

Understanding the Structure of Pd/ZnO Methanol Steaming Reforming Catalysts for Hydrogen Production

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Introduction

Alcohols, due to their easy storage and transport, have been proposed as possible sources of hydrogen. To convert alcohols to hydrogen via onboard reforming requires highly active, selective and stable catalysts. Pd supported on ZnO has shown promising properties as a catalyst for onboard steam reforming of methanol to produce hydrogen [1]. The formation of PdZn alloy nanoparticles has been considered to be responsible for the improved catalytic performance of Pd/ZnO catalysts [1]. The alloy formation processes and detailed surface atomic structures of the PdZn nanoparticles, however, are not well understood [2-3]. We have recently developed a unique model nanocatalyst by preparing precursor materials consisting of Pd dispersed onto well-defined surfaces of ZnO nanobelts. *In situ* study of the reduction processes of the Pd/ZnO precursor materials, using an electron microscope with sub-Ångström image resolution, has provided deep insights into the PdZn alloy formation processes, their structural evolution and the nature of the final Pd/ZnO catalysts.

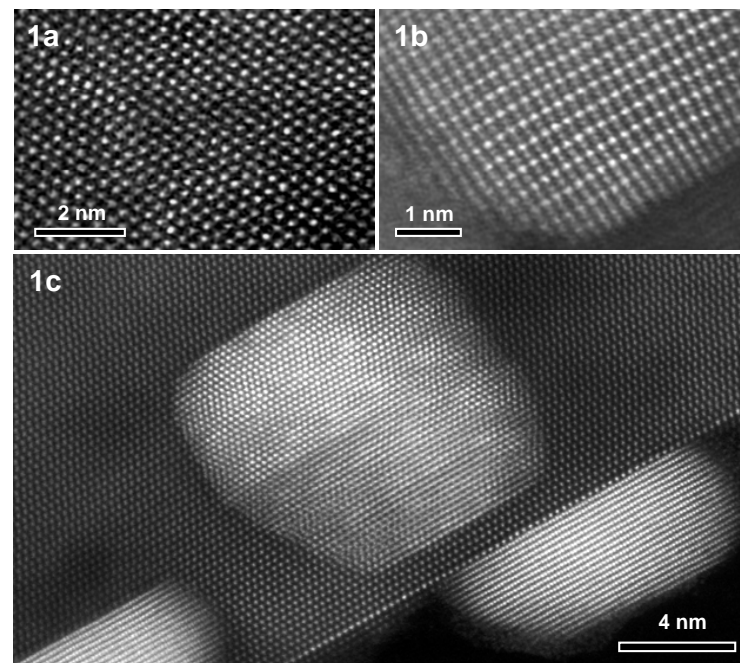
Materials and Methods

ZnO nanobelts or nanoribbons were fabricated by a thermal evaporation-condensation method in a high temperature tube furnace [4]. The deposition-precipitation of Pd was accomplished by dipping the ZnO nanobelts into an aqueous solution containing Pd(NO₃)₂ as precursor salts. Because ZnO nanobelts dissolve quickly in an acidic solution, the pH value of the aqueous solution was maintained, by adding NaOH, between 6 and 7. The precursor materials were then either reduced in a tube furnace with flowing H₂/Ar gases or were reduced *in situ* inside a JEOL 2200FS scanning transmission electron microscope (STEM) equipped with a CEOS Co. aberration corrector which provides a nominal imaging resolution of about 0.07 nm. A novel heater assembly, provided by Protochips Inc. (Raleigh, NC), was used to heat up the precursor materials to desired temperatures.

Results and Discussion

Figure 1a shows an atomic resolution high-angle annular dark-field (HAADF) [5] STEM image of the Pd/ZnO nanobelt precursor material. The brighter dots represent individual Pd atoms located on top of Zn columns (grey dots). It is interesting to note that some of the Pd atoms are aligned together to adapt to the lattice spacing of the Zn layers of the ZnO single crystals. Figure 1b shows an atomic resolution HAADF image of a PdZn alloy nanoparticle, obtained after *in situ* heating of the precursor sample at 400°C for about 55 minutes. The bright dots (layers) represent columns of Pd atoms and the grey dots (layers) represent columns of Zn atoms. The HAADF image reveals that the most outside surface layer of the PdZn alloy nanoparticles probably consists of primarily Zn atoms. Figure 1c shows an atomic resolution HAADF image of the Pd/ZnO sample, obtained after further *in situ* heating of the precursor at

500°C for about 30 minutes, clearly revealing an epitaxial relationship between the PdZn alloy nanoparticles and the ZnO nanobelts (PdZn (111)|| ZnO (0001)). The epitaxial growth of PdZn on ZnO support makes the catalyst more resistant to sintering. The PdZn nanoparticles display dominant {111} facets. The interaction of Pd with ZnO has also been investigated.



Significance

The *in situ* investigation of the Pd/ZnO nanobelt model catalyst inside a sub-Ångström resolution electron microscope provided deep insights into the formation processes of PdZn alloy nanoparticles, their structural evolution and the surface atomic structure of the catalyst.

References

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