Catalytic Behavior of Au Core / Pd Shell Bimetallic Nanoparticles on Silica Prepared by Sonochemical and Sol–Gel Processes

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A unique catalyst, Au core and Pd shell bimetallic nanoparticles immobilized on porous silica exhibiting a considerable high activity for the hydrogenation of cyclohexene, was prepared via two steps composed of the sonochemical reduction method and the sol–gel process under a low temperature condition.

During the last decade a number of excellent techniques in the preparation of metallic nanoparticles with various compositions, structures, shapes and sizes have been developed in the controlled colloidal dispersions systems.[1,2] Structure-controlled bimetallic nanoparticles such as a core–shell structure, a random alloy structure, etc. are also expected to exhibit diverse and unusual catalytic activities.[2–5] On the other hand, it has also been reported that bimetallic nanoparticles composed of Au core and Pd shell could be selectively prepared by the sonochemical method in an aqueous solution.[6] It is an important subject from the practical point of view how to disperse and stabilize such functional nanoparticles onto the surface of porous materials. An objective of this report is how to prepare Au/Pd nanoparticles supported on porous silica via successive processes composed of the sonochemical method and the sol–gel method at low temperatures. The obtained catalyst was characterized by TEM, XRD, XPS, etc., and furthermore the catalytic property was investigated for the hydrogenation of cyclohexene.

Ultrasonic irradiation was carried out using an ultrasonic generator (200 kHz, 6 W/cm^2) and a barium titanate oscillator (65 mm ϕ). An aqueous solution (65 mL) of $NaAuCl_4$ (Au(III)) and Na_2PdCl_4 (Pd(II)) containing poly(ethylene(40)glycol monostearate) (PEG, 0.4 mM) was sonicated at 20 °C under Ar atmosphere. The initial combined concentration of Au(III) and Pd(II) was held constant at 1 mM. The stepwise reduction[6] was observed to proceed during the ultrasonic irradiation, i.e., the reduction of Pd(II) proceeded after the reduction of Au(III) finished. The reduction of both ions was completed in 20 min irradiation, in which PEG acted not only as a stabilizer for the formed colloidal particles but also as a radical source for the reduction of noble metal ions under sonication.[7] The formation of Au/Pd bimetallic nanoparticles composed of Au core and Pd shell was recognized by UV–vis,[8] XPS and XRD analyses. Next, to the colloidal Au/Pd dispersion $Si(OC_2H_5)_4$ and NH_3 were added and refluxed for 2 h at 75 °C. The solution was then evaporated by heating at below 80 °C with vigorous stirring, resulting in the porous silica powders[9] including the Au/Pd nanoparticles. The powders were washed sufficiently with distilled water and dried at 50 °C in an oven for several days.

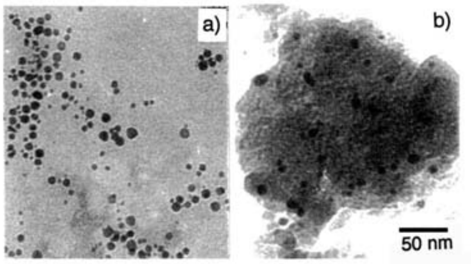

Figure 1. TEM photographs of a) Au/Pd bimetallic nanoparticles prepared by sonochemical method and b) silica supported Au/Pd nanoparticles catalyst after sol-gel process. Ratio of Au/Pd composition is 1/1. Noble metal loading on silica is 0.3 mol%.

Figure 1 shows transmission electron micrographs of the Au/Pd particles obtained by ultrasonic irradiation (a) and those supported silica after the sol–gel process (b), respectively. It was confirmed that the sonochemically prepared Au/Pd particles were of nanometer size with a fairly sharp distribution (average size: 6.3 nm, standard deviation: 2.2 nm). Since no appreciable difference was observed in the size and distribution of the particles before and after the sol–gel process, highly dispersed Au/Pd particles in and on the porous silica matrix could be successfully prepared. It was also confirmed by XPS analysis[10] that the core–shell structure of the Au/Pd particle was retained during the sol–gel process.

To evaluate the catalytic activity of silica supported bimetallic Au/Pd core–shell catalysts, the hydrogenation of cyclohexene in a 1-propanol solution was employed. Figure 2 shows the effect of various Au/Pd composition on the rate of hydrogenation in addition to the average sizes of supported Au/Pd particles. In comparison with the bimetallic catalysts, the monometallic catalyst supported on silica was also prepared by the same procedure. It was found that the rates of hydrogenation over the Au/Pd supported on silica were distinctly higher than that over the monometallic Pd silica, although the sizes of their particles were almost equal to each other. Pure Au supported on silica exhibited no catalytic activity in this reaction. The catalytic activity con-

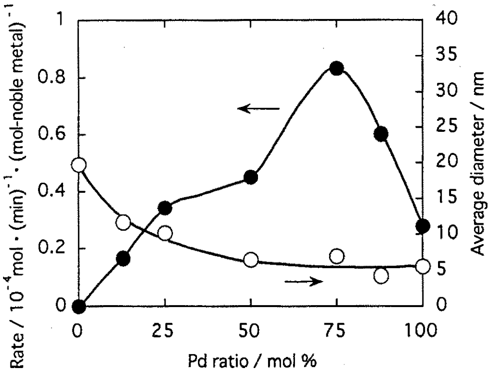

Figure 2. Catalytic activities (●) for the hydrogenation of cyclohexene over catalysts with various Au/Pd composition and average sizes (○) of loading noble metal. The reaction was carried out in a conventional closed system at 23 ± 0.5 ℃. Conditions: initial H_2 pressure of 1 atm, cyclohexene of 1.18 mmol, 1-propanol solution of 30 mL.

siderably depended on the composition of Au/Pd and the highest activity was recognized at the composition of 75 mol% Pd. In colloidal dispersions of bimetallic nanoparticles, Toshima et al. have proposed the roll of ligand effect derived from an electrostatic effect between Au core part and atomic Pd shell.[2,4,11] The high activity of the present Au/Pd supported on porous silica could be elucidated by the ligand effect although the average size of the present Au/Pd particles was considerably larger in comparison with their catalyst. For example in the case of the composition at 75 mol% of Pd, the layer of Pd shell and the core of Au could be estimated to be ca. 1.1 nm in thickness and ca. 4.2 nm in diameter, respectively, assuming that monodispersed Au/Pd particles of 6.4 nm could be formed. This thickness of Pd shell corresponds to several atomic layers. Because of the quantum sized structure, the ligand effect might be affected by any quantum size effects[12,13] with respect to the optimum size effect of the Pd layer or the Au cluster of the core part.

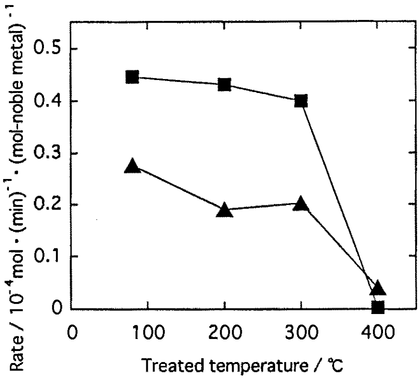

Figure 3. Effect of thermal treatment of silica supported catalysts on the catalytic activity. (■) : Au/Pd=1/1, (▲) : Pd.

The effect of thermal treatment of Au/Pd silica on the activity was examined to clarify the role of core–shell structure in the catalytic activity. Figure 3 shows the relation between the thermal treatment of the catalysts at several temperatures under H_2 atmosphere and the activity for the hydrogenation of cyclohexene. It was recognized that the catalytic activity of bimetallic Au/Pd silica gradually decreased with temperature and almost completely disappeared by the treatment at 400 °C. The activity of monometallic Pd silica decreased with temperature of the H_2 treatment in analogy with the Au/Pd silica. The decrease ratio in the activity of monometallic Pd catalyst from 300 °C to 400 °C was, however, fairly smaller than that of the Au/Pd silica. This decrease in the catalytic activity would not be attributed to the decrease in the surface area of the Au/Pd nanoparticles because the size of the particles hardly changed by the thermal treatment which was confirmed by the TEM observation. Figure 4 represents the XRD patterns of the Au/Pd silica treated with H_2 at various temperatures. In the XRD pattern of as-prepared sample, a broad peak was observed at 38.2 degrees assigned to Au(111) line. Pd shell was presumably too thin to appear as the sufficient diffraction of Pd metal. The diffraction pattern did not change until the treated temperature at 400 °C, where the peak shifted to a higher angle and exactly located at the middle of Au(111) and Pd(111) line which was consistent with that of bulk alloy state.[14] The color of the sample also varied from reddish gray to dark gray at this temperature. These results indicated that the core–shell structure was destroyed at 300–400 °C to form the random alloy structure, while the size of the bimetallic particles did not change by the treatment. From these points of view, it might be concluded that the extremely low activity at 400 °C was attributed to the change in the Au/Pd structure from the core–shell to the random alloy structure. It was also suggested that the core–shell structure of Au/Pd played an important role for the hydrogenation of cyclohexene. Further detailed investigations are, of course, required to gain insight into the relations between the structure of Au/Pd nanoparticles and the catalytic activity.

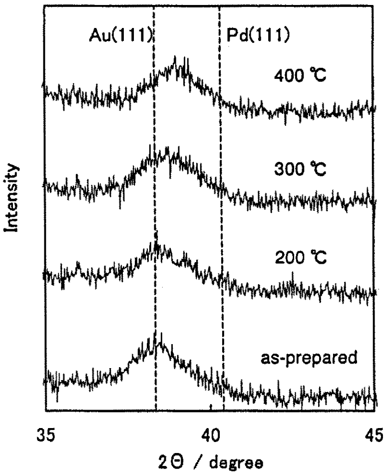

Figure 4. Effect of thermal treatment of silica supported Au/Pd bimetallic catalyst on the XRD pattern. (Cu Kα).

References and Notes

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8 The plasmon absorption peak assigned to Au colloid was initially emerged at ca. 540 nm, but the peak was bule-shifted and became obscure when the reduction of Pd(II) ions proceeded. This phenomenon was in good agreement with that of the spectral change in the formation processes of Au core and Pd shell structure described in ref 6.
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10 Relative photoelectron intensity of Pd to Au corrected by the sensitivity factor was obtained as 1.36, although the ratio of Au/Pd composition was equal to 1. This result supported the formation and the existence of Au core and Pd shell structure, assuming that the photoelectron emitted from the inner Au was absorbed by the outer Pd layer. This speculation was also supported by ref 3.
11 It has been suggested that a positive charged Pd shell deposited on Au core in the bimetallic particles is more active than non-charged monometallic Pd particles, since olefin having a double bond favors the electron-deficient surface.
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