

***In situ* Imaging and Spectroscopy of the Carbon Deposition Mechanism on Ni/CeO₂ Solid Oxide Fuel Cell Anode Catalyst**

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Ceria is a promising anode material for intermediate temperature (350-550°C) solid oxide fuel cells (SOFCs) due to its relatively high oxygen ion conductivity at these temperatures. Long-term stability of SOFCs may be limited by carbon deposition from the fuels onto the active anode (fuel oxidation) catalyst, causing deactivation or destruction of the ceramic-metal composite structure. Ceria has been shown to inhibit carbon deposition by quickly exchanging oxygen from its lattice to oxidize carbon on the surface of the electrode [1]. We are interested in understanding how ceria can affect carbon deposition at the gas-solid interface by observing structural and chemical changes at the nanoscale. Environmental transmission electron microscopy (ETEM) provides the ability to observe nano-level structural changes under simulated reaction conditions which can be correlated with nanomaterials' performance through *in situ* and *operando* techniques [2]. *In situ* electron energy-loss spectroscopy (EELS) has also allowed dynamic changes in the local oxidation state of nanomaterials to be determined during catalysis [3]. A fundamental study of the local structural and chemical changes in a Ni/CeO₂ catalyst occurring under reaction conditions will provide information on the carbon deposition and may suggest mitigation strategies.

An FEI Titan ETEM was used to study gas-solid interactions of a model Ni/CeO₂ catalyst with two carbon source gases, ethane (C₂H₆) and ethylene (C₂H₄), to gain insight into carbon deposition processes relevant to SOFC applications. NiO was loaded onto CeO₂ cubes which were then reduced *in situ* in 1 Torr H₂ at 400°C. The hydrocarbon gas (C₂H₆ or C₂H₄) was introduced and samples were heated to 550°C. Figure 1 shows the structural changes that occurred during hydrocarbon exposure. When exposed to C₂H₄, carbon was deposited in the form of graphite layers whereas Ni surfaces remained free of graphite during C₂H₆ exposure. *In situ* EELS was used to monitor the valence state of Ce^{3+/4+}, which varies with the oxygen content of the ceria according to Ce_x³⁺Ce_{1-x}⁴⁺O_{2-x/2}. Ce valence can thus be used to interpret carbon deposition behaviors in terms of oxygen deficiency of the ceria support. Figure 2 a) and b) show high-angular angle dark-field (HAADF) images where EELS lines scans were acquired in each source gas. Typical EELS spectra of the O K and Ce M₄₅ edges are shown as insets. The integrated intensity ratio of the M₄/M₅ peaks was used to correlate the EELS spectra to Ce valence. The table in Figure 2 c) indicates that no changes in local Ce valence states were observed during C₂H₄ exposure when compared to Ce valence state in H₂. During C₂H₆ exposure under identical conditions, however, localized reduction zones were observed in the ceria support near Ni particles. Therefore, ceria inhibited carbon deposition during C₂H₆ exposure through localized oxygen exchange but was unable to do so during C₂H₄ exposure [4]. These results will be discussed in terms of a Mars van Krevelen carbon oxidation mechanism.

References:

- [1] Wang, W., *et al*, Chemical Reviews, **113** (2013), p. 8104-8151.
- [2] Tao, F. and P.A. Crozier, Chemical Reviews, **116** (2016), p. 3487-3539.
- [3] Sharma, R., *et al*, Philosophical Magazine, **84** (2004), p. 2731-2747.
- [4] We gratefully acknowledge support of NSF grant DMR-1308085 and ASU's John M. Cowley Center for High Resolution Electron Microscopy.

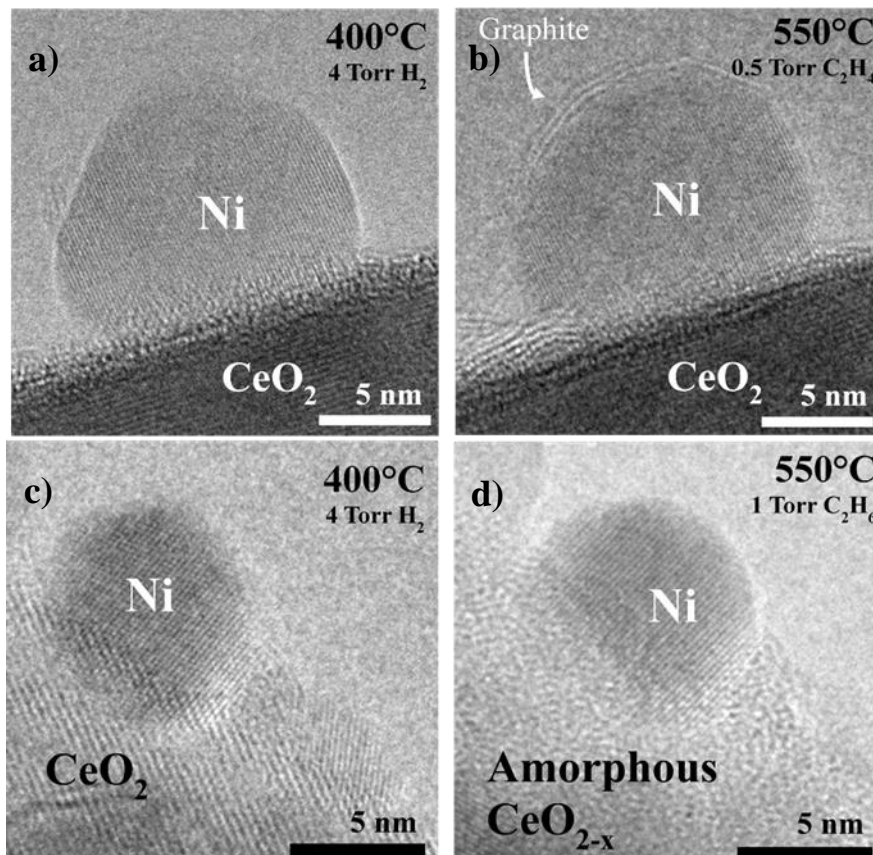


Figure 1. a) & c) Ni/CeO₂ at 400°C in 4 Torr H₂ b) Ni/CeO₂ in 0.5 Torr C₂H₄ at 550°C with several graphite layers covering the Ni particle. d) Ni/CeO₂ in 1 Torr C₂H₆ at 550°C. The Ni particle surface remains clear of graphite and the crystalline ceria becomes amorphous.

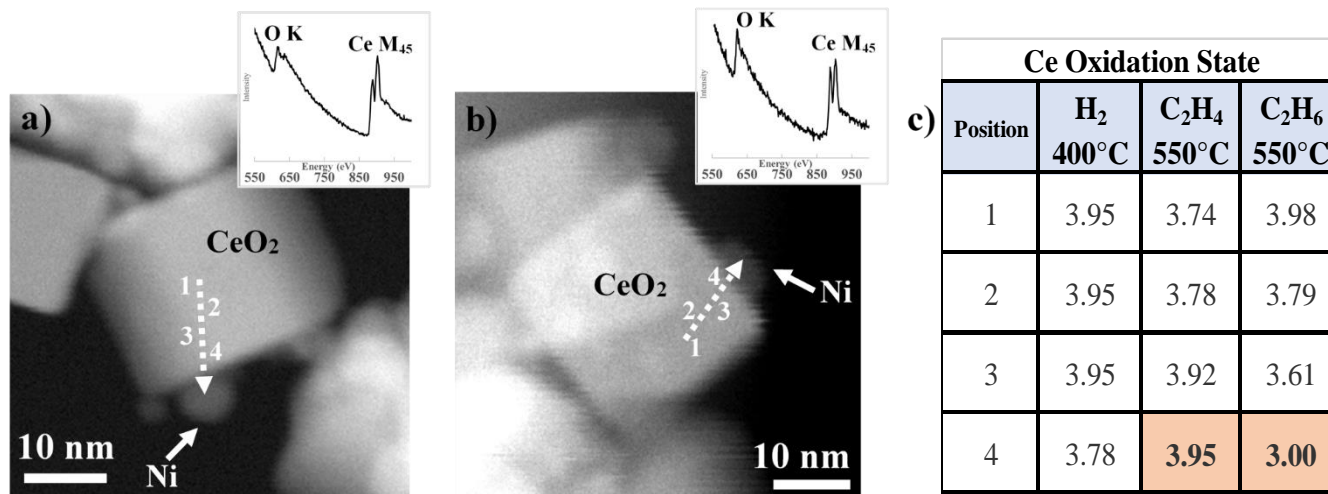


Figure 2. HAADF images of Ni/CeO₂ in a) 0.5 Torr C₂H₄ at 550°C and b) 1 Torr C₂H₆ at 550°C. Dotted lines indicate EELS line scan directions with position markers 1-4. The insets are typical EELS spectra of the O K and Ce M₄₅ edges near Ni particles. The table in c) shows the oxidation state of Ce along the line scans of a) and b) compared to a typical line scan in H₂. The highlighted values indicate that localized reduction zones of the ceria cube were observed near the Ni particle in C₂H₆ but no reduction zones were seen in C₂H₄.