

Sonochemical Preparation of Supported Metal Catalysts

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Noble metal nanoparticles dispersed on metal oxides were prepared via the sonochemical reduction of the corresponding metal ions in an aqueous solution. The reduction was induced by reducing radicals formed from the sonolysis of organic additives such as alcohols and surfactants, and the rates were controllable by selecting the type of the additives. The average particles size of metallic Pd formed on the alumina surface changed clearly with the type of alcohols; methanol < ethanol < 1-propanol. It was also found that the size of formed Pd particles increased with decreasing the rate of Pd(II) reduction (corresponding to the rate of Pd nucleation). The formation mechanism of the supported materials was also proposed. In addition, Au core / Pd shell nanoparticles supported on silica were prepared by successive processes composed of the sonochemical method and the sol-gel method. The catalytic activities of these materials were also discussed.

Key words: Sonochemistry, Cavitation, Noble Metal Catalyst, Nanostructured Materials

1. INTRODUCTION

Nanostructured materials, such as metal nanoparticles, their supported materials and organic-inorganic nanocomposites, have attracted considerable attention for their application to catalysts, absorbents and sensors as well as optical, electronic and magnetic devices.¹⁻³ Therefore, a wide variety of the preparation methods have been extensively studied. On the other hand, during the past decade high power ultrasound have been increasing interest to its application for preparing nanostructured materials because of unique phenomena induced by ultrasonic cavitation.⁴⁻⁷

The cavitation, which is caused by ultrasonic irradiation of a liquid, is comprised of the formation, growth and collapse of bubbles in a liquid. When the cavitation bubbles are violently collapsing, the inside of the bubbles reach several thousands of degrees and hundreds of atmospheres together with a shock wave generation.^{4,8,9}

We have been reported that a new application of organic radicals, which were formed from sonochemical decomposition of organic additives such as surfactants, water soluble polymers, alcohols, etc., to the reduction of noble metal ions and the formation of their nanoparticles in aqueous solutions.¹⁰⁻¹² In this paper, from the fundamental viewpoint of fabricating a novel nanostructured material including a catalyst, Pd nanoparticles supported on alumina^{12,13} and Au core / Pd shell nanoparticles supported on silica¹⁴ were prepared via one or two steps composed of the sonochemical method and the sol-gel method at low temperatures. Characterization of the prepared materials by TEM, XRD, XPS, etc., and the catalytic activity for

hydrogenation of olefins at ambient temperature are described.

2. EXPERIMENTAL

2.1 Preparation of Pd supported on Al₂O₃

Ultrasonic irradiation was carried out at 20°C in a water bath using an ultrasonic generator (Kaijo 4021, 200kHz, 6W/cm²) and a 65mm ϕ barium titanate oscillator. The irradiation set-up is similar to that previously reported.¹⁵ A cylindrical glass vessel (volume: 190mL) was used for ultrasonic irradiation, which had a silicon rubber septum for gas bubbling or sample extraction without exposing the sample to air. The bottom of the vessel was planar, 1mm in thickness, and 55mm ϕ in diameter. The vessel was fixed directly on the oscillator.

An aqueous solution of Na₂PdCl₄ (Pd(II), 1mM, 65mL) containing α -alumina (2.02 or 10.5g/L) was prepared in the reaction vessel, and then it was bubbled with argon for 30min. An alcohol, which acts as an effective accelerator for the reduction of Pd(II), was injected into the solution using a micro-syringe through the septum just before the irradiation.

2.2 Preparation of Au/Pd supported on SiO₂

An aqueous solution (65mL) of NaAuCl₄ (Au(III)) and Pd(II) containing poly(ethylene(40)glycol monostearate) (PEG, 0.4mM) was sonicated at 20°C under argon atmosphere. The reduction of Au(III) and Pd(II) smoothly proceeded stepwise as reported previously⁷ and completed in 20min irradiation, in which PEG acted not only as a stabilizer for the formed colloidal particles but also a radical source for the

reduction of noble metal ions under sonication.^{10,11} Next, to the colloidal Au/Pd dispersion $\text{Si}(\text{OC}_2\text{H}_5)_4$ (21mmol) and NH_3 (1.9mmol) were added and refluxed for 2h at 75°C. The solution was then evaporated by heating at less than 80°C with vigorous stirring, resulting in the drying silica powders including Au/Pd nanoparticles. The powders were washed sufficiently with distilled water and dried in a 50°C oven for several days.

3. RESULTS AND DISCUSSION

3.1 Formation of Pd nanoparticles supported on Al_2O_3

Figure 1 shows a transmission electron micrograph of the sonochemically prepared Pd/ Al_2O_3 . It was observed that spherical Pd particles were formed on alumina and were of nanometer size with a fairly narrow distribution. Furthermore, they were highly dispersed on the surface of the alumina. The formation of metallic Pd was also confirmed by the X-ray diffraction pattern. The average size and standard deviation of the Pd particles under several preparation conditions were summarized in Table 1. In this experiment, the initial concentrations of

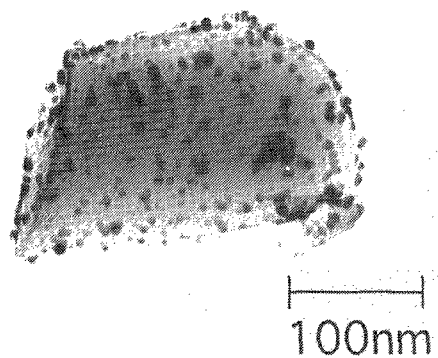


Figure 1. Transmission electron micrograph of sonochemically prepared 1wt% Pd/ Al_2O_3 . Irradiation time: 30min.

Table 1. Average size and standard deviation of sonochemically formed Pd particles on Al_2O_3 .

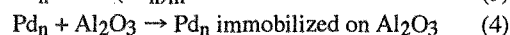
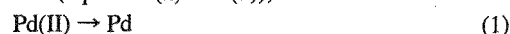
Conditions ^a	Average size / nm	SD ^b / nm
1 wt%, 1-Propanol	6.8	1.8
1 wt%, Ethanol	7.4	2.5
1 wt%, Methanol	7.9	3.4
5 wt%, 1-Propanol	8.6	2.8
5 wt%, Ethanol	10.0	2.9
5 wt%, Methanol	11.3	5.8

^a Weight ratio of Pd / Al_2O_3 . ^b Standard deviation.

Pd(II), concentration of alcohols and the irradiation time are fixed at 1mM, 20mM and 30min, respectively. As shown in Table 1, it was found that the size of the formed Pd particles and their distribution were dependent on the kinds of alcohol additives. Under our sonication system, since alcohol is an important additive for controlling the rate of Pd(II) reduction, the size of Pd particles formed from the reduction would be controllable. The average size of Pd particles decreased in the order of methanol > ethanol > 1-propanol. The standard deviation, also, decreased in the same order.

To investigate the effect of alumina on the formation of Pd particles, the preparation of 1wt% and 5wt% of Pd/ Al_2O_3 were carried out by changing the amount of coexisting alumina. The obtained results were also indicated in Table 1. The size of the formed Pd particles and its standard deviation became smaller when larger amount of alumina existed. Since the rate of reduction was almost the same between 1wt% and 5wt% of Pd/ Al_2O_3 in the same alcohol additive, the rates of Pd nucleation were suggested to be almost equal to each other. Therefore, the growth and/or the agglomeration of the Pd particles in solution would be suppressed by its adsorption onto alumina so that the size of the formed Pd particles was smaller as the amount of alumina increased. In other words, alumina acts as a stabilizer for the Pd particles under sonication.

The formation process of the supported materials is suggested as follows: the nucleation (equation (1)) and growth (equation (2) and (3)) of Pd nuclei occurs in the bulk solution, and the immobilization (equation (4)) of the Pd particles proceed competitively toward its growth process (equation (2) and (3)),



where Pd_n denotes a Pd particle and $(\text{Pd}_n)_m$ a more aggregated one. According to this proposed mechanism, it should be noted that the formed Pd particles are selectively immobilized only on the surface of the alumina.

3.2 Formation of Au Core / Pd Shell Nanoparticles Supported on Silica

Figure 2 shows transmission electron micrographs of the Au/Pd particles obtained by ultrasound and their supported silica after the sol-gel processes, respectively. It was confirmed that the sonochemically prepared Au/Pd particles were of nanometer size with a fairly sharp distribution (average size: 6.3nm, standard deviation: 2.2nm). After the sol-gel processes, the size and distribution of the particles (average size: 6.4nm, standard deviation: 2.0nm) also did not change so that highly dispersed Au/Pd nanoparticles on silica could be

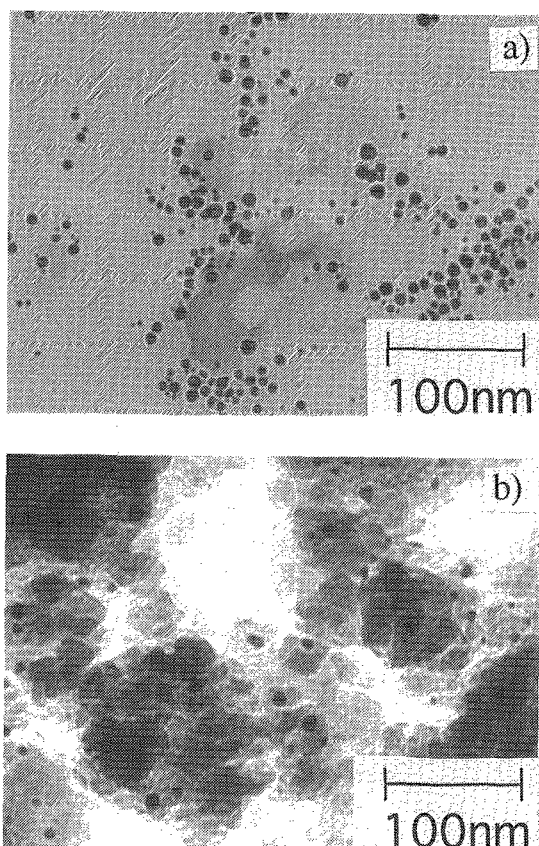


Figure 2. Transmission electron micrographs of a) the Au/Pd particles obtained by the 20min irradiation and b) their supported silica after sol-gel processes.

successfully prepared. The XPS analysis showed that the core-shell structure in the Au/Pd particle was remained; Relative XPS 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. The result of this speculation was in good agreement with the previous reports.¹⁶ In the XRD pattern of the prepared sample (Au/Pd = 1), a broad peak was also observed at 38.2 degrees ($\text{CuK}\alpha 1$) assigned to Au (111) line, while Pd shell was presumably too thin to appear as the sufficient diffraction of Pd metal. For example in the case of the composition at 50mol% of Pd, the layer of Pd shell and the core of Au could be estimated to be ca. 0.6nm in thickness and ca. 5.2nm in diameter, respectively, assuming that monodispersed Au/Pd particles of 6.4nm was formed. This Pd thickness corresponds to two or three atomic layers.

3.3 Catalytic activity of Pd supported on Al_2O_3

For the measurement of the catalytic activity of the sonochemically prepared catalysts, hydrogenation of

olefin (1-hexene, trans-3-hexene, cyclohexene) was carried out in a 1-propanol solution (Condition: $23 \pm 0.5^\circ\text{C}$, 1atm of hydrogen). All Pd/ Al_2O_3 catalysts were treated with H_2 gas at 200°C for 2h to remove any carbon and oxide species before the catalytic studies. The catalyst was added to 1-propanol solution (30mL) in a reaction vessel and kept under 1atm hydrogen atmosphere for 60min at room temperature before the reaction, then olefin was introduced.

The hydrogenation of 1-hexene over Pd catalyst was investigated. In comparison with the sonochemically prepared Pd/ Al_2O_3 (sonocatalyst), a conventional Pd/ Al_2O_3 prepared by an impregnation method and a commercial available Pd black were used as a catalyst. The rates of the hydrogenation were clearly different among the different catalysts. The initial rates over the Pd black, the conventional Pd/ Al_2O_3 , and the sonocatalysts prepared in methanol and in 1-propanol were 30, 96, 320, and 700 mmol/min · g-Pd, respectively. It is noted that the activity of the sonocatalysts were three to eight times higher than that of the conventionally prepared one. The reason was considered that the active site of Pd metal would exist only on the surface of the alumina and/or the size effect of the Pd particles.

The hydrogenation of trans-3-hexene, which have internal C-C double bond, also most readily proceeded over the sonocatalysts, but the rate for trans-3-hexene was considerably slow compared with that for 1-hexene. Since trans-3-hexene has a bulky group around the C-C double bond, namely because of the steric effect of the substrate, the rate for trans-3-hexene was slower than that for 1-hexene.

3.4 Catalytic activity of Au/Pd supported on SiO_2

Figure 3 shows the effect of various Au/Pd

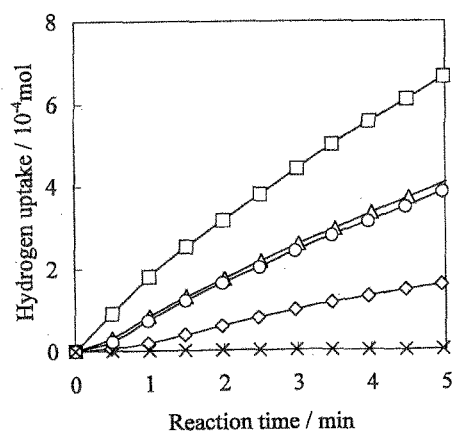


Figure 3. Effect of various Au/Pd composition on the catalytic hydrogenation of cyclohexene. (\times); Au, (Δ); Au: Pd=3:1, (\circ); Au: Pd=1:1, (\square); Au: Pd=1:3, (\diamond); Pd. Noble-metal supported silica (0.3mol%) was used for the catalytic reaction.

composition on the catalytic hydrogenation of cyclohexene. In comparison with the bimetallic catalysts, the monometallic Au and Pd supported on silica were also prepared by the same procedures, respectively. It was found that the rates of hydrogenation over the Au/Pd supported on silica exhibited higher activity rather than that over the monometallic Pd silica, while pure Au supported on silica had no activity. The catalytic activity considerably varied by changing the composition of Au/Pd and the composition at 75mol% of Pd content showed the highest activity. The high activity of the Au/Pd nanoparticles on silica might be attributed to an electrostatic effect¹⁷ between Au atom and Pd atom and/or a quantum size effect.¹⁸ It seems that the core-shell structure in the Au/Pd nanoparticles supported on silica play an important role in the catalytic activity as well as does the colloidal dispersion.

4. REFERENCES

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