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Atomic Scale Spectroscopy of Supported Pd-Cu/γ-Al_2O_3 Bimetallic Catalysts

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One of the key issues in developing supported bimetallic catalysts with desired properties is to understand and control the alloy composition and preferential surface segregation of individual nanoparticles. Although alloying is a well-known and well-understood phenomenon in metallurgy, which deals with bulk materials, the alloying and surface segregation behavior of bimetallic nanoparticles is still poorly understood. In this paper we will describe our recent study, using atomic resolution imaging and spectroscopy techniques, of the alloying and surface segregation properties of a gamma-alumina supported Pd-Cu bimetallic catalysts. The interest in supported Pd-Cu bimetallic catalysts arises from its potential applications to denitrification of drinking water, oxidation of carbon monoxide, and catalytic combustion of methane.

The experimental analysis was carried out on a 200kV JEOL 2010F STEM/TEM. For all the experimental results reported here an electron probe of about 0.2 nm in diameter was used to obtain the Z-contrast images and the EELS spectra. Supported Pd-Cu/γ-Al_2O_3 catalyst (containing 2% Pd and 1% Cu) samples obtained by reducing at various temperatures were studied.

Our study showed that the alloying behavior of the bimetallic nanoparticles strongly depends on the reduction temperature of the precursor materials. When the final catalyst was formed by reducing the precursor material at 773 K, EELS analysis showed nanoparticles with compositions varying from that of pure Pd to Pd-Cu bimetallic alloy nanoparticles. For example, figure 1a is a high-resolution Z-contrast image showing many nanoparticles with sizes ranging from 2-5 nm. The EELS spectra in figure 1b clearly show that the small particle (indicated by the arrow in figure 1a) contains pure Pd. The oxygen signal revealed in the spectra #2 and #3 originates from the alumina substrate. Other nanoparticles, such as the one shown in figure 2a, however, contain both Pd and Cu. The EELS spectra in figure 2b also suggest that for this particular Pd-Cu bimetallic nanoparticle, Pd has been preferentially segregated to the surface since both spectra #1 and #3, obtained from the edge of the nanoparticle, do not show any detectable Cu signal. When the catalyst was obtained by reducing the precursor material at 1073 K, however, most of the nanoparticles grew bigger (figure 3a) and they all contain both Pd and Cu. There was no significant preferential surface segregation of either Cu or Pd when the catalyst is reduced at 1073 K. Figure 3b shows the EELS spectra that clearly demonstrate this point. Further experiments on the quantitative description of the preferential surface segregation and alloying phenomenon of supported bimetallic alloy nanoparticles will be performed. The dependence of preferential surface segregation of bimetallic nanoparticles on the reduction temperature, size of the nanoparticles, and reducing environment will be discussed [1].

References

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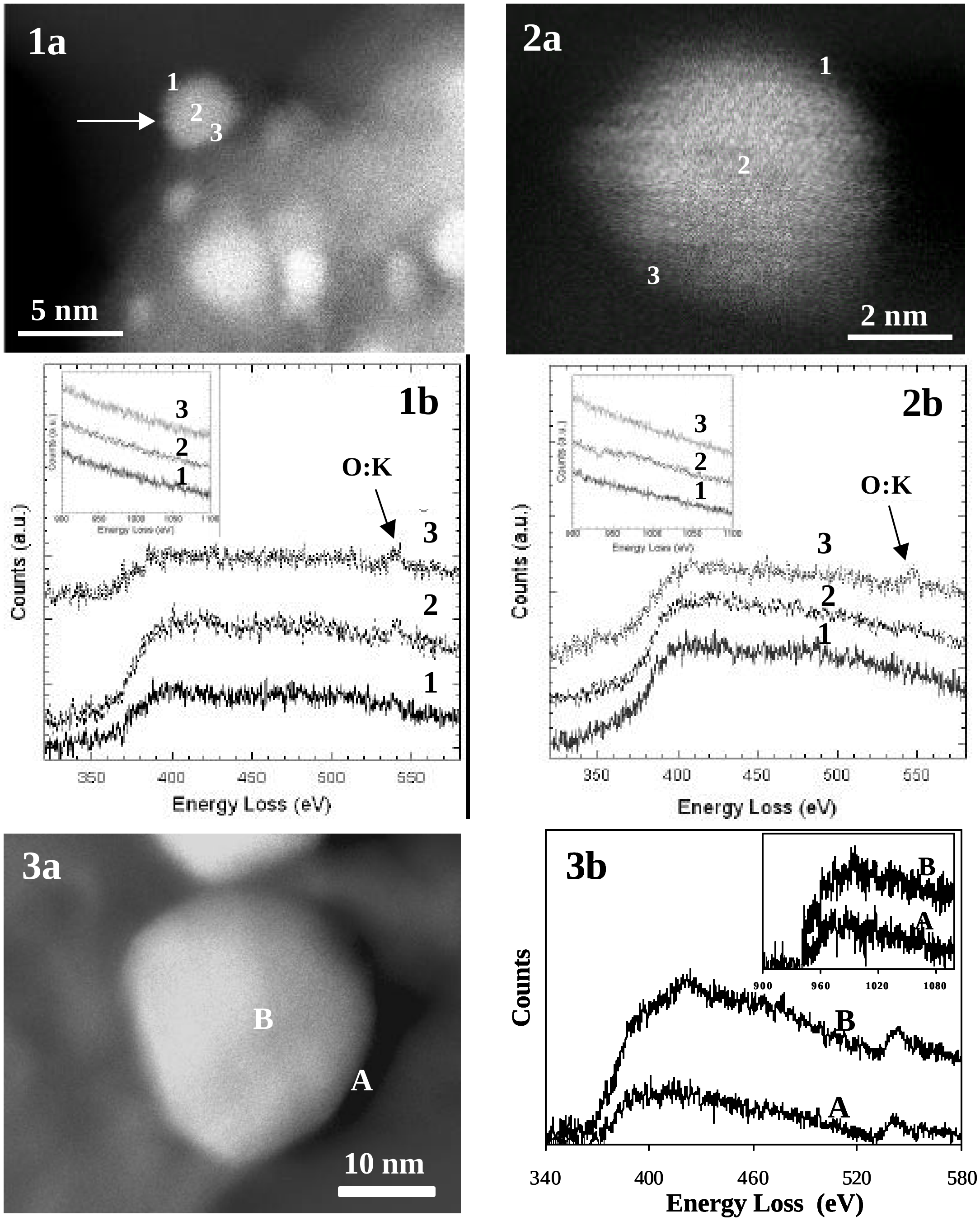

FIG. 1. Z-contrast image (a) and EELS spectra (b) show the presence of pure Pd nanoparticles in the Pd-Cu/Al_2O_3 catalyst reduced at 773 K.

FIG. 2. Z-contrast image (a) and EELS spectra (b) show the presence of Pd-Cu alloy nanoparticles and the preferential surface segregation of Pd in the Pd-Cu/Al_2O_3 catalyst reduced at 773 K.

FIG 3. Z-contrast image (a) and EELS (b) show alloyed nanoparticles with no surface segregation.

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