Atomic-level In situ Imaging and Spectroscopy of Interfacial Interactions during Carbon Deposition on a Ni/CeO_2 Catalyst

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Internal reforming of hydrocarbons in solid oxide fuel cells (SOFCs) can enhance electrochemical conversion efficiencies by eliminating the need for external fuel reforming[1]. Long-term stability of SOFCs may be limited by carbon deposition from the fuels onto the anode catalyst, causing deactivation of the ceramic-metal composite structure. Ni/CeO_2-based catalysts may inhibit carbon deposition through a process involving lattice oxygen exchange. Natural gas consists primarily of methane (CH_4) but also contains several percent of higher hydrocarbons such as ethane (C_2H_6) and propane (C_3H_8), which have been shown to deposit carbon more easily than CH_4[2]. We are interested in understanding how CeO_2 can affect carbon deposition at the gas-solid interface by observing structural and chemical changes at the nanoscale. *In situ* environmental transmission electron microscopy (ETEM) provides the ability to observe atomic-level structural changes under simulated reaction conditions[3]. *In situ* electron energy-loss spectroscopy (EELS) has allowed dynamic changes in the local oxidation state of CeO_2 to be determined during reduction[4]. A fundamental study of the local structural and chemical changes occurring at Ni/CeO_2 interfaces under reaction conditions will elucidate the mechanisms that enable Ni/CeO_2-based catalysts to inhibit carbon deposition from light hydrocarbons.

In situ ETEM techniques were employed to investigate the atomic-level three-phase interactions occurring at the metal-support interface during carbon deposition from C_2H_6 and C_2H_4 over a model Ni/CeO_2 catalyst[5]. Structural and chemical interfacial changes occurring during species-dependent carbon deposition were determined using atomic-level imaging and EELS. Figure 1 shows the structural changes that occurred during hydrocarbon exposure. During exposure to C_2H_4, graphite layers formed on the Ni surface. In contrast, no carbon deposition occurred and crystalline ceria became amorphous during C_2H_6 exposure. A high-angle annular dark-field (HAADF) image of Ni/CeO_2 is shown in Figure 2 and insets of energy-loss spectra acquired near a Ni/CeO_2 interface show an intensity ratio change in the Ce M_{45} edge during C_2H_6 exposure, indicating the removal of oxygen. EELS linescans showed localized reduction zones in the ceria support near Ni/CeO_2 interfaces during C_2H_6 exposure while less pronounced reduction zones were observed during C_2H_4 exposure. Rapid dehydrogenation caused graphite formation to occur on Ni surfaces during C_2H_4 exposure, whereas the metal-support interface catalyzed the oxidative dehydrogenation of C_2H_6 and oxidized the resulting carbonaceous species during C_2H_6 exposure. These experiments demonstrate that the ability of the interfacial sites on Ni/CeO_2 to inhibit carbon deposition during reforming is strongly influenced by thermodynamic and kinetic considerations which may show significant variation among different hydrocarbon species[6].

References:

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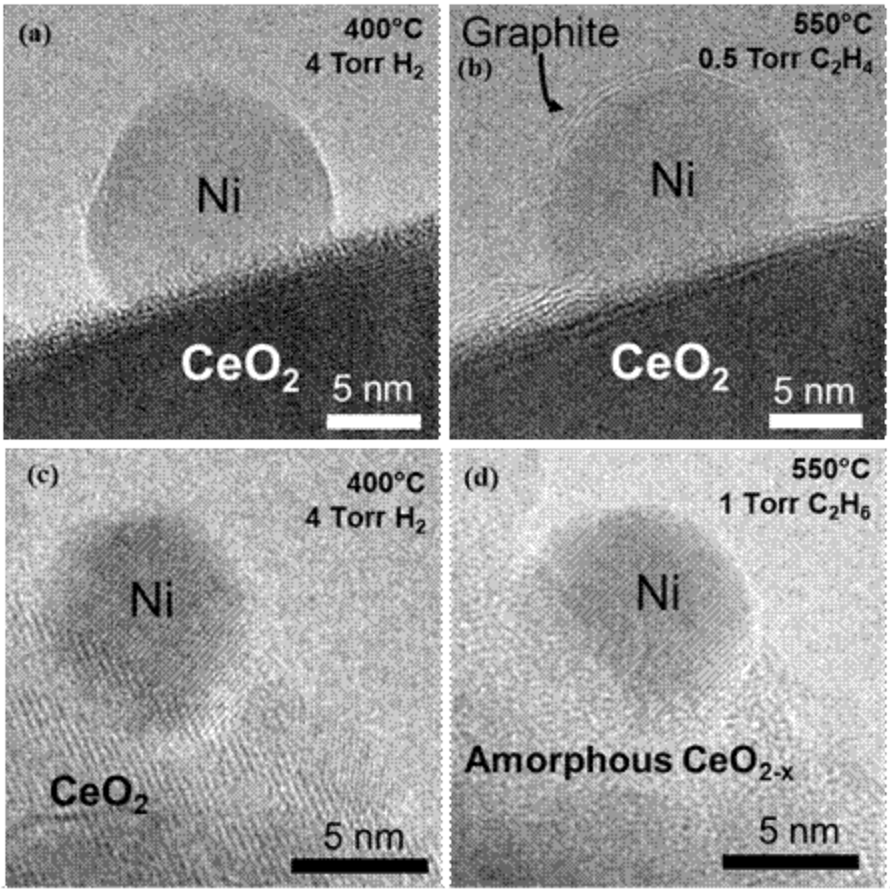

Figure 1. a) & c) Ni/CeO_2 at 400°C in 4 Torr H_2 b) Ni/CeO_2 in 0.5 Torr C_2H_4 at 550°C with several graphite layers covering the Ni particle. d) Ni/CeO_2 in 1 Torr C_2H_6 at 550°C. The Ni particle surface remains clear of graphite and the crystalline ceria becomes amorphous.

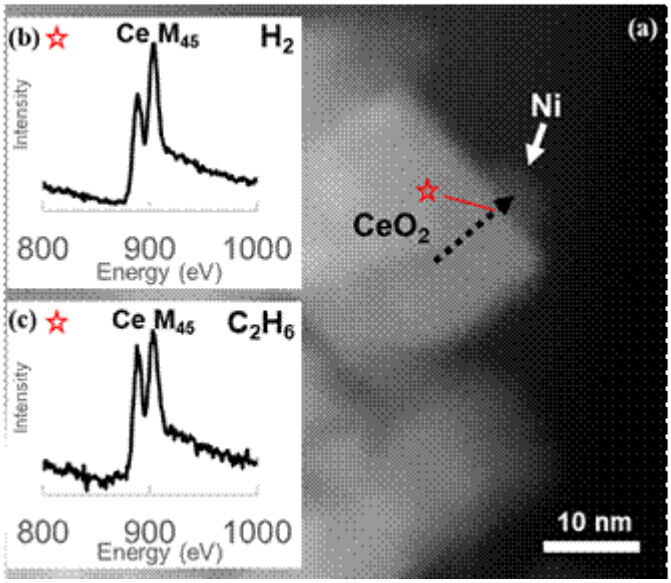

Figure 2. (a) HAADF-STEM image of Ni/CeO_2 catalyst. Dotted line indicates EELS linescan. Red star indicates the position on the linescan where the inserts were taken. (b) Energy-loss spectrum near Ni/CeO_2 interface (red star position) in 4 Torr H_2 at 400°C. (c) Energy-loss spectrum near Ni/CeO_2 interface (red star position) in 1 Torr C_2H_6 at 550°C. Ce M_{45} edge intensity ratio changes during C_2H_6 exposure indicating a transition from Ce^{4+} to Ce^{3+}.