

Atomic Resolution Imaging and Spectroscopy Of Supported Nanoparticle Catalysts

Jingyue Liu* and Nabin Nag**

* Science & Technology, Monsanto Company, 800 N. Lindbergh Blvd., St. Louis, MO, USA

** Process Technologies, Engelhard Corporation, 23800 Mercantile Road, Beachwood, OH, USA

Supported nanoparticle catalysts are widely used in many catalytic reactions. To better understand the catalytic performance of supported nanoparticle catalysts and to design better bimetallic catalysts, we need to know the nanostructure, surface composition, and the electronic structure of the individual nanoparticles as well as their interaction with the support materials. The combination of atomic resolution imaging with electron energy-loss spectroscopy (EELS) in a FEG TEM/STEM has proved powerful for characterizing individual nanoparticles and interfaces on an atomic scale. We report here the study of metal-support interactions in Pd/TiO₂ and Pd-Ni/TiO₂ nanoparticle catalysts.

The catalyst samples were prepared by an incipient wetting technique. The metal-loaded dried precursors of 5wt%Pd and 5wt%Pd3wt%Ni, both supported on TiO₂, were reduced at 650° C for 2 hours in a flow of 4% hydrogen in nitrogen to get the final catalyst. The EELS spectra and images were obtained on a JEOL 2010F FEG TEM/STEM microscope. An electron probe size of 0.2 nm was used to acquire the EELS spectra.

Figure 1 shows a HREM profile image of a Pd nanoparticle supported on a TiO₂ crystal; a thin layer of material seems to decorate the surface of the Pd nanoparticle. Although it is quite likely that the thin layer consists of TiO_x species, other explanations, such as contamination, cannot be ruled out. To determine the nature of the surface material, atomic resolution EELS spectra from different regions of the individual Pd nanoparticles were obtained. Figure 2a shows a HAADF image of the Pd/TiO₂ catalyst revealing a faceted Pd nanoparticle attached to a TiO₂ crystal. The EELS spectra obtained from different regions on the Pd nanoparticle showed the presence of Ti signal (figure 2b). The Ti signal in the edge spectra A and C (indicated by the letters A and C in figure 2a) is much higher than that in the spectrum B which was obtained from the center of the Pd nanoparticle. These results suggest that a layer of Ti-containing species encapsulates the Pd nanoparticle. Detection and quantification of the oxygen signal cannot be reliably done because the oxygen K-edge overlaps with the Pd M_{2,3}-edge. The EELS results unambiguously, however, show that the encapsulating layer on the Pd nanoparticles originated from the titania support.

Figure 3 shows a HREM profile image of a Pd-Ni/TiO₂ bimetallic catalyst revealing a large particle supported on TiO₂. The lattice fringes show that the particle structure is complicated; in fact, the particle seems to be composed of many domains. HAADF images showed contrast variations across the Pd-Ni nanoparticles; figure 4a shows such a HAADF image revealing the presence of bright patches across the particle. XEDS spectra showed that the particle contains Pd and Ni as well as a small Ti signal. Since the Ti signal in the XEDS spectra could originate from scattering effects, EELS spectra obtained from these bright patches (e.g., the regions indicated by the letters A, C, and D in figure 4a) were obtained and clearly showed the presence of strong Ti signal (spectrum A in figure 4b). The EELS spectra obtained from the regions that were not covered by the bright patches (indicated by the letter B in figure 4a), however, did not reveal any detectable Ti signal (spectrum B in figure 4b). The presence of oxygen in the bright patches is also clearly revealed in spectrum A. We concluded that the bright patches contain TiO_x species and discontinuously decorate the surfaces of the Pd-Ni nanoparticles, which is in contrast to the encapsulation of Pd nanoparticles in the Pd/TiO₂ nanoparticle catalyst. The observed differences in the surface decoration effects may

originate from the different surface structures of the nanoparticle systems. Mechanisms governing the metal-support interactions and their dependence on the reduction temperature, surface structure, and alloying will be given [1].

Reference

1. The author (JL) thanks Dr. Alan Nicholls for assistance with the microscope.

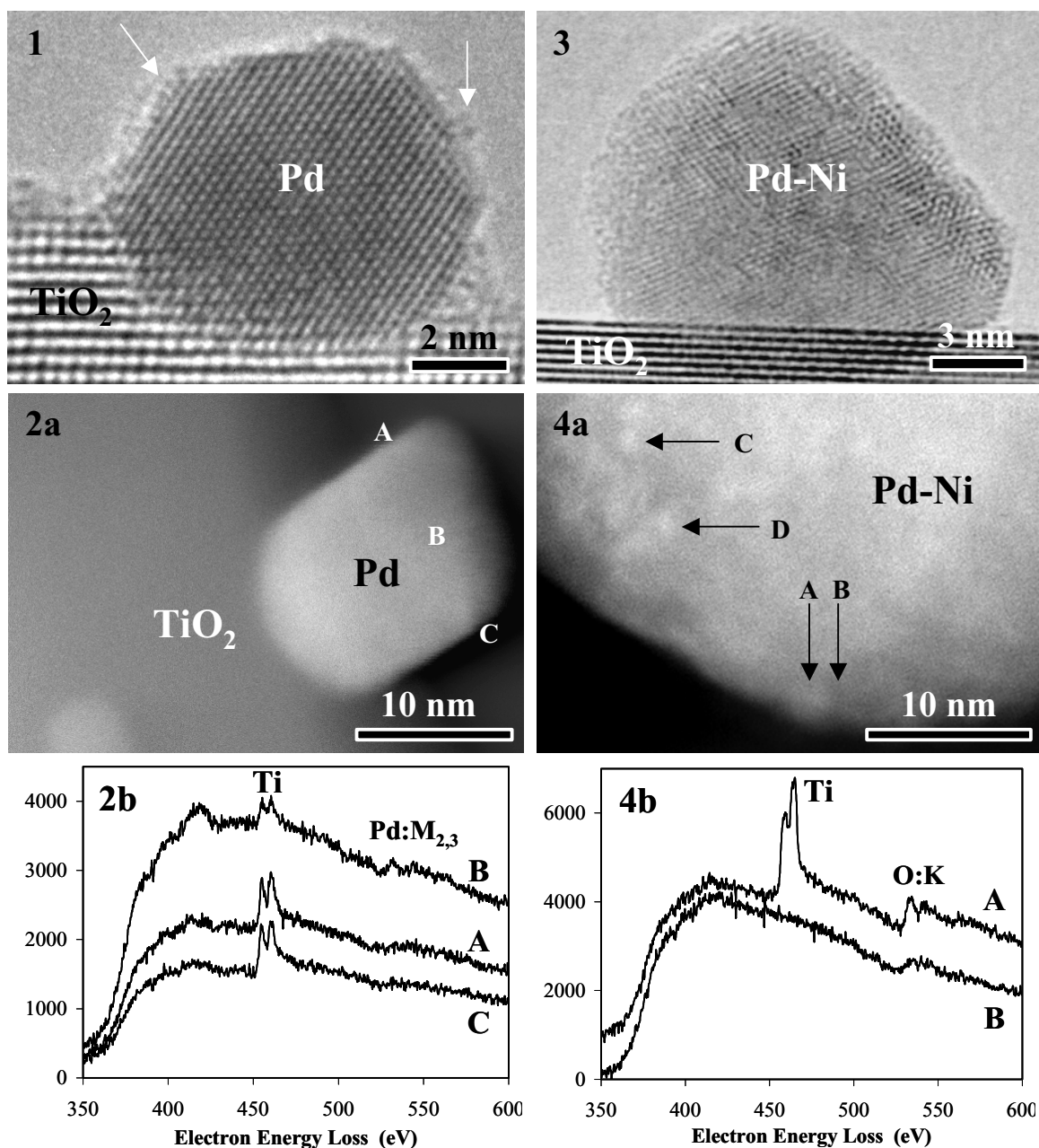


Fig. 1 HREM profile image of Pd nanoparticle in a Pd/TiO₂ catalyst shows surface decoration effect.

Fig. 2 HAADF image (a) and EELS spectra (b) show presence of Ti-containing species on Pd nanoparticle.

Fig. 3 HREM profile image of Pd-Ni nanoparticle shows complicated domain structures.

Fig. 4 HAADF image (a) and EELS spectra (b) show that the bright patches are TiO_x species.