

Redox Behavior and Activity Measurement of Individual Ceria-Zirconia Nanoparticles

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Introduction

The ability of cerium oxides to reversibly form mixed +3 and +4 valence oxides (CeO_2 and Ce_2O_3) leads to excellent oxygen storage capacity (OSC). It has been reported that the addition of zirconia not only improves the life of the redox cycles but also lowers the reduction temperature [1]. Therefore nanoscale ceria zirconia particles have been widely used in automobile three-way catalysts to adjust the local oxygen environment in order to remove the unwanted gases from exhaust to reduce pollution. It is easily accepted that nano and bulk properties are different due to their size-dependent effects, for example, surface-to-bulk ratio, the number of active sites and possible composition variation at nanometer level etc. However, extrapolations from “bulk properties” to understand nanoscale materials are frequently problematic, as bulk characterization such as x-ray diffraction (XRD), temperature programmed reduction (TPR) and thermalgravimetric analysis (TGA) etc normally averages or sums the properties a large ensemble of nanoparticles. Identification of structural and chemical features of individual nanoparticles could offer substantial opportunities for manipulating nanostructured catalytic materials and understanding their properties. For this reason, we have undertaken a detailed *in situ* environmental transmission electron microscopy (E-TEM) study of the dynamic nanostructural and nanochemical changes that take place in ceria zirconia during redox cycles. The simultaneous dynamic nanostructure and nanochemistry evolution from individual nanoparticles opens up the possibility to distinguish and optimize their redox activity.

Materials and Methods

The ceria zirconia solid solution nanopowder was prepared by a spray freezing method. Experimental raw materials and synthesis procedures are described elsewhere [1]. A Tecnai F20 E-TEM with an environment cell was used for the *in situ* nano-characterization to monitor the changes that occurred under different reducing conditions. High resolution electron microscopy (HREM), scanning transmission electron microscopy (STEM) imaging and electron energy-loss spectroscopy (EELS) were used to follow the structural and oxidation state changes during reduction in H_2 . Parallel *ex situ* TGA reduction and *in situ* E-TEM characterization have been carried out to compare and understand their redox properties. The *in situ* E-TEM characterization reported here is corresponding to the second reduction cycle [1].

Results and Discussion

Figure 1 shows the HREM images and associated EELS (inserts) of two individual ceria zirconia nanoparticles at 586°C in 1.5 torr H_2 . The change in the relative height of the peaks at the beginning of Ce M_{45} edge in the energy-loss spectrum shows that the right nanoparticle (active) has transformed from the Ce^{+4} to Ce^{+3} oxidation state, but the left one (inactive) has not. Figure 2 (a) shows the oxidation state for same two nanoparticles as a function of temperature and Figure 2 (b) shows *in situ* EELS spectra during *in situ* reduction for the active nanoparticle. EELS line scan analysis in STEM mode at 572°C (not shown) revealed a 10~15% composition variation between these two nanoparticles. The chemical

composition analysis of active nanoparticle shows lower Ce/Zr atomic ratio. This result is consistent with *ex situ* TGA reduction cycling characterization that the reduction fraction decreased with redox cycling, as there is a significant redox activity difference between nanoparticles after the first TGA reduction cycling. Detailed results will be presented and discussed in terms of the correlation between redox activity and nanostructure, nanochemistry of individual nanoparticles.

Significance

Correlating *in situ* atomic-scale structural and chemical changes taking place on individual nanoparticles and comparing with *ex situ* TGA reduction characterization will give insights into the origin of the enhanced redox properties and also help identify their structural and chemical features of active ceria zirconia nanoparticles.

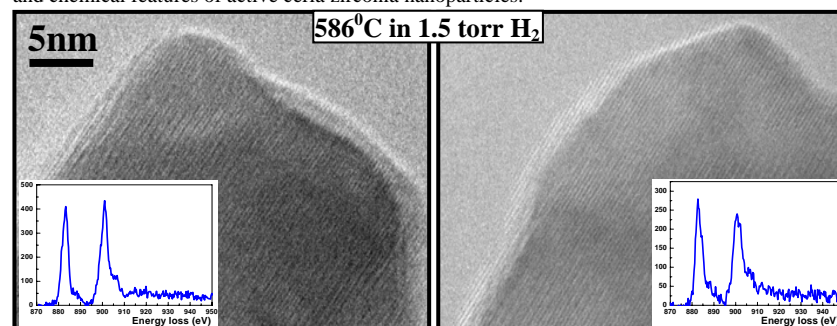


Figure 1. HREM images and associated electron energy-loss spectrum (insert) for two individual ceria zirconia nanoparticles at 586°C in 1.5 torr H_2 . The *in situ* EELS (inserts) shows that the particle on the right is more strongly reduced than the particle on the left.

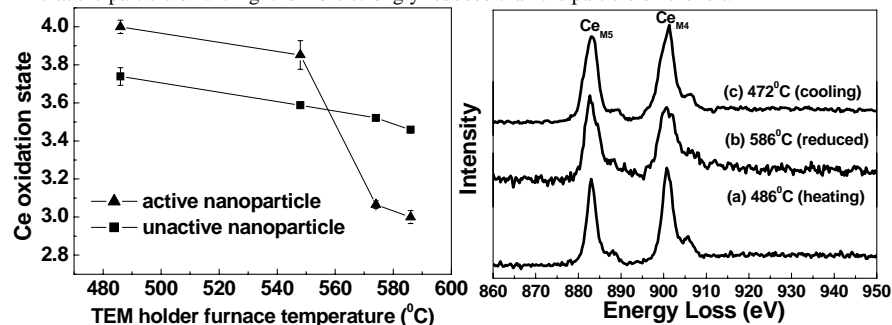


Figure 2. A) oxidation state for same two particles shown in Figure 1 as a function a temperature. B) *in situ* EELS spectra during reduction for the active nanoparticle.

References

1. Wang RG, Crozier PA, Sharma R, Adams JB, *J. Phys. Chem. B.* 110(37), 18278 (2006).
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