doi:10.1017/S1431927610058381
Microsc. Microanal. 16 (Suppl 2), 2010

In-situ Observations of Interfacial Interactions Between Ni Catalyst and Pr Doped Ceria Support During Reduction

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In the past decade, CeO_2-based ceramics have become potential candidates for anode material in solid oxide fuel cells (SOFC's) due to their desirable electrochemical behavior at low temperatures. These ceramics have been used as supports for metal catalysts like Rh, Pt, Pd, and Ni and their behavior in various fuel atmospheres have been investigated [1]. Metal-support interactions can play an important role in overall catalytic performance of the material. In this research, we have investigated the interfacial interactions between Ni catalyst and 10 mol% Pr-doped CeO_2 support during *in situ* reduction in H_2 using an environmental transmission electron microscope (ETEM). *In situ* observation in an ETEM is the only way to observe these metal-support interactions occurring at atomic scale under various reducing atmospheres and not only gives information about local composition and structure but also the reactivity of individual nanoparticles.

Nanoparticles of 10 mol% Pr-doped CeO_2 were synthesized using a spray drying technique. 10 wt% Ni was loaded onto the doped CeO_2 support via an impregnation technique in which $Ni(NO_3)_2.6H_2O$ dissolved in ethanol was mixed with the support, dried in air at 120°C followed by reduction in $5\%H_2$/He mixture at 400°C for 3 hrs. *In situ* characterization was performed on a FEI Tecnai F20 environmental transmission electron microscope (ETEM) operated at 200kV. The TEM sample was prepared by dry loading the nanopowder onto 200 mesh Pt TEM grids. The sample was progressively heated to up to 650ºC using a Gatan hot-stage under 67 Pa (0.5 Torr) of dry H_2 in the sample area. Electron energy-loss spectra (EELS) and high resolution electron microscopy (HREM) images were recorded from selected regions.

The support was first investigated for structural changes during *in situ* reduction. Figures 1(a) and (b) show the HREM images and energy-loss spectra of Pr doped CeO_2 nanoparticles before and after reduction in H_2 respectively. It was observed that the doped CeO_2 nanoparticles undergo a structural change upon reduction at 650°C, wherein a disordered structure is formed. EELS from such nanoparticles showed the reversal in the height of CeM_{45} white lines (an indication of Ce^{4+} reducing to Ce^{3+} oxidation state [2]) demonstrating that the structural change is associated with reduction of the support. Unreduced nanoparticles did not show this structural change. Similar effects have been found in the Ni-loaded, Pr-doped CeO_2. Figure 2 (a) shows a high resolution image of the Ni/support interface at 216°C and a sharp interface is clearly seen. Fringes of 0.31 nm and 0.20 nm, typical of CeO_2(111) and Ni(111) lattice spacings, were observed. It was also observed that the Ni particles were initially covered by a thin film of NiO which reduced to Ni metal at 400°C in the presence of H_2. At 650°C a disordered structure appears to form at the interface which may be attributed to the formation of a reduction zone in the support around the Ni particle, possibly due to hydrogen 'spillover'. We are currently investigating this effect in more detail and the findings will be presented in terms of structural changes and their effect on redox properties of the doped CeO_2 supports.

References
[1] A. Trovarelli, *Catalysis by Ceria and Related Materials*, Imperial College Press, 2002.
[2] R. Sharma et al., Phil. Mag. 84 (2004) 2731.
[3] The support from US Department of Energy (DE-FG02-07ER46442) and the use of ETEM at John M. Cowley center for High Resolution Microscopy at Arizona State University is highly acknowledged

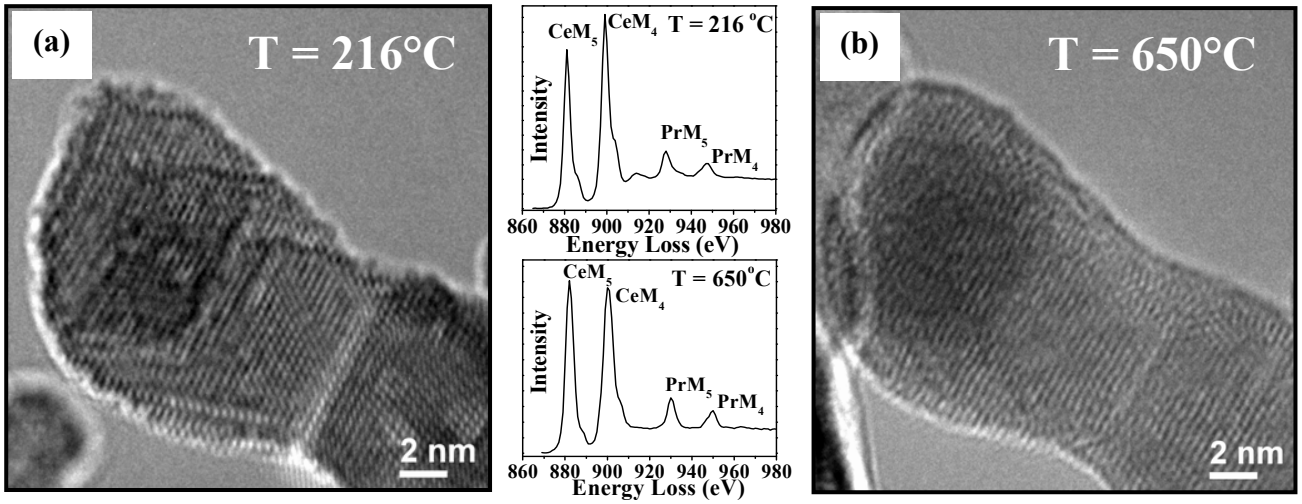

FIG. 1. HREM images and EELS spectra of Pr doped CeO_2 nanoparticles at (a) 216°C and (b) after reduction in 67 Pa (0.5 Torr) of dry H_2 at 650°C.

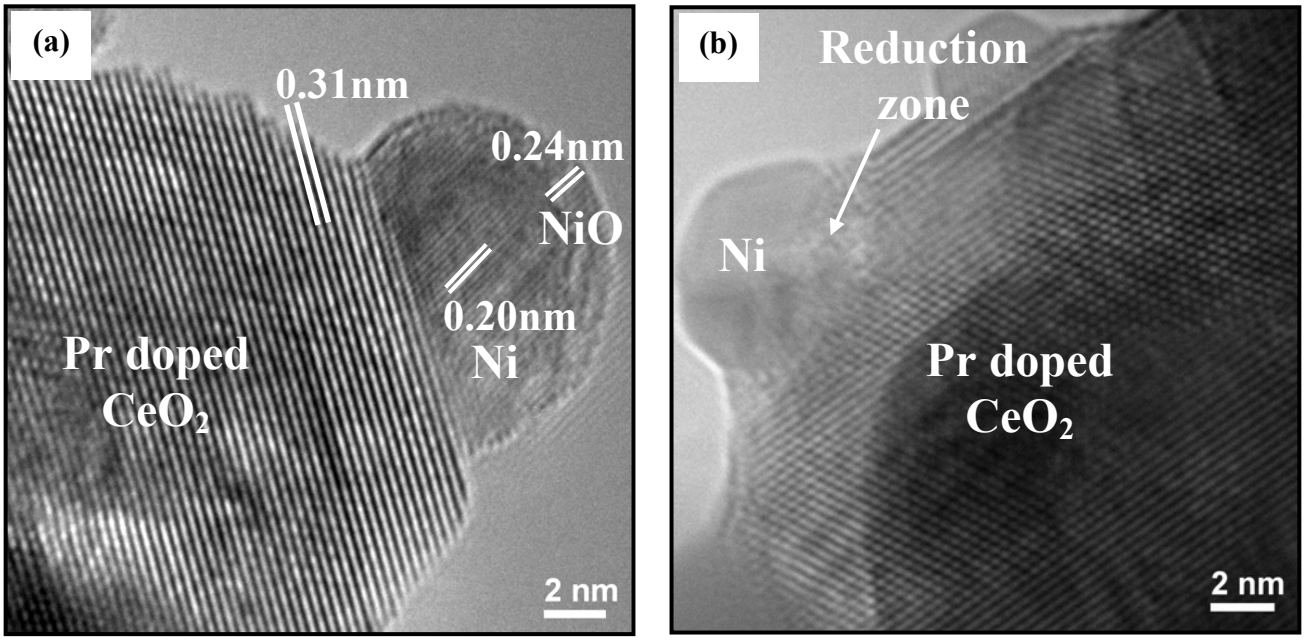

FIG. 2. HREM images of Ni/Pr doped CeO_2 interface, (a) at 216°C, and (b) at 650°C in 67 Pa (0.5 Torr) of H_2 showing a disordered structure around the particle indicating possible formation of a reduction zone at the interfacial region.

https://doi.org/10.1017/S1431927610058381 Published online by Cambridge University Press