Catalysis Letters Vol. 105, Nos. 1–2, November 2005 (© 2005)
DOI: 10.1007/s10562-005-8006-0

Preparation of polymer-stabilized palladium–silver bimetallic nanoparticles by γ-irradiation and their catalytic properties for hydrogenation of *cis,cis*-1,3-cyclooctadiene

Seong-Ho Choi[a],*, Seungho Lee[a], Sang-Jun Kim[a], Sang-Ho Sohn[b], Hee-Dong Kang[b], Yu-Ping Zhang[c], Kwang-Pill Lee[c], and Jong-Han Chun[d]

[a]*Department of Chemistry, Hannam University, 133 Ojung-Dong, Daeduck-Gu, Daejeon 306–791, South Korea*
[b]*Department of Physics, Kyungpook National University, Daegu 702–701, South Korea*
[c]*Department of Chemistry Graduate School, Kyungpook National University, Daegu 702–701, South Korea*
[d]*Department of Applied Chemistry, Hanbat National Univerisity, Daejeon 305–719, South Korea*

Received 2 April 2005; accepted 23 July 2005

Polyvinypyrrolidone (PVP)-stabilized Pd-Ag bimetallic colloids were successfully prepared in an acetone:2-propanol solution mixture of palladium acetate and silver perchlorate, and in an aqueous solution of palladium nitrate and silver nitrate by γ-irradiation. The prepared PVP-stabilized bimetallic nanoparticles were characterized by UV, TEM, XRD, and XPS. In Pd–Ag bimetallic nanoparticles, the XPS data indicated that the constituent elements were in the metallic state, and the palladium atoms were concentrated on the surface of the alloy cluster. These PVP-stabilized bimetallic nanoparticles were used as catalysts for hydrogenation of *cis,cis*-1,3-cyclooctadiene (COD).

KEY WORDS: γ-irradiation; precious bimetallic nanoparticles; Pd–Ag nanoparticles; polyvinylpyrrolidone; *cis,cis*-1,3-cyclooctadiene (COD); hydrogenation catalysts.

1. Introduction

Alloy nanoparticles [1–5] of various compositions were studied because of their catalytic properties, optical and nonlinear optical properties. They have been prepared by both chemical and physical methods.

From the catalytic point of view, bimetallic particles were studied in efforts to improve catalytic activity and also to create new properties which monometallic catalysis may not possess [6,7].

Many researchers prepared the monometallic and bimetallic nanoparticles in an aqueous solution in the presence of a stabilizer using chemical reducing agents, because most of the monometallic and bimetallic precursors, which are called salts, have good-enough solubility in aqueous solution [8,9].

In previous papers [10,11], the precious metallic nanoparticles were successfully prepared by γ -irradiation without chemical reducing agents. They were prepared using hydrated electrons induced by γ -irradiation in aqueous solution. However, less has been reported about the preparation of precious metallic nanoparticles in organic solvents by γ-irradiation, since the particle precursors show only a very low solubility in organic solvents and the hydrated electrons were not generated in organic solvents by γ-irradiation. Furthermore, little has been reported about the preparation of alloy nanoparticles by γ-irradiation in organic solvent and aqueous solution.

K. Meguro *et al.* [12] reported the preparation of gold nanoparticles in organic solvent by reduction of extracted chloroauric acid with hydrazine/formaldehyde/benzaldehyde. K. Esumi *et al.* [13] also reported the preparation of a platinum nanoparticles by thermal decomposition of platinum complex in organic solvent.

We report here about the preparation of PVP-stabilized Pd, Ag, and Pd–Ag nanoparticles by γ-irradiation in some organic solvents and in aqueous solution. The samples were characterized by UV spectroscopy, Transmission Electron Microscope (TEM), X-Ray Diffraction (XRD) and X-Ray Photoelectron Spectroscopy (XPS). The hydrogenation of *cis,cis*-1,3-COD over Pd–Ag nanoparticles was also examined.

2. Experimental

2.1. Materials

Palladium acetate [$(CH_3CO_2)_2Pd$], palladium nitrate [$PdNO_3$], silver perchlorate hydrate ($AgClO_4 \cdot xH_2O$), and *cis,cis*-1,3-cyclooctadiene (COD) were the analytical reagents supplied by Aldrich-Sigma Co.. Silver nitrate ($AgNO_3$) was purchased from Kojima Chemicals Co., Ltd. (Japan). The polyvinylpyrrolidone (PVP, MW. av. 40,000) colloidal stabilizer was obtained from Tokyo

---

* To whom correspondence should be addressed.
E-mail: shchoi@hannam.ac.kr

1011-372X/05/1100–0059/0

Kasi (Japan). The hydrogen source (99.9%) was supplied by Korea Standard Gas Co. (Korea). The other chemicals of reagent grade were also used without further purification.

2.2. *Preparation of PVP-stabilized Pd–Ag bimetallic nanoparticles by γ-irradiation in organic solvents*

A monometallic solution was prepared by dissolving analytically pure (CH_3CO_2)2Pd (224 mg, 1.0 mmol) and $AgClO_4 \cdot xH_2O$ (207 mg, 1.0 mmol) in acetone:2-propanol (1000 mL, 1/1 vol-%) in the presence of PVP as a colloidal stabilizer. The weight ratio (%) of the PVP-to-precursor was adjusted to 25. Secondly, the bimetallic solution was prepared from the above prepared monometallic solution. The monometallic solution was taken by pipette, respectively, and then the monometallic solution was added in reaction bottle. The concentration of the mixture solution was adjusted to 4.0×10^{-4} M. The solution was bubbled for 30 min using nitrogen gas in order to remove oxygen, and then was irradiated by γ-ray of Co-60 source under atmospheric pressure and ambient temperature. The total irradiation dose was 30 kGy (a dose rate $= 1.0 \times 10^4$ Gy/h). A homogeneous Pd–Ag colloid with a dark brown color was formed (designated PVP-stabilized Pd/Ag (1/1)).

2.3. *Preparation of PVP-stabilized Pd–Ag bimetallic nanoparticles by γ-irradiation in aqueous solution*

A monometallic ion solution was prepared by dissolving analytically pure PdNO3 (43.4 mg, 0.18 mmol) and AgNO3 (31.4 mg, 0.18 mmol) in pure water (200 mL) in the presence of PVP (8.68 mg) as a colloidal stabilizer. The weight ratio (%) of the precusior-to-PVP was adjusted to 25 because of precipitation of alloy nanoparticles. Secondly, the bimetallic solution was prepared from the above prepared monometallic solution. The concentration of the mixture solution was adjusted to 1.0×10^{-2} M. The solution was bubbled for 30 min by using nitrogen gas in order to remove oxygen, and then was irradiated by γ-ray of Co-60 source under atmospheric pressure and ambient temperature. The total irradiation dose was 30 kGy (a dose rate $= 1.0 \times 10^4$ Gy/h). The Pd, Pd–Ag, and Ag nanoparticles with a dark brown color were obtained as solid state.

2.4. *Hydrogenation of cis,cis-1,3-cyclooctadine*

Hydrogenation of *cis,cis*-1,3-COD was performed by using mono- and bimetallic nanoparticles prepared by γ-irradiation in organic solvent. The solvent was removed by a rotary evaporator to remove a acetone. The obtained solid nanoparticles were redispersed in MeOH. The mono- and bimetallic nanoparticles in MeOH were bubbled using hydrogen gas to remove oxygen. The catalyst (ca. 1.5×10^{-3} mmol, 40 mL) was activated under hydrogen atmosphere with magnetic stirring for 1 h at 30 °C. The *cis,cis*-1,3-COD compound was added into a reaction flask. Hydrogen gas flow was continued for the desired time. The solutions were filtered with a syringe filter with a 0.2 μm pore diameter, then analyzed by high-performed liquid chromatography (HPLC) with RI detector using C18 column (25×0.46 cm (i.d)).

2.5. *Measurements*

The absorption of the PVP-stabilized mono- and bimetallic colloids were recorded with a UV-240 Shimadzu UV–vis spectrophotometer using quartz cells. The PVP-stabilized mono- and bimetallic nanopowders were obtained by evaporation in organic solvent. While the PVP-stabilized mono- and bimetallic nanopowders prepared in aqueous solution were obtained by centrifuge. The XRD spectra of the solid powder samples were obtained from a X-ray diffractometer (Enraf Nonius, RA/FR 571). TEM photographs of the sample were obtained using a transmission electron microscope (TEM) (HITACHI, H-7100) or Carlzeiss (EM912 EF-TEM, Germany). The x-ray photoelectron spectra (XPS) of the sample were obtained using the ESCALab 220i (VG Scientific) equipped with a full 180° hemispherical electrostatic analyzer to examine the chemical state of the constituent elements.

3. Results and Discussion

3.1. *Preparation and characterization of PVP-stabilized Pd–Ag bimetallic colloids in organic solvents by γ-irradiation*

Various combinations of palladium acetate and silver perchlorate were irradiated by γ-ray of Co-60 source in a mixed solvent of acetone and 2-propanol (vol-% , 1/1) in the presence of PVP as a stabilizer. A homogeneous precious mono- and bimetallic colloid with a dark brown color was obtained after γ-irradiation.

Figure 1 shows the UV–vis spectra of the PVP-stabilized Pd/Ag colloids prepared by γ-irradiation in acetone:2-propanol mixture: **1**. Pd/Ag (100/0, mol-%), **2**. Pd/Ag (80/20, mol-%), **3**. Pd/Ag (60/40, mol-%), **4**. Pd/Ag (40/60, mol-%), **5**. Pd/Ag (20/80, mol-%), **6**. Pd/Ag (0/100, mol-%). In PVP-stabilized Ag colloids **(6)**, a characteristic surface plasma absorption peak appeared at 400 nm [14–16], while characteristic visible absorption peak did not appear in PVP-stabilized monometallic Pd colloids (**1**). In PVP-stabilized Pd/Ag colloids (**2, 3**, **4**, and **5**), the very broad absorption band of bimetallic nanoparticles appeared because of the broad size distribution of the nanoparticles.

In an acetone:methanol mixture, the acetone ketyl radials may be induced by γ-irradiation as following reactions.

$$(CH_3)_2CO \rightarrow (CH_3)_2C{\cdot}OH \qquad (1)$$

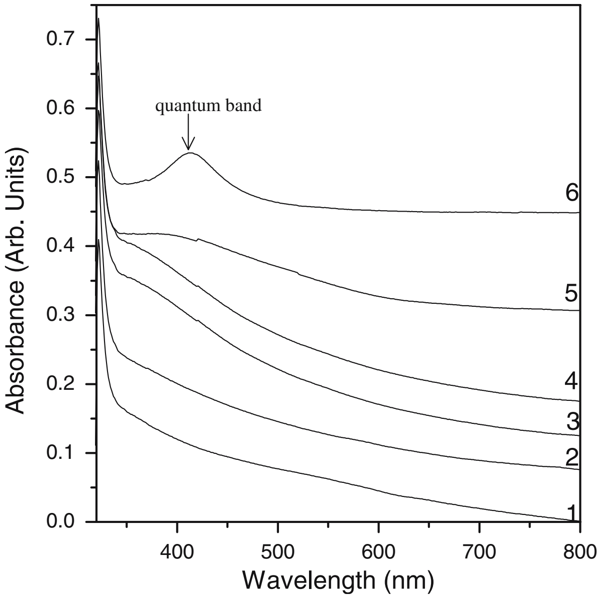

Figure 1. UV–vis spectra of the PVP-stabilized Pd/Ag colloids in acetone-2-propanol mixture. (1). Pd/Ag (100/0, mol-%), (2). Pd/Ag (80/20, mol-%), (3). Pd/Ag (60/40, mol-%), (4). Pd/Ag (40/60, mol-%), (5). Pd/Ag (20/80, mol-%), (6). Pd/Ag (0/100, mol-%).

The Ag^+ and Pd^{2+} ions are reduced by acetone ketyl radical induced by γ-irradiation as following reactions.

$$Ag^+ + (CH_3)_2C{\cdot}OH \rightarrow Ag^0 + (CH_3)_2CO + H^+ \quad (2)$$

$$Pd^{2+} + 2(CH_3)_2C{\cdot}OH \rightarrow Pd^0 + 2(CH_3)_2CO + 2H^+ \quad (3)$$

Thus, the formation of an acetone ketyl radical is very important to obtain precious metal particles. After γ-irradiation, the solution pH was determined to be ~ 2.7 indicating that H^+ ions were generated during γ-irradiation as shown in the above mechanisms (2) and (3). K. Eusmi *et al.* [17] reported about the preparation of colloidal silver–palladium alloys by UV-irradiation in mixture of acetone and 2-propanol. They also pointed out that the silver–palladium alloys were prepared by acetone ketyl radical induced by UV irradiation.

In order to obtain solid nanoparticles, the organic solvent was removed by a rotary evaporator. Subsequently, the nanoparticles as solid state were washed with MeOH to remove unreacted metallic ions. Figure 2 shows TEM images of the PVP-stabilized Pd/Ag nanoparticles: **1**. Pd/Ag (100/0, mol-%), **2**. Pd/Ag (80/20, mol-%), **3**. Pd/Ag (60/40, mol-%), **4**. Pd/Ag (40/60, mol-%), **5**. Pd/Ag (20/80, mol-%), **6**. Pd/Ag (0/100, mol-%). In **1** and **6** of figure 2, the Pd and Ag nanoparticles are showing a uniform distribution, but small particles have aggregated into secondary particles during solvent evaporation. The alloy nanoparticles with broad size distributions were obtained as shown in **2, 3, 4**, and **5** of figure 2. The size of alloy nanoparticles was increased by adding silver ions.

Figure 3 show the X-ray diffraction patterns of the PVP-stabilized Pd/Ag nanoparticles. The broken lines shows the different peak positions of Ag and Pd. The peaks for nanoparticles were broad because of the small sizes of the nanoparticles. This was previously reported by K. Esumi *et al.* [17]. They determined alloy nanoparticles from a different peak position of Ag and Pd by an XRD profile.

In order to investigate the composition of the nanoparticles, each of the alloy nanoparticles were characterized by XPS. Figure 4 shows an XPS survey scan spectra of the PVP-stabilized Pd/Ag nanoparticles. Regarding XPS studies of PVP-protected Pd colloids, the signals of the Pd nanoparticles were too weak to be exactly detected because of the coverage of protective polymer on the particle surface (**1** of figure 4). On the other hand, regarding the binding energy of the constituent elements ($Pd_{3d,5/2}$: 335.4 eV, $Ag_{3d,5/2}$: 367.9 eV) palladium and silver appeared to be in the mono- and bimetallic nanoparticles except for Pd nanoparticles. In **4** (40/60, Pd/Ag mol-%) of figure 4, the intensities of XPS peaks of Pd nanoparticles are higher than that of Ag nanoparticles. These results clearly indicate that the palladium was concentrated on the surface of the alloy cluster. These phenomena of concentrated Pd on the surface of palladium–silver bimetallic alloys are similar to the case of the concentrated palladium on palladium–gold bimetallic alloys, characterized using XPS by Liu *et al.* [9].

In aqueous solution, the prepared PVP-stabilized Pd/Ag bimetallic nanoparticles with a 25 weight ratio (%) of PVP-to-precursors were stable without any metal precipitate for months. The bimetallic nanoparticles in aqueous solution were difficult to analyze and to use for

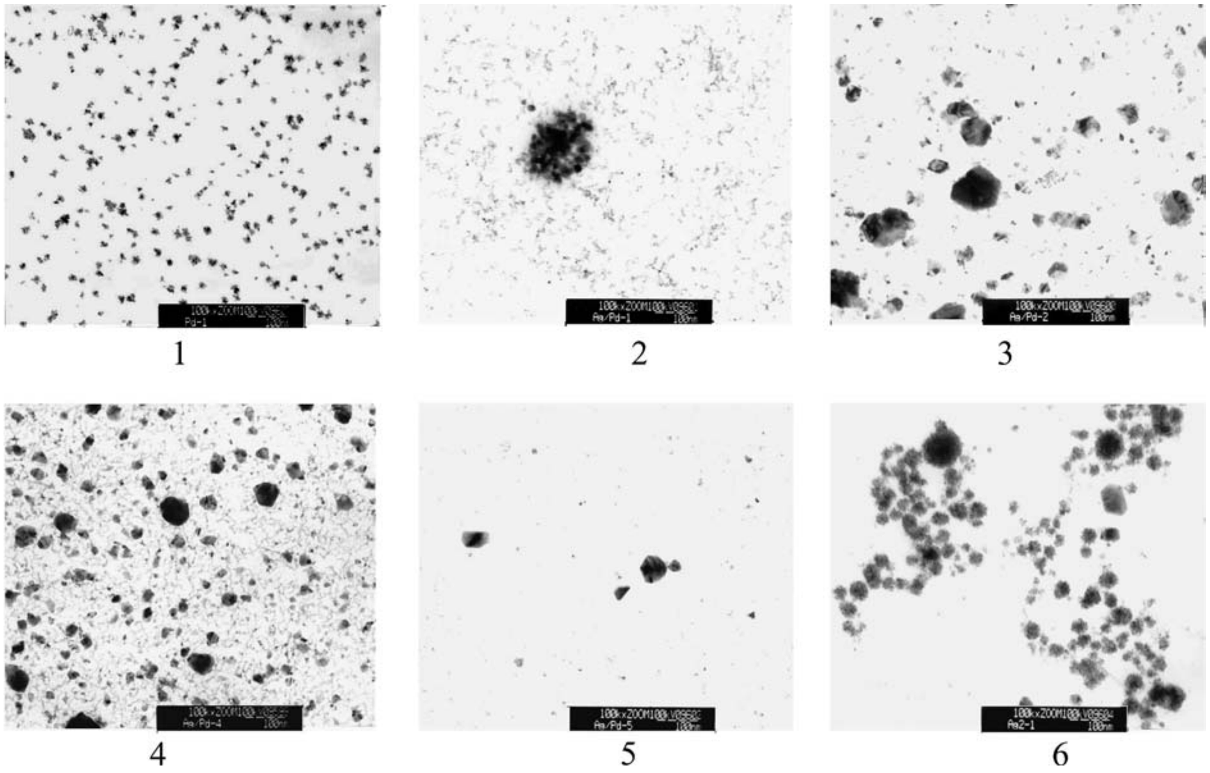

Figure 2. TEM photography of the PVP-stabilized Pd/Ag nanoparticles. (1). Pd/Ag (100/0, mol-%), (2). Pd/Ag (80/20, mol-%), (3). Pd/Ag (60/40, mol-%), (4). Pd/Ag (40/60, mol-%), (5). Pd/Ag (20/80, mol-%), (6). Pd/Ag (0/100, mol-%).

hydrogenation catalysts. In order to obtain bimetallic nanoparticles in solid state, the weight ratio (%) of PVP-to-precursors was adjusted to 1/25. The PVP-stabilized nanoparticles with a dark brown color were obtained in solid state.

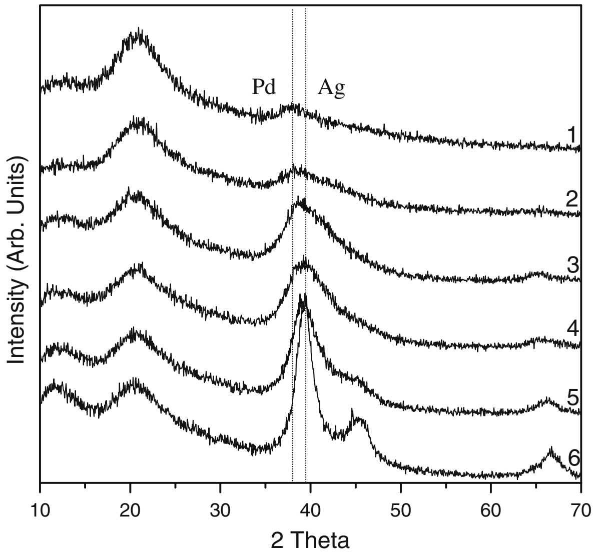

Figure 3. X-ray diffraction patterns of the PVP-stabilized Pd/Ag nanoparticles. (1). Pd/Ag (100/0, mol-%), (2). Pd/Ag (80/20, mol-%), (3). Pd/Ag (60/40, mol-%), (4). Pd/Ag (40/60, mol-%), (5). Pd/Ag (20/80, mol-%), (6). Pd/Ag (0/100, mol-%).

Figure 5 shows TEM images of PVP-stabilized mono- and bimetallic nanoparticles prepared by γ-irradiation in aqueous solutions. The Pd nanoparticles were uniformly distributed, but small particles had aggregated into secondary particles because the Pd nanoparticles were not protected by the PVP. The small bimetallic nanoparticles with uniform distribution were also aggregated as shown in **2, 3, 4**, and **5** of figure 5. The size distribution of bimetallic nanoparticles was relatively uniform, while the size of bimetallic nanoparticles was increased by adding silver ions. In the case of silver particles, size distribution was irregular, and the size of silver nanoparticle was larger than bimetallic nanoparticles. In a previous paper [10], in aqueous solution by using γ-irradiation, the PVP-stabilized silver nanoparticles with a 25 weight ratio (%) of PVP-to-precursors were uniformly distributed and below 20 nm size. This means that the ratio of PVP to precursors plays a very important role for the size, size distribution, morphology, and stability of nanoparticles.

3.2. *Hydrogenation of cis,cis-1,3-COD over PVP-stabilized Pd and Pd/Ag (50/50, mol-%) nanoparticles in methanol*

PVP-stabilized Pd/Ag (100/0, mol-%) and Pd/Ag (50/50, mol-%) nanoparticles prepared by γ-irradiation in organic solvents were tested for use as catalysts for hydrogenation of *cis,cis*-1,3-COD. Figure 6 shows the

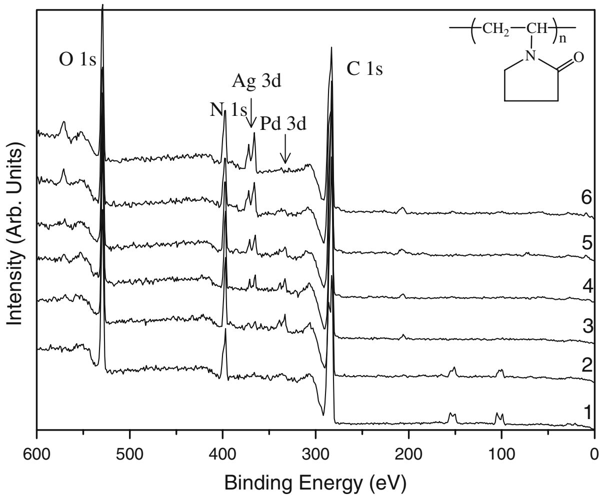

Figure 4. XPS survey scan spectra of the PVP-stabilized Pd/Ag nanoparticle. (1). Pd/Ag (100/0, mol-%), (2). Pd/Ag (80/20, mol-%), (3). Pd/Ag (60/40, mol-%), (4). Pd/Ag (40/60, mol-%), (5). Pd/Ag (20/80, mol-%), (6). Pd/Ag (0/100, mol-%).

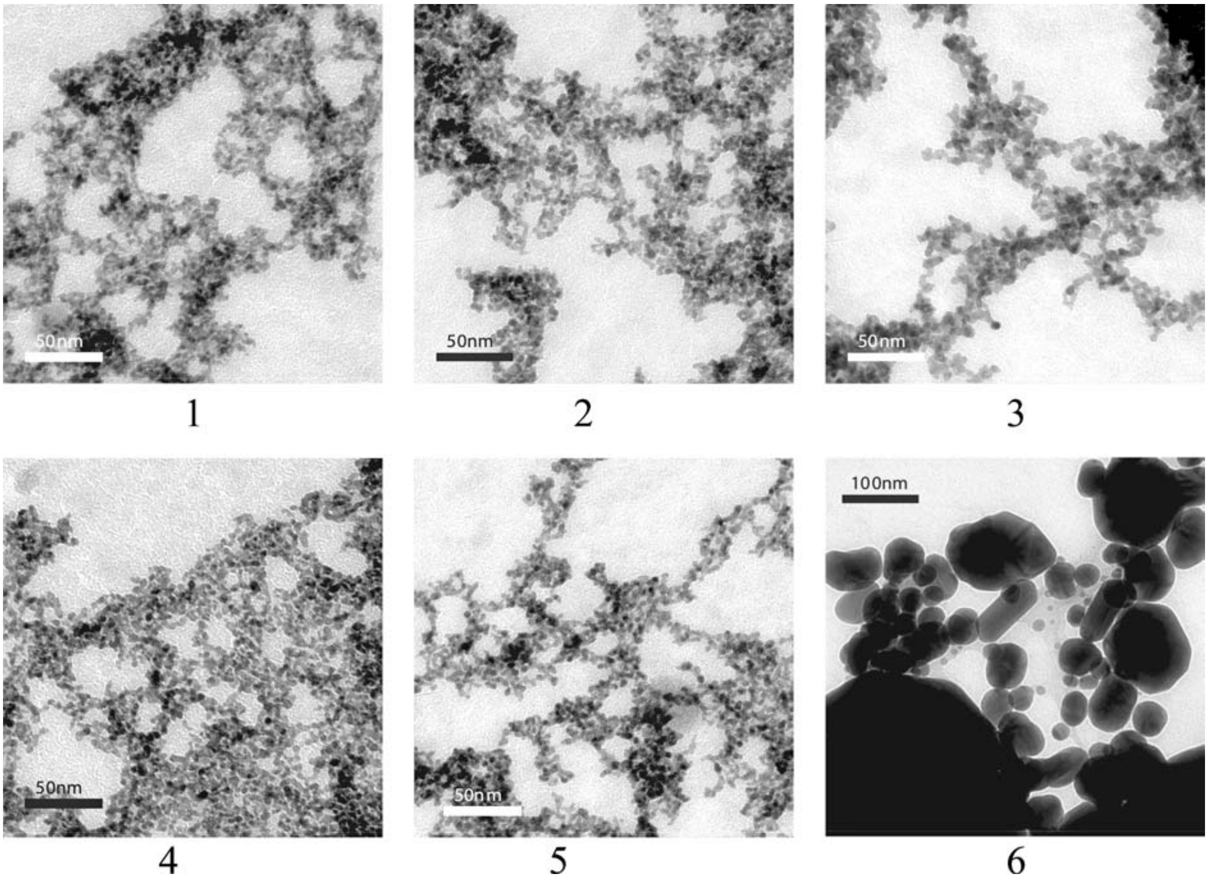

Figure 5. TEM images PVP-stabilized Pd/Ag nanoparticles prepared in aqueous solution. (1). Pd/Ag (100/0, mol-%), (2). Pd/Ag (80/20, mol-%), (3). Pd/Ag (60/40, mol-%), (4). Pd/Ag (40/60, mol-%), (5). Pd/Ag (20/80, mol-%), (6). Pd/Ag (0/100, mol-%).

chromatograms of *cis,cis*-1,3-COD during hydrogenation process in MeOH in the presence of Pd/Ag (100/0, mol-%) nanoparticles (a) and Pd/Ag (50/50, mol-%) nanoparticles (b), respectively. In figure 6(a), the resolution time of *cis,cis*-1,3-COD before hydrogenation appeared at 4.6 min. After 20 min, the resolution times of cyclooctadiene and cyclooctane over Pd nanoparticles were at 5.0 min and 5.8 min, respectively. After 40 min, the resolution time of cyclooctane was only shown at 5.8 min. From the results, cyclooctane was obtained

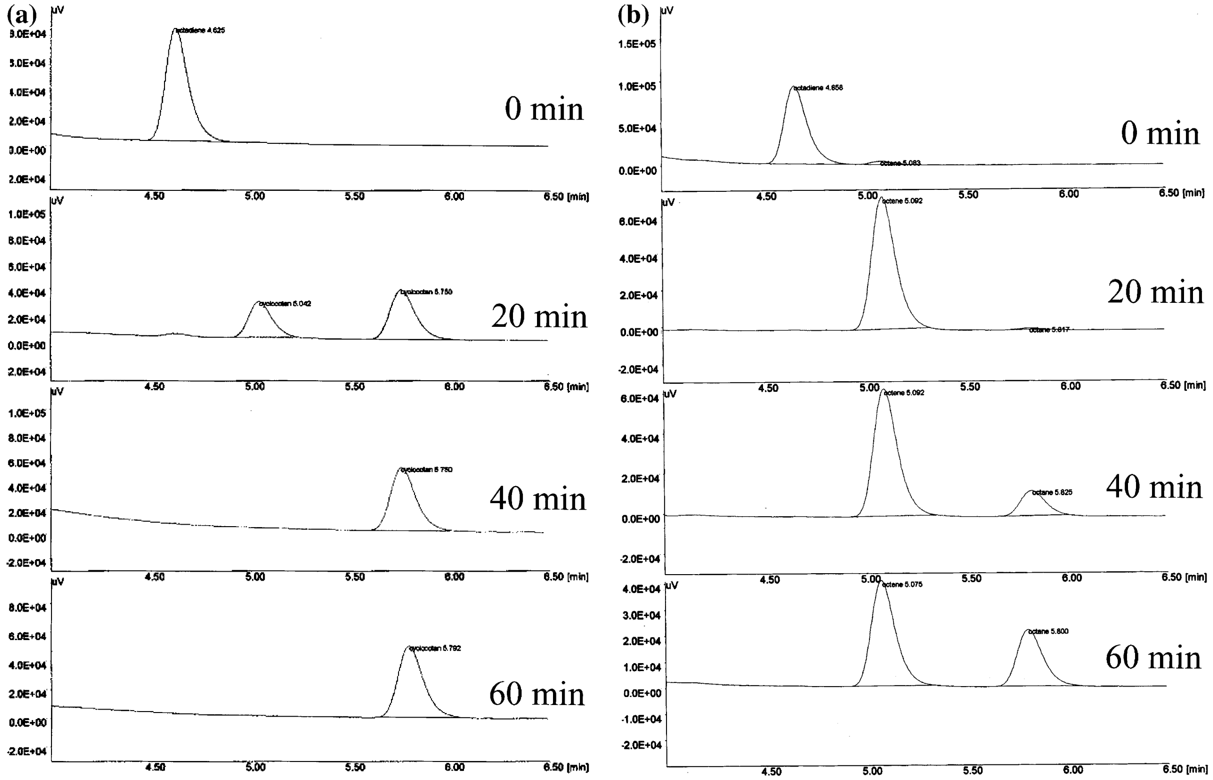

Figure 6. Chromatograms of hydrogenation process of *cis, cis*-1,3-COD over (100/0, mol-%) (a) Pd/Ag (50/50, mol-%) (b) in MeOH.

from *cis,cis*-1,3-COD over Pd nanoparticles as shown below:

In figure 6(b), the resolution time of *cis,cis*-1,3-COD before hydrogenation also appeared at 4.6 min. Cyclooctene was fully obtained after a hydrogenation time of 20 min. The area of cyclooctane peak was increased by increasing hydrogenation time. At 180 min, the *cis,cis*-1,3-COD was perfectly converted to cyclooctane over Pd/Ag (50/50, mol-%) prepared by γ-irradiation in organic solvents.

Table I summarizes the hydrogenation results of *cis,cis*-1,3-COD over mono- and bimetallic nanoparticles in MeOH for 20 and 60 min. The *cis,cis*-1,3-COD was converted to cyclooctane over PVP-stabilized Pd/Ag (100/0, mol-%) nanoparticles for 60 min, while *cis,cis*-1,3-COD did not proceed to cyclooctane over PVP-stabilized Pd/Ag (0/100, mol-%) nanoparticles in MeOH for 60 min.

Conclusions

1. PVP-stabilized mono- and bimetallic nanoparticles were successfully prepared by γ-irradiation in organic solvents and in aqueous solution.
2. PVP-stabilized mono- and bimetallic Pd/Ag nanoparticles were characterized by UV, TEM, XRD, and XPS. The TEM, XRD and XPS data elucidated the

Table 1

Hydrogenation of *cis,cis*-1,3-COD over PVP-Stabilized Mono- and bimetallic nanoparticles in MeOH[a]

Catalyst	Selectivity (%) for 20 min			Selectivity (%) for 60 min		
	cis,cis-1,3-COD	Cyclooctene	Cyclooctane	*cis,cis*-1,3-COD	Cyclooctane	Cyclooctane
PVP–Pd/Ag(100/0)	0	38.5	61.5	0	0	100
PVP–Pd/Ag(80/20)	0	85	15.0	0	1.8	98.2
PVP–Pd/Ag(60/40)	0	93.8	6.2	0	35.0	65.0
PVP–Pd/Ag(50/50)	0	98.0	2.0	0	57.1	42.9
PVP–Pd/Ag(40/60)	7.5	92.5	0	27.2	38.6	34.2
PVP–Pd/Ag(20/80)	61.5	38.5	0	68.5	22.9	8.6
PVP–Pd/Ag(0/100)	98.6	1.4	0	96.0	4.0	0

[a] Hydrogenation condition: Concentration of *cis,cis*-1,3-COD $= 1.5\times10^{-3}$ M; Total volume = 40 mL; Reaction temperature = 30 °C; Amount of $H_2 = 0.15$ L/min in flow-cell; Concentration of mono- and bimetallic nanoparticles $= 1.5\times101^{-3}$ M (calculated by precious metal ions). Selectivity (%) was calculated by HPLC with RI deterctor.

formation of PVP-stabilized bimetallic nanoparticles. XPS data indicated that the constituent elements were in the metallic state and that palladium atoms were concentrated on the surface of the alloy cluster.

3. These PVP-stabilized mono- and bimetallic nanoparticles were used for hydrogenation catalysts of *cis,cis*-1,3-cyclooctadiene.

Acknowledgments

This work was supported by the Ministry of Commerce, Industry and Energy (MOCIE) through the Advanced Material Research Center for Better Environment at Hanbat National University.

References

[1] M. Liu, W. Yu, H. Liu and J. Zheng, J. Colloid Interf. Sci. 214 (1999) 213.
[2] M.P. Mallin and C.J. Murphy, Nano Lett. 2 (2002) 235.
[3] Y.-M. Chung and H.-K. Rhee, Catal. Lett. 85 (2003) 59.
[4] S. Takenaka, Y. Shigeta, E. Tanabe and K. Otsuka, J. Catal. 220 (2003) 468.
[5] Y.-C. Liu, X.-P. Qiu, Y.-Q. Huang and W.-T. Zhu, J. Power Sources 111 (2002) 160.
[6] M.S. Löffler, H. Natter, R. Hempelmann and K. Wippermann, Electrochim. Acta 48 (2003) 3047.
[7] Y. Takasu, T. Kawaguchi, W. Sugimoto and Y. Murakami, Electrochim. Acta 48 (2003) 3861.
[8] W. Yu, M. Liu, H. Liu and J. Zhen, J. Colloid Interf. Sci. 210 (1999) 218.
[9] H. Liu, G. Mao and S. Meng, J. Mol. Catal. 74 (1992) 275.
[10] S.-H. Choi, S.H. Lee, Y.M. Hwang, K.P. Lee and H.D. Kang, Radiat. Phys. Chem. 67 (2003) 517.
[11] S.-H. Choi, K.-P. Lee and S.-B. Park, Stud. Surf. Sci. and Catal. 146 (2003) 93.
[12] K. Meguro, T. Tano, K. Torigoe, H. Nakamura and K. Esumi, Colloid. Surfaces 34 (1988) 381.
[13] K. Esumi, O. Sadakane, K. Torigoe and K. Meguro, Colloid. Surfaces 62 (1992) 255.
[14] G. Suyal, Thin Solid Films 426 (2003) 53.
[15] F.H. Scholes, S.A. Furman, D. Lau, C.J. Rossouw and T.J. Davis, J. Non-Crystalline Solids 347(1–3) (2004) 93.
[16] A.M. Whelan, M.E. Brennan, W.J. Blau and J.M. Kelly, J. Nanosci. Nanotech. 4(1/2) (2004) 66.
[17] K. Esumi, M. Wakabayashi and K. Torigoe, Colloid. Surfaces 109 (1996) 55.