the air condition. The resulted samples were labeled

as nano-CeO_{2-x}-RT(sample3), nano-CeO_{2-x}-473K(sample4), nano-CeO_{2-x}-623K(sample5), nano-CeO_{2-x}-873K(sample6). Further, it was observed from HRTEM that the size of nanocrystal CeO₂ was about 6nm.

XANES spectra at the Ce L₃ edge were measured in transmission mode at the EXAFS station (Beam line 4W1B) of Beijing Synchrotron Radiation Facility. The storage ring was run at typical energy 2.2 GeV with the electron current about 80 mA. A Si (111) double crystal monochromator was used, providing an energy resolution of 1.5eV. To suppress the unwanted harmonics, the monochromatic crystal faces were detuned, reducing the incident beam by 30%. The incident and output beam intensities were recorded using ionization chambers, filled with nitrogen gas and a 50% argon-doped nitrogen mixture respectively. The spectra were recorded in the range of 5.5-6.2 KeV, which cover the L₃ edge absorption of Cerium atoms.

3. Results and discussion

Figure 1 compares the normalized Ce L₃-edge XANES spectra of CeO₂ nanoparticles at different temperature (ambient, 473K, 623K, 773K, 873K, respectively), along with two standard spectra of crystalline Ce(NO₃)₃·6H₂O in triclinic phase and CeO₂ in cubic phase. The Ce L₃-edge spectrum of CeO₂ is in agreement with the results of Kaindl *et al.* (1988), Bianconi *et al.* (1994), and Douillard *et al.* (1995). The pre-edge structure, labeled A, is assigned to final states with delocalized *d* character at the bottom of the conduction band. Due to the cubic crystal-field splitting of Ce 5*d* states, features B and D are associated to the transitions of Ce 2*p* to the Ce 4*f*¹5*d* e_g $\underline{\underline{L}}$ and Ce 4*f*¹5*d* t_{2g} $\underline{\underline{L}}$ states, where, $\underline{\underline{L}}$ denotes an oxygen ligand 2*p* hole; 4*f*¹ refers to an electron from an oxygen 2*p* orbital to a cerium 4*f* one(charge transfer-like). The energy separation between peaks B and D is about 3.6 eV, which is in agreement with previous works (Bianconi *et al.* 1994). The feature E is attributed to the contribution of a different final state configuration 4*f*⁰5*d*. For the Ce L₃-edge spectrum of Ce(NO₃)₃·6H₂O, the strongest peak C at about 5725.5 eV, due to the dipole-allowed transition of Ce 2*p* to Ce 4*f*¹5*d* final states, characterizes the Ce in trivalent state (Capehart *et al.* 1992). The peak positions and the assignments of the electronic transition of all materials investigated, are tabulated in Table 1.

Table 1 The peak positions and assignments in Ce L₃-edge XANES spectra of CeO₂ nanoparticles at different temperature.

Sample	Peak(eV)				
	A	B	C	D	E
	5717.8	5724.6	5725.5	5728.2	5735.3
1			2p→4f ¹ 5d		
2	2p→5d	2p→4f ¹ 5de _g $\underline{\underline{L}}$		2p→4f ¹ 5dt _{2g} $\underline{\underline{L}}$	2p→4f ⁰ 5d
3			2p→4f ¹ 5d		
4			2p→4f ¹ 5d		
5			2p→4f ¹ 5d	2p→4f ¹ 5dt _{2g} $\underline{\underline{L}}$	2p→4f ⁰ 5d
6	2p→5d	2p→4f ¹ 5de _g $\underline{\underline{L}}$		2p→4f ¹ 5dt _{2g} $\underline{\underline{L}}$	2p→4f ⁰ 5d

$\underline{\underline{L}}$ denotes an oxygen ligand 2*p* hole

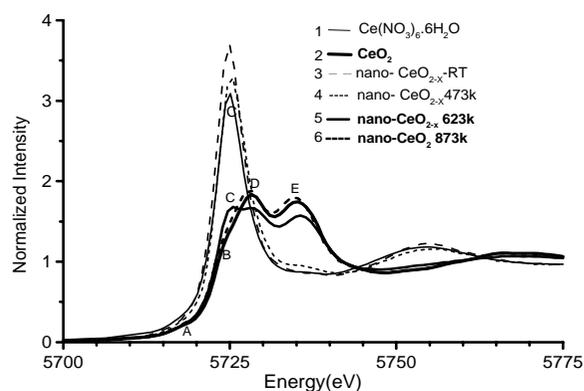


Fig.1 The normalized Ce L_3 -edge XANES spectra of Cerium Oxide nanoparticles at different annealing temperature, along with two standard spectra of crystal $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and CeO_2 .

It is immediately apparent that the XANES spectra at Ce L_3 edge of the annealing temperature below 473K has a single peak, and is similar to that of crystalline sample $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and different from the spectrum of standard CeO_2 . The peak C is significantly intensified in the sample of nano- CeO_{2-x} -RT, with respect to that of the spectrum of $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, indicating that the first nearest neighbors are less distorted. As the calcination temperature increases up to 623K, the spectra show three features (C,D,E): C is due to Ce^{3+} ; while D,E are spectral features of Ce^{4+} . This shows that Ce^{3+} and Ce^{4+} coexist in the nanoparticles when the annealing temperature is in the range between 473K and 623K. When the temperature is above 623K, four different features, labeled, A,B,D and E, are presented, which are characteristic spectral features of CeO_2 in cubic phase. Based on the above results, we deduced that the cerium oxide colloids, formed from cetyltrimethyl ammonium bromide, butanol and $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ in cyclohexane, are essentially cerium oxide nanoparticles coated with CTAB. XANES spectra shows that Ce is trivalent in nano- CeO_{2-x} -RT. With increasing temperature, the CTAB around the cerium oxide nanoparticles decomposes and can easily react with oxygen under air condition (Bin *et al.*, 1999). This results in a valence change from Ce^{3+} to Ce^{4+} and in the formation of CeO_2 nanocrystal. In fact, the experimental XANES spectra have revealed already that the valence of nanoparticles changes from Ce^{3+} to Ce^{4+} with the increasing of temperature and the CeO_2 nanocrystal form when the annealing temperature is above 623K.

4. Conclusion

The structure of Cerium oxide nanoparticles, investigated as a function of the annealing temperature, changes from triclinic structure to cubic one (CeO_2) and its valence varies from Ce^{3+} to Ce^{4+} by increasing of calcination temperature. The present XANES results provide the evidence of local structure and valence state in the formation of nanocrystalline CeO_2 . Further effort is doing in our Lab. to confirm the formation mechanism of CeO_2 nanocrystal. A complete discussion of the XANES part of the Ce L_3 X-ray absorption spectra will be published in a forthcoming paper.

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