Promotion Effect of Polymer-Immobilized Neodymium Ions on Catalytic Activity of Ultrafine Palladium Particles

Toshiharu Teranishi, Ken Nakata,[†] Mikio Miyake, and Naoki Toshima*[†]
School of Materials Science, Japan Advanced Institute of Science and Technology, 15 Asahidai, Tatsunokuchi, Ishikawa 923-12
[†]*Department of Applied Chemistry, School of Engineering, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113*

(Received December 19, 1995)

Neodymium ions, which are placed close to ultrafine palladium particles by immobilization on water-soluble polymers, did promote the catalytic activity of the palladium particles for hydrogenation of acrylic acid. The acrylic acid is considered to be concentrated around ultrafine palladium particles by coordinating to neodymium ions bound to the protecting polymer.

Much attention has been paid to nanostructured ultrafine transition metal particles from fundamental and practical viewpoints.[1] Nano-size ultrafine particles are promised to be advanced materials with new electronic, magnetic, and optic properties.[1-3] They have been also applied to catalysts[1-4] for hydrogenation, hydroformylation, hydration and so on.

The colloidal dispersion of nano-size ultrafine particles is often stabilized by the water-soluble polymers. These polymers will be able to work not only as stabilizers of the ultrafine particles but also as the materials functionalizing the ultrafine particles, since it is an advantage for polymer catalysts to be attached by two functional groups or active sites on the polymer support, resulting in cooperative and multi step catalysts.[5]

Lanthanoids (rare earths) have been investigated and utilized in many fields.[6] Recently, lanthanoid-catalyzed reactions are of great interest and importance. The first report on the promotion effect of lanthanoid upon catalytic activity of metals appeared in the study of supported catalysts for synthesis gas conversion.[7] For adsorption characteristics, lanthanoid and transition metals were more efficient when they were used together than used separately. Therefore, immobilization of lanthanoid around transition metals and interaction between transition metals and lanthanoids are considered to be important in order to investigate the promotion effect by lanthanoids. We have reported the promotion effect by anchored lanthanoid ions upon the hydrogenation activity of the ultrafine Pd particle catalyst supported on the resin beads.[8] Thus, the promotion effect of lanthanoids has been observed only in the heterogeneous system, and it remains as an unsettled question whether lanthanoids promote the catalytic activity even in a homogeneous system.

To the best of our knowledge, there is no reports to functionalize the ultrafine metal particle catalyst by protecting polymers. This is the first report to functionalize the colloidal metal catalysts by the lanthanoid ions immobilized by water-soluble protective polymer.

In this letter, monodispersed ultrafine Pd particles protected by polyacrylate-Nd^{3+} complexes were first successfully prepared, in which Nd^{3+} are placed close to the ultrafine Pd particles. They were used for investigation of the promotion effect of Nd^{3+} upon the catalytic activity of Pd particles. It should be emphasized that no promotion effect was observed in colloidal dispersions of poly(*N*-vinyl-2-pyrrolidone)-protected Pd particles, while the effect is obvious for those of polyacrylate-protected Pd particles. The speculated mechanism of the promotion effect is also discussed.

Colloidal dispersions of ultrafine Pd particles were prepared by alcohol-reduction in the presence of sodium polyacrylate (PAA, average molecular weight 2,200). The mixture of 15 cm^3 of a 2 mmol dm^{-3} $H_2[PdCl_4]$ aqueous solution (30 μmol of Pd), 10 cm^3 of water, 25 cm^3 of ethanol and 56.6 mg of PAA (600 μmol as monomeric unit) was refluxed in 50 cm^3 flask for 3 h under air. The dispersions of ultrafine Pd particles protected by PAA (abbreviated as PAA-Pd) have brown color and are stable for months at room temperature. The formation of the ultrafine Pd particles was confirmed by the electronic spectra and the TEM photographs. Complexation of Nd^{3+} to PAA was conducted by adding $NdCl_3{\bullet}6H_2O$ to the dispersion of PAA-Pd at designed concentration, and confirmed by the FT-IR spectra. Homogeneous colloidal dispersion of ultrafine Pd particles protected by poly(*N*-vinyl-2-pyrrolidone) (PVP, average molecular weight 40,000) was prepared (abbreviated as PVP-Pd), complexed with Nd^{3+}, and characterized as well as PAA-Pd. Catalytic hydrogenation of acrylic acid and 1-hexene was carried out in ethanol at 30°C under 1 atm of hydrogen. Hydrogen uptake was measured with a gas burette to determine the initial rate of hydrogenation.

It was confirmed from the electronic spectra that $PdCl_4^{2-}$ ions disappeared within 30 min and the formation of ultrafine Pd particles was completed for 2 h in both cases of PAA-Pd and PVP-Pd. The mean diameter of monodispersed PAA-Pd and PVP-Pd particles are 44 Å and 28 Å, respectively.

In order to investigate the promotion effect of Nd^{3+} on the catalytic activity of ultrafine Pd particles, hydrogenation of acrylic acid in ethanol, catalyzed by PAA-Pd and PVP-Pd, was carried out in the presence of Nd^{3+}, the amount of which was varied from 0.01 to 0.2 in molar ratio to Pd. In both cases, hydrogenation product was propionic acid and no other products were detected. Figure 1 demonstrates the change in the catalytic activity by the addition of Nd^{3+}. When PVP was used as a protective polymer, the catalytic activity of ultrafine Pd particles decreased with increasing the amount of added Nd^{3+}. This is probably due to the adsorption of Nd^{3+} on the surface of Pd particles, because the Pd particles are negatively charged, resulting in decreasing in the number of active sites for hydrogen of the Pd surface. On the other hand, when PAA was used instead of PVP, addition of Nd^{3+} made the catalytic activity increase at any ratio of Nd^{3+} to Pd. The promotion effect of Nd^{3+} is thought to require Nd^{3+} placed close to Pd particles but not adsorbed on the surface of particles. FT-IR measurement indicates that Nd^{3+} coordinate to PAA by ion exchange, whereas such coordination is not detected for PVP probably because PVP has a weak coordination ability to the Nd^{3+}. ICP analysis also supports the coordination of Nd^{3+} to PAA, that is, the amount of Nd^{3+} could coordinate to PAA four times as large as Pd. These facts support the above suggestion, that is, close placement of

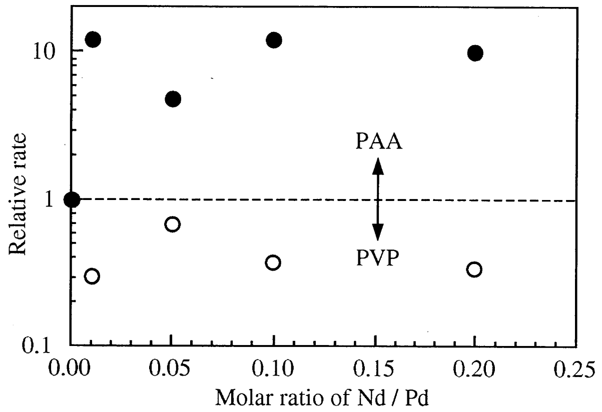

Figure 1. Addition effect of neodymium ions on the catalytic activity of PAA-Pd (●) and PVP-Pd (○) for the hydrogenation of acrylic acid in ethanol at 30 °C under 1 atm of H_2.

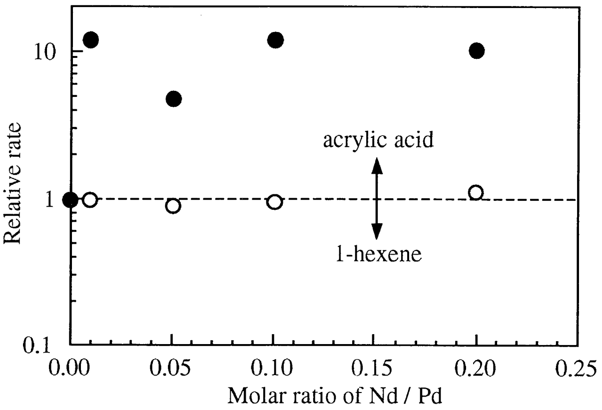

Figure 2. Addition effect of neodymium ions on the catalytic activity of PAA-Pd for the hydrogenation of acrylic acid (●) and 1-hexene (○) in ethanol at 30 °C under 1 atm of H_2.

Nd^{3+} to Pd particles is required for the promotion effect.

Hydrogenation of 1-hexene, instead of acrylic acid, catalyzed by PAA-Pd was carried out in ethanol in the presence of Nd^{3+} in order to investigate the influence of the substrate. The effect of addition of Nd^{3+} on the catalytic activity of Pd particles are shown in Figure 2. Although the Nd^{3+} were located close to the Pd particles, the catalytic activity didn't increase at all in the case of 1-hexene. It may be concluded from these facts that the promotion effect of Nd^{3+} is not mainly based on an electronic interaction between Nd^{3+} and Pd particles, but on an interaction between Nd^{3+} and substrates; the coordination of specific substrates containing oxygen or nitrogen atoms to Nd^{3+}. This is supported by the result that PAA-Pd with Nd^{3+} also have the promotion effect on the hydrogenation of allyl amine. Figure 3 illustrates a speculated mechanism of the promotion effect, where acrylic acid is concentrated around ultrafine Pd particles by coordinating to Nd^{3+}, which are bound to the PAA but not adsorbed on the Pd particles.

The present work was supported by a Grant-in-Aid for Scientific Research on Priority Areas "New Development of Rare Earth Complexes" (Nos. 06241215 and 07228213) from the Ministry of Education, Science, Sports and Culture, Japan.

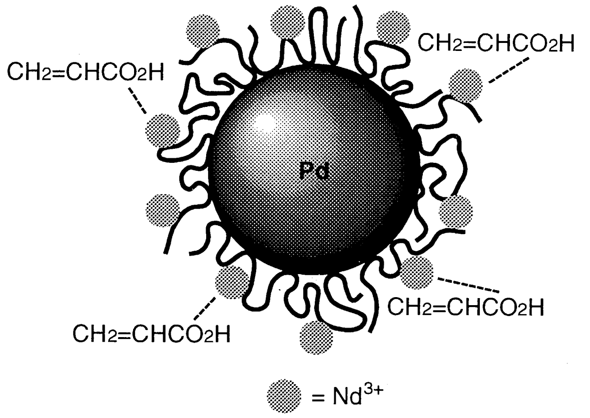

Figure 3. Schematic illustration of the speculated mechanism of the promotion effect of neodymium ions on the catalytic activity of PAA-Pd.

References

1 *Clusters and Colloids*, ed by G. Schmid, VCH, Weinheim, (1994).
2 A. Henglein, *J. Phys. Chem.*, **97**, 5457 (1993).
3 H. Weller, *Angew. Chem., Int. Ed. Engl.*, **32**, 41 (1993).
4 L. N. Lewis, *Chem. Rev.*, **93**, 2693 (1993).
5 H. Hirai and N. Toshima, in "Tailored Metal Catalysts," ed by Y. Iwasawa, Reidel, Dordrecht (1986), pp. 87-140.
6 Handbook on the Physics and Chemistry of Rare Earth, ed by K. A. Gschneider, Jr., and L. Eyring, North-Holland, Amsterdam (1978-84), Vol. 1-7; New-Frontiers in Rare Earth Science and Applications, ed by X. Guangxian and X. Jime, Science Press, Beijing (1985); K. A. Gschneider, Jr., Industial Applications of Rare Earth Elements, Am. Chem. Soc. (1981).
7 J. S. Rieck and A. T. Bell, *J. Catal.*, **99**, 278 (1986).
8 T. Teranishi and N. Toshima, *J. Chem. Soc., Dalton Trans.*, **20**, 2967 (1994).