

CHARACTERIZATION OF NOBLE METAL ALLOY NANOPARTICLES PREPARED BY ULTRASOUND IRRADIATION

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Abstract. Solutions containing $\text{Au}^{3+}/\text{Pd}^{2+}$ and $\text{Au}^{3+}/\text{Pt}^{4+}$ ions were reduced in the presence of surfactants (SDS or PEG-MS) by ultrasound irradiation (200kHz, 4.2W/cm²). The obtained colloidal bimetallic nanoparticles of Au/Pd or Au/Pt were examined by UV-vis spectra, XRD, TEM, HRTEM, EDX, hydrogenation catalysis measurements and ¹⁹⁷Au Mössbauer spectroscopy. It was found that the prepared nanoparticles exhibited different morphologies with changing the irradiation parameters and the surfactants. The ¹⁹⁷Au Mössbauer spectroscopy clearly indicated that electronic structures of Au atoms of the core-shell structured nanoparticles are different from the bulk materials.

1. INTRODUCTION

It has been proposed that making less in size of materials to nano-order brings out peculiar properties which have not been observed in the bulk materials [1]. A variety of preparation methods of nanoparticles have been developed, such as the reduction by chemical reductants [2, 3], photochemical or radiation chemical reduction [4, 5] and/or gas evaporation [6, 7]. Sonochemistry is a novel technique to prepare nanoparticles more easily than those methods and to control the particle sizes or structures by adjusting parameters [8-13].

In this study, Au^{3+} and Pd^{2+} or Au^{3+} and Pt^{4+} ions were simultaneously reduced by ultrasonic irradiation in the presence of additives of either sodium dodecyl sulfate (SDS) or polyethylene glycol monostearate (PEG-MS). The additives were used to increase amounts of reducing radicals to accelerate the reaction. Prepared binary Au/Pd or Au/Pt nanoparticles were characterized by various methods, and hydrogenation catalytic activities of the prepared nanoparticles were also investigated.

2. EXPERIMENTAL

A multiwave ultrasonic generator with a barium titanate oscillator of 64 mm diameter was used for sonication at 200 kHz with an input power of 4.2 W/cm². Aqueous solutions with a given concentration of noble metal complex ($\text{NaAuCl}_4 \cdot 2\text{H}_2\text{O}$ / $\text{PdCl}_2 \cdot 2\text{NaCl} \cdot 3\text{H}_2\text{O}$ or $\text{NaAuCl}_4 \cdot 2\text{H}_2\text{O}$ / $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$) with an additive of either SDS or PEG-MS were argon purged and sealed in glass vessels. They were sonicated in a water bath kept at about 20 °C, and the reactions were traced by using UV-vis spectra. The colloidal products were examined by X-ray diffraction (XRD), transmission electron microscopy (TEM), high resolution transmission electron microscopy (HRTEM), energy dispersive X-ray spectroscopy (EDX) and ¹⁹⁷Au Mössbauer spectroscopy. The Mössbauer measurements were performed at about 8K. For comparison, Au_3Pd , AuPd and AuPd_3 alloys were also examined. Hydrogenation catalysis measurements were performed using 4-pentenoic acid for prepared colloidal nanoparticles and commercial Pd black.

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Table 1. Summary on sample preparation conditions.

	(a)	(b)	(c)	(d)	(e)	(f)	(g)	(h)	(i)
Au ³⁺	0.5mM	—	1.0mM	0.5mM	0.5mM	0.25mM	0.5mM	0.25mM	0.25mM
Pd ²⁺	—	0.5mM	1.0mM	0.5mM	0.5mM	0.25mM	0.5mM	—	—
Pt ⁴⁺	—	—	—	—	—	—	—	0.25mM	0.25mM
SDS	8 mM	8 mM	8 mM	8 mM	12 mM	12 mM	—	8 mM	—
PEG-MS	—	—	—	—	—	—	0.4mM	—	0.4mM
Irradiation time	15min	20min	38min	20min	21min	12min	10min	60min	160min

3. RESULTS AND DISCUSSION

Materials. Table 1 summarizes the sample preparation conditions of the present study. The precursor for Au³⁺, Pd²⁺ and Pt⁴⁺ ions are NaAuCl₄·2H₂O, PdCl₂·2NaCl·3H₂O, and H₂PtCl₆·6H₂O, respectively. The concentrations of SDS of 8 mM and PEG-MS of 0.4 mM are corresponding to the critical micelle concentration, respectively. The irradiation times indicate the period required for complete reduction of the system, in other words, all the Au³⁺, Pd²⁺ and Pt⁴⁺ ions were consumed, respectively.

Sonochemical preparation of Au/Pd and Au/Pt nanoparticles. (1) Au/Pd. The color of the aqueous solutions containing Au³⁺, Pd²⁺ and surfactants (SDS or PEG-MS) was pale yellow (the color typical for Au³⁺- and Pd²⁺-containing solutions). With ultrasound irradiation, the color changed to reddish-violet indicating the formation of Au nanoparticles and finally into dark brown originated from Pd nanoparticles [12, 14]. In response to the change in the solution color, the UV-vis absorption spectra also changed: The absorption of Au³⁺ and Pd²⁺ ions (around 313 nm) before sonication faded away, running into the appearance of the surface plasmon absorption of Au nanoparticles (about 530 nm) and followed by that of Pd nanoparticles to cover the Au peak. The UV-vis spectrum change indicates that the reduction reaction is successive; Au³⁺ ions are reduced at first, and then Pd²⁺ ions begin to be reduced after consumption of Au³⁺ ions, suggesting formation of a core-shell structure with Au core and Pd shell. The above considerations are applied to both Au/Pd nanoparticles prepared using SDS (hereafter Au/Pd/SDS) and PEG-MS (hereafter Au/Pd/PEG-MS), and marked differences between them were not found in the absorbance spectroscopy.

(2) Au/Pt. When using SDS, the surface plasmon absorption of Au nanoparticles (about 530 nm) appeared shortly after the beginning of the sonica-

tion. Consecutively the surface plasmon absorption of Pt nanoparticles emerged, and that of Au nanoparticles was remained for the last time. The spectrum change indicates that Au³⁺ ions are reduced at first, and then Pt⁴⁺ ions are reduced to Pt²⁺. Because of overlapping of the surface plasmon absorption of Au and Pt, Au and Pt nanoparticles may coexist individually. Antithetically, in case of PEG-MS, although the above gradual reaction was observed partly, the surface plasmon absorption of Au finally disappeared, suggesting formation of an intermingle structure of Au and Pt.

Structures and ¹⁹⁷Au Mössbauer spectroscopy of Au/Pd and Au/Pt nanoparticles. The XRD results of Au/Pd/SDS suggested formation of a core-shell structure [15]. On the other hand, all Au/Pd/PEG-MS nanoparticles were found to show random alloy structures, indicating that Au and Pd exhibit different interactions in this reaction system.

TEM and HRTEM micrographs of Au/Pd/SDS nanoparticles are shown in Figs. 1a and 1b, respectively. The nanoparticles are spherical and monodispersed. They were confirmed to be a core-shell structure with Au-core and Pd-shell by EDX analyses. The widths of the Au-core and the Pd-shell measured by HRTEM were in good agreement with calculated values using the Au and Pd atom ratios. The average particle sizes were varied from 7.0±1.2 nm to 11.7±2.3 nm by changing the sample preparation conditions; the sizes were decreased with increasing SDS concentrations or decreasing initial noble metal concentrations. The former effect was considered to be protection effect of SDS. In addition, all the nanoparticles exhibited the identical core-shell structure.

Figs. 1c and 1d demonstrates TEM and HRTEM micrographs of Au/Pd/PEG-MS, respectively. The size distributions are relatively broad comparing with Au/Pd/SDS, and their mean particle diameters pre-

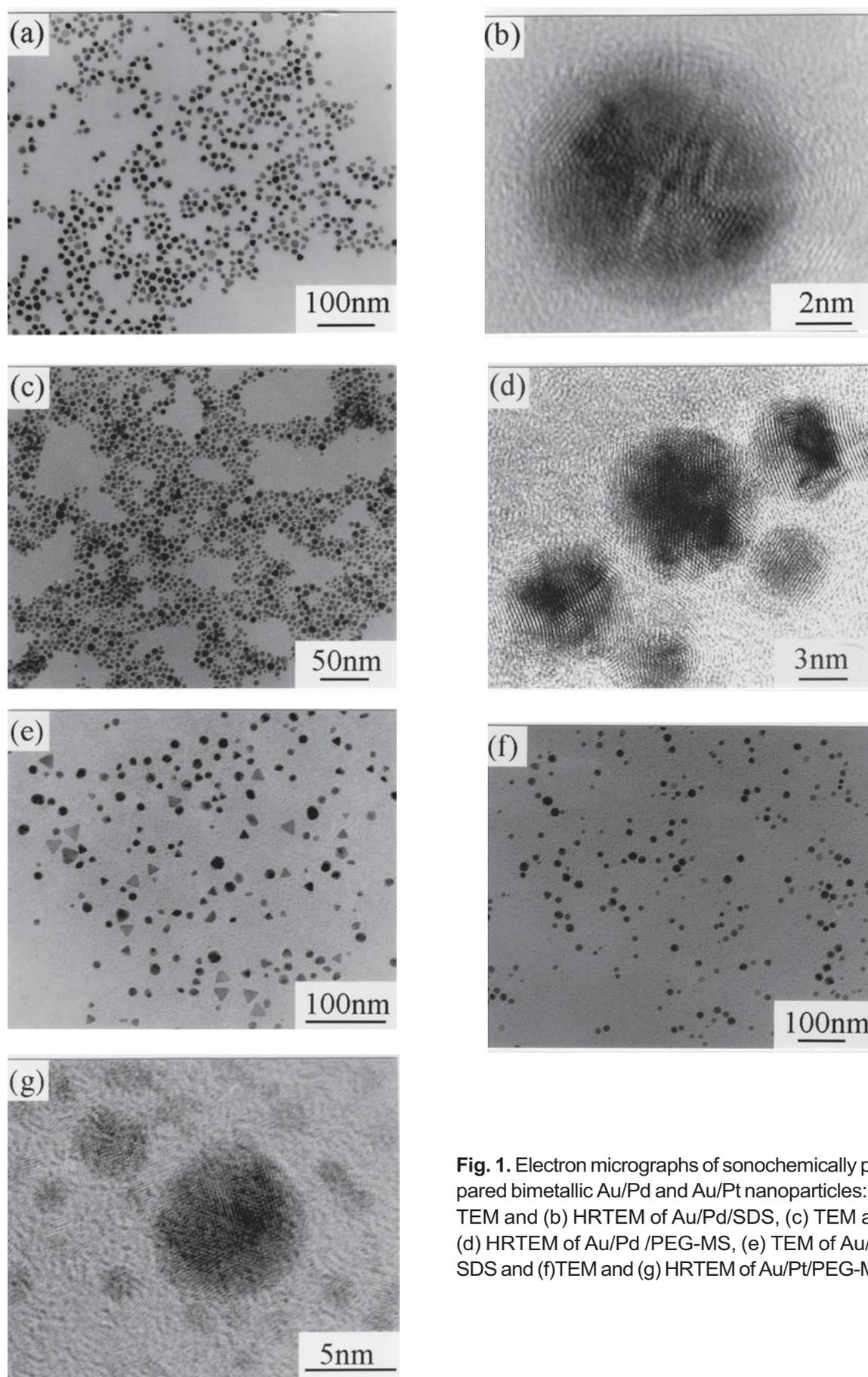


Fig. 1. Electron micrographs of sonochemically prepared bimetallic Au/Pd and Au/Pt nanoparticles: (a) TEM and (b) HRTEM of Au/Pd/SDS, (c) TEM and (d) HRTEM of Au/Pd /PEG-MS, (e) TEM of Au/Pt/SDS and (f)TEM and (g) HRTEM of Au/Pt/PEG-MS.

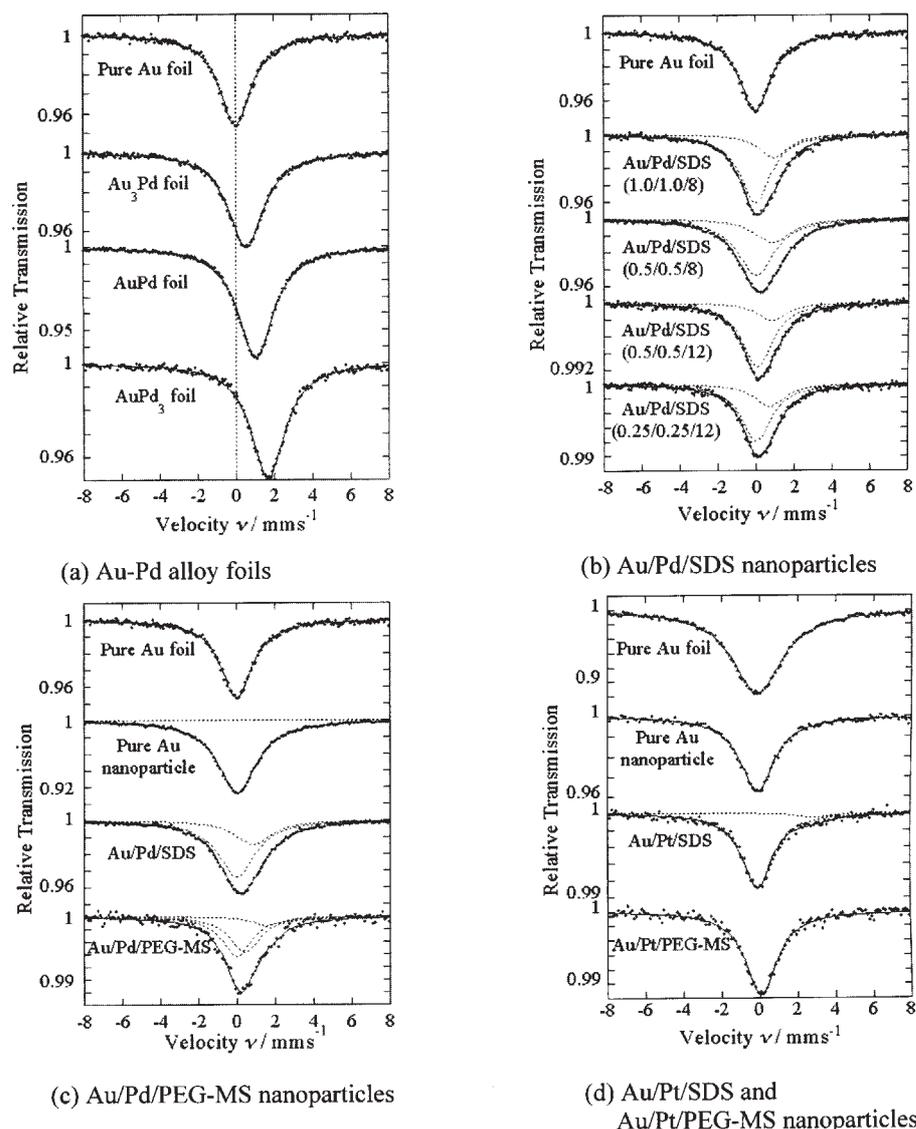


Fig. 2. Results of ^{197}Au Mössbauer measurements; (a) Au/Pd alloy foils, (b) size-different Au/Pd/SDS nanoparticles, (c) Au/Pd/PEG-MS nanoparticles and (d) Au/Pt/SDS and Au/Pt/PEG-MS nanoparticles.

pared by the same concentrations ratios of Au^{3+} and Pd^{2+} ions are smaller than those of Au/Pd/SDS. EDX analyses indicate the particles are mixtures of a core-shell structure with Au-core and Pd-shell and random alloys.

In the XRD spectra of Au/Pt/SDS, broad Au peaks were observed, but no Pt diffraction peaks. Taking the UV-vis spectroscopy into consideration, it was thought that the Au/Pt/SDS nanoparticles were not an Au/Pt random alloy structure, but Au and Pt nanoparticles coexisted individually. The XRD spectra of Au/Pt/PEG-MS exhibited Au diffraction peaks in a wide reflection angle range, and a small number of Pt diffraction peaks. Because the obtained

Au peaks corresponded to pure Au diffraction positions, it was considered that the Au/Pt/PEG-MS nanoparticles were not complete random alloys. Fig. 1e shows a TEM micrograph of Au/Pt/SDS. In addition to particles with the size of about 10 nm, smaller particles than 1 nm are seen. It was confirmed from EDX analyses that the large and small particles were Au and Pt nanoparticles, respectively. TEM and HRTEM micrographs of Au/Pt/PEG-MS are shown in Figs. 1f and 1g, respectively. There are two kinds of particles with the sizes of about 1 nm and about 6.5 nm similar to Au/Pt/SDS. The selected area diffraction of the larger particles included not only Au diffraction lined but also a portion of Pt

diffraction lines. The EDX measurements showed that the particles had a core-shell like structure composed of Au-core and Pt-shell, in which the Pt content of edge region is higher than that of center. The smaller particles were confirmed to be Pt nanoparticles.

Fig. 2a shows the ^{197}Au Mössbauer spectra of Au-Pd alloy foils. The absorption peaks shift to the positive velocity side as the Pd concentration increases. The Mössbauer spectra of the core-shell structured Au/Pd/SDS with different particle sizes are shown in Fig. 2b. It is found that a subcomponent with a positive isomer shift appears in the alloy spectra. The Mössbauer spectra are considered to reflect the core-shell structure of the Au/Pd/SDS nanoparticles as seen by HRTEM. Therefore the positive isomer shift of Fig. 2b may be concluded to associate with the Au atoms near the core-shell interfaces. Table 2 summarizes the Mössbauer data of Au/Pd foils and nanoparticles. Provided that only Au atoms of one interface layer of the core-shell structure are affected by Pd atoms, the area ratio is calculated to be about 10 and a few %. However, the observed ratios (about 20~30%) were considerably larger than the calculated value. Hence it was considered that several layers of Au atoms of the interfaces interact with Pd atoms between Au-core and Pd-shell. At the bottom of Fig. 2c, the Mössbauer spectrum of Au/Pd/PEG-MS is shown compared to that prepared with SDS. This spectrum contains not only a pair of a pure Au component and a subcomponent with a positive isomer shift as well as Au/Pd/SDS but also a tertiary component which considerably shifts to a positive velocity side. In light of EDX analyses, it is consid-

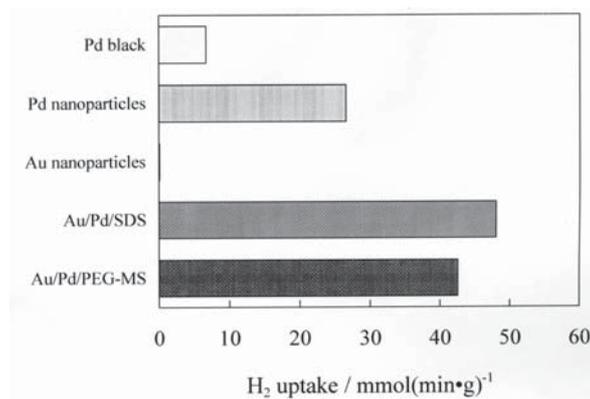


Fig. 3. Hydrogenation catalytic activity of 4-pentenoic acid over Au-Pd nanoparticles prepared with SDS and PEG-MS, Au and Pd nanoparticles and commercially available Pd black.

ered that the 0-velocity component corresponds to Au atoms in the Au-core and the subcomponent to Au atoms near the core-shell interfaces of the Au/Pd nanoparticles, and the tertiary component to Au atoms within Au/Pd alloy nanoparticles.

The Mössbauer spectra of Au/Pt/SDS and Au/Pt/PEG-MS nanoparticles are shown in Fig. 2d. It is observed that the spectrum of Au/Pt/SDS nanoparticles contains a pure Au component and a subcomponent with a positive isomer shift. The subcomponent was considered to be related to Au atoms sitting at the surface, as the case of Au/Pd. Regarding a positive isomer shift of Au/Pt/PEG-MS, further detailed discussion is difficult at moment.

Hydrogenation catalytic activity of Au-Pd nanoparticles. Fig. 3 shows the hydrogenation catalytic

Table 2. Summarized results of ^{197}Au Mössbauer spectroscopy for the AuPd foils and the Au/Pd nanoparticles.

	Composition	Isomer shift / mms ⁻¹	Area ratio / %
Spectra of AuPd foil	3 : 1	0.539	—
	1 : 1	1.037	—
	1 : 3	1.659	—
<i>Subspectra of nanoparticles</i>			
Au ³⁺ /Pd ²⁺ /Surfactant(mM)	1.0/1.0/8 SDS	1.059	23.6
	0.5/0.5/8 SDS	0.861	30.0
	0.5/0.5/12 SDS	0.839	21.9
	0.25/0.25/12 SDS	0.709	28.2
	0.5/0.5/0.4 PEG-MS	0.421	42.6
		1.597	10.8
Au ³⁺ /Pt ⁴⁺ /Surfactant(mM)	0.25/0.25/8 SDS	3.008	5.88
	0.25/0.25/0.4 PEG-MS	0.179	—

Table 3. Summarized data of binary Au/Pd and Au/Pt nanoparticles prepared by ultrasonic irradiation.

	Surfactant	Structure	Mean diameter
Au ³⁺ /Pd ²⁺ 0.5/0.5mM	SDS 8 mM	core-shell	10.2±1.5 nm
	PEG-MS 0.4 mM	core-shell + random alloy	4.9±1.4 nm
Au ³⁺ /Pt ⁴⁺ 0.25/0.25 mM	SDS 8 mM	monometallic mixture	Au 10.5±2.6 nm, Pt off the register
	PEG-MS 0.4 mM	core-shell like	6.5±1.5 nm

activities of sonochemically prepared Au/Pd/SDS and Au/Pd/PEG-MS nanoparticles, Au, Pd nanoparticles and commercial Pd black. High catalytic activity of Pd nanoparticles is clearly seen as compared to Pd black. This is due to the effect of particles sizes. On the other hand no catalytic activity is found in Au nanoparticles, indicating that Pd functions as catalysis in the present reaction system. It is remarkable that Au/Pd/SDS exhibits superior catalytic activity to Au/Pd/PEG-MS, though the latter is smaller than the former. Recalling that Au/Pd/PEG-MS nanoparticles have not the entire core-shell structure, it is concluded that the core-shell structure hold the key of high catalytic activity.

4. CONCLUSIONS

We have obtained binary Au/Pd and Au/Pt nanoparticles by sonochemical reduction of aqueous solutions containing noble metal complexes and surfactants. In Table 3 is shown the summarized data of the structures of nanoparticles. The particle sizes were reduced by increasing SDS concentrations or decreasing initial noble metal concentrations.

The hydrogenation catalysis measurement showed that complete core-shell structured Au/Pd/SDS nanoparticles exhibited the best hydrogenation catalysis activity among materials examined. It was found that the catalytic activities of Au/Pd/SDS and Au/Pd/PEG-MS nanoparticles are associated with the electronic factor of Au and Pd rather than the size or surface effect factor. The ¹⁹⁷Au Mössbauer spectra of core-shell Au/Pd nanoparticles exhibited a subcomponent with positive isomer shifts, which were considered to be associated with Au atoms at the core-shell interfaces.

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REFERENCES

- [1] R. Kubo // *J. Phys. Soc. Japan* **17** (1962) 975.
- [2] L. Zeiri and S. Efrima // *J. Phys. Chem.* **96** (1992) 5908.
- [3] R. Seshadri G.N. Sabbanna, G.U. Kulkarni, G. Ananthakrishna and C.N. Rao // *J. Phys. Chem.* **99** (1995) 5639.
- [4] D. Lawless, S. Kapoor, P. Kennepohl, D. Meisel and N. Serponr // *J. Phys. Chem.* **98** (1994) 9619.
- [5] N. L. Pocard, D. C. Alsmeyer, R. L. McCreery, T. X. Neeman and M. R. Callstorm // *J. Am. Chem. Soc.* **114** (1992) 769.
- [6] N. Satoh and K. Kimura // *Bull. Chem. Soc. Jpn.* **62** (1989) 1758.
- [7] R. P. Andres R.S. Averback, W.L. Brown, L.E. Brus, W.A. Goddard, A. Kaldor, S.G. Louie, M. Moscovits, P.S. Peercy, S.J. Riley, R.W. Siegel, F. Spaepen and Y. Wang // *J. Mater. Res.* **4** (1989) 704.
- [8] E. B. Flint and K. S. Suslick // *Science* **253** (1991) 1397.
- [9] D. Peters // *J. Mater. Chem.* **6** (1996) 1605.

- [10] G. J. Price, *Current Trends in Sonochemistry* (The Royal Society of Chemistry, Cambridge, 1992).
- [11] T. J. Mason and J. P. Lorimer, *Sonochemistry: Theory, Applications and Uses of Ultrasound in Chemistry* (Ellis Horwood, Chichester, 1988).
- [12] K. Okitsu, H. Bandow, Y. Maeda and Y. Nagata // *Chem. Mater.* **8** (1996) 315.
- [13] K. Okitsu, S. Nagaoka, S. Tanabe, H. Matsumoto, Y. Mizukoshi and Y. Nagata // *Chem. Lett.* **13** (1999) 271.
- [14] Y. Nagata, Y. Mizukoshi, K. Okitsu and Y. Maeda // *Radiat. Res.* **146** (1996) 333.
- [15] A. Mealand, T. B. Flanagan // *J. Phys. Chem.* **69** (1965) 3575.