


EELS Analysis of Ce Valence State of SiO₂ Supported CeO₂ Nanoparticles, CeO_x Nanoclusters and Ce Single Atoms

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Recent advances in catalysis by supported single metal atoms have demonstrated their superior performance for many important catalytic reactions [1]. We previously reported the anchoring of metal atoms by dispersing CeO_x nanoglues onto high-surface-area SiO₂ support to confine the movement of supported metal atoms and to significantly enhance the activity/stability of the Pt₁/CeO_x/SiO₂ for CO oxidation reaction [2]. The redox capability of CeO₂ surfaces and CeO_x clusters play an important role in determining both the activity and stability of ceria supported metal atoms. Spatially resolving the distribution of Ce³⁺ and Ce⁴⁺ in supported CeO_x particles/clusters is of importance for understanding the catalytic behavior of CeO_x supported single metal atoms and clusters. The electron energy loss spectroscopy (EELS) in an aberration-corrected STEM instrument can be utilized to provide such information on an atomic scale. Recent report has demonstrated that the distribution of Ce valence states of CeO₂ nanoparticles strongly depends on particle size and facet [3]. However, most of the previous work focused on CeO₂ nanoparticles with sizes > 3 nm. In this work, we investigate the change of valence state of Ce in the form of CeO₂ nanoparticles, CeO_x nanoclusters ( 1 nm) and supported Ce single atoms.

The preparation of CeO_x-SiO₂ nanocomposites was accomplished by adsorbing Ce salt precursors onto SiO₂ powders via a wet chemistry method [2]. The Ce-containing SiO₂ precipitates were washed with deionized water, dried overnight and calcined at 600°C for 5 hours to form CeO_x clusters on the SiO₂ surfaces. STEM EELS analysis was conducted on a NION UltraSTEM 100 aberration-corrected microscope equipped with a monochromator and operated at 60 KV.

The surface layers of larger CeO₂ particles consist primarily Ce³⁺ while the center part of larger CeO₂ particles consist primarily of Ce⁴⁺. However, when the size of the CeO₂ nanoparticle decreases the fraction of Ce³⁺ in the center region of the particle increases [3-4]. In this work, we acquired EELS spectra from the center (area 1) and edge (area 2) regions of the CeO₂ nanoparticle with a size of ~ 4 nm (Figure 1a). The result shows that Ce³⁺ and Ce⁴⁺ cations co-exist at the center of the particle but Ce³⁺ dominates at the edge (Figure 1c spectrum 1 and 2, respectively). The existence of the Ce³⁺ signal in the center region of the small CeO₂ nanoparticles partially originates from the expanded lattice which facilitates the formation of oxygen vacancies due to the lower formation energy on smaller size CeO₂ (< 5 nm) [5]. The EELS spectrum (Figure 1c spectrum # 3) obtained from a typical CeO_x cluster (~1 nm) (area 3 in Figure 1b) shows red-shift but not as much as that taken from the edge of a smaller CeO₂ nanoparticle (Figure 1c spectrum 2). For such small CeO_x clusters it would not be possible to define the surface from the interior regions of the cluster so the EELS spectrum reflect the average valence state of the CeO_x cluster. The Ce oxidation state of such CeO_x nanoclusters seems to be between 3+ and 4+. We have also analyzed the

oxidation state of loosely aggregated Ce single atoms (area 4 in Figure 1b and spectrum # 4 in Figure 1c). Compared to the EELS spectrum obtained from the CeO_x nanocluster a blue-shift is clearly observable, suggesting that the supported Ce single atoms are most probably oxidized to Ce⁴⁺. The strong bonding between the supported Ce single atoms with the SiO₂ support under high temperature calcination conditions also suggests that the Ce single atoms are strongly anchored by the oxygen ligands of the SiO₂ support. These initial results provide an interesting perspective on understanding the redox capabilities of small CeO₂ nanoparticles, CeO_x nanoclusters and supported Ce single atoms. Detailed analysis of the dependence of Ce valence state on the particle size and cluster configurations will be discussed [6].

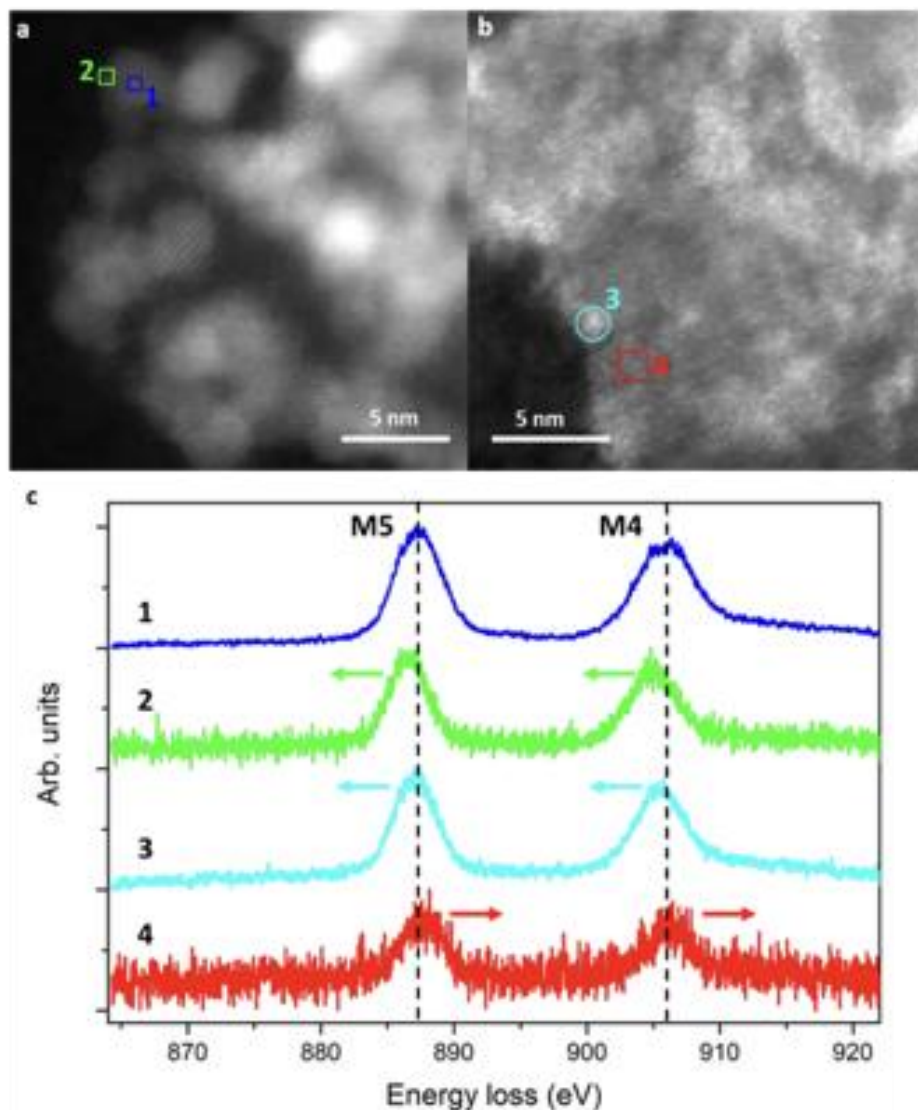


Figure 1. HAADF image of SiO₂-supported CeO₂ nanoparticles (a) and Ce nanoclusters/atoms (b). EELS spectra acquired from the center (1) and edge (2) region of a CeO₂ nanoparticle, CeO_x cluster (3) and Ce single atoms (4). The Ce³⁺ seems to be dominant near the edge of the CeO₂ particles and the fraction of the Ce³⁺ decreases for 1 nm CeO_x nanoclusters to Ce single atoms. Such analysis suggests that the SiO₂-supported Ce atoms are fully oxidized after the high temperature calcination treatment.

References

- [1] JY Liu, *ACS Catalysis* **7** (2017), p. 34.
- [2] X Li *et al.*, *Microscopy and Microanalysis* **24** (S1) (2018), p. 1660.
- [3] B Goris *et al.*, *ACS Nano* **10** (2014), p. 10878.
- [4] S Turner *et al.*, *Nanoscale* **8** (2011), p. 3385.
- [5] XD Hao *et al.*, *Small* **42** (2018), p. 1802915.
- [6] We acknowledge the use of facilities within The Eyring Materials Center and the John M. Cowley Center for High Resolution Electron Microscopy at Arizona State University.