Preparation of Silica-Coated Rhodium Nanoparticles Using Water-in-Oil Microemulsion

Masahiro Kishida, Teruoki Tago, Takatoshi Hatsuta, and Katsuhiko Wakabayashi
Chemical Engineering Group, Department of Materials Process Engineering, Graduate School of Engineering,
Kyushu University, 6-10-1 Hakozaki, Higashi-ku, Fukuoka 812-8581

(Received April 10, 2000; CL-000329)

Monodispersed silica-coated rhodium nanoparticles were synthesized by using the w/o microemulsion of polyoxyethylene (15) cetyl ether / cyclohexane / water system. By hydrolysis of tetraethyl orthosilicate in the presence of rhodium complex nanoparticles followed by thermal treatment, the silica-coated metallic rhodium nanoparticles were obtained in the microemulsion. In the composite nanoparticles, a metallic rhodium particle with a diameter of 4 nm was located nearly at the center of a spherical silica particle. The thickness of silica layer was 14 nm.

Nanometer-sized particles have a potential for new materials with novel properties. The synthesis of monodispersed nanoparticles of homogeneous structure has been widely studied by many researchers. However, it has become more important to synthesize nanoparticles having heterogeneous structure in order to improve physical and/or chemical properties of the homogeneous nanoparticles. One way of preparing the heteogeneous nanoparticle is coating, and the coating of the nanoparticle with silica has received a considerable attention in the field of sol–gel chemistry.

In fact, some groups reported the preparation for silica-coated nanoparticles of metal,[1–6] metal oxide,[7–9] and metal compound.[10] However, the coating procedure has still been complicated since the procedure always needed the pretreatment of nanoparticle surface with some reagents to promote silica growth on the nanoparticle surface. For example, gold nanoparticles were pretreated with 3-aminopropyltrimethoxysilane, prior to silica-coating.

It is desirable in view of industrial technology to coat the nanoparticles by a more convenient method. In this work, we demonstrate a simple method by which monodispersed silica-coated rhodium nanoparticles can be prepared using a water-in-oil (w/o) microemulsion of polyoxyethylene (15) cetyl ether / cyclohexane / water.

Silica-coated rhodium nanoparticles were prepared through a three-step procedure (coating was one step): 1) synthesis of nanoparticles of rhodium–hydrazine complex, 2) coating of rhodium–hydrazine complex nanoparticles with silica, 3) conversion of rhodium–hydrazine complex nanoparticles to metallic rhodium ones. In this procedure, no pretreatment of rhodium–hydrazine nanoparticles was conducted before the silica-coating.

The yellow nanoparticles of rhodium–hydrazine complex were synthesized by injecting hydrazine hydrate ($N_2H_4/RhCl_3$ = 3) directly into a w/o microemulsion consisting of an aqueous $RhCl_3 \cdot 3H_2O$ solution of 0.38 mol/dm^3 and an organic surfactant solution of 0.50 mol/dm^3 (water-to-surfactant molar ratio, W, was 3). The surfactants were polyoxyethylene (15) cetyl ether (C-15), polyoxyethylene (23) lauryl ether (L-23), polyoxyethylene (5) *p*-nonylphenyl ether (NP-5) and sodium bis(2-ethylhexyl) sulfosuccinate (AOT). Cyclohexane was used as an organic solvent, but 1-hexanol was used in the case of L-23 since L-23 was insoluble in cyclohexane.

Coating of the rhodium–hydrazine nanoparticles with silica was done by using hydrolysis of tetraethyl orthosilicate (TEOS). The hydrolysis was conducted in the microemulsion containing the rhodium–hydrazine nanoparticles at 50 °C for 2 h. Before the hydrolysis, W and a pH of the microemulsion were adjusted with an aqueous ammonia at 23 and 9, respectively. After the hydrolysis, the yellowish white precipitates were obtained by adding 50 mL (volume fraction of total one, ca. 20 vol%) of ethanol to the microemulsion.

The precipitates were filtered, washed thoroughly with propanol, dried at 80 °C overnight, and calcined under air flow at 500 °C for 2 h to remove the surfactant. Finally, the samples thus obtained were reduced with hydrogen at 450 °C for 2 h.

When the ICP measurement of a supernatant solution after precipitation was carried on, the amount of <0.1 % rhodium charged initially was detected in the solution. Thus, it was confirmed that almost all the rhodium charged initially was included in the precipitates. The silica yield from TEOS can be calculated from both the amount of TEOS charged initially and the weights of silica obtained after the hydrogen reduction. The silica yield and rhodium content of samples were shown in Table 1. As can be seen in Table 1, no significant difference in silica yield was whether different surfactants were used.

Table 1 Rhodium content and its size in rhodium-silica samples

Surfactant used for preparation	Rh content / wt%	SiO_2 yield / mol%	Rh size[a)] by XRD / nm	Rh size[a)] by TEM / nm
C-15	2.4	83	4.1	3.8
L-23	1.3	77	3.8	4.0
NP-5	2.6	77	3.1	3.0
AOT	1.1	91	n.d.[b)]	1.5

a) Measured after H_2 reduction, b) the Rh size coud not be determined by XRD.

The precipitates obtained using C-15 before the air-calcination were observed with transmission electron microscope (JEOL 2000FX). The TEM micrograph is shown in Figure 1. All rhodium–hydrazine nanoparticles were included in spherical silica particles. It was noteworthy that each silica particle included a fixed number (average 4) of rhodium–hydrazine nanoparticles, and that the nanoparticles were located near the center of each silica particle.

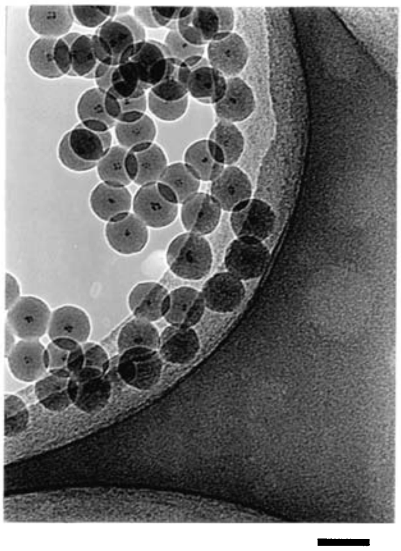

Figure 1. TEM (x250 K) micrograph of silica-coated Rh-N_2H_4 particles synthesized using polyoxyethylene(15)cetyl ether before air-calcination (bar = 40 nm).

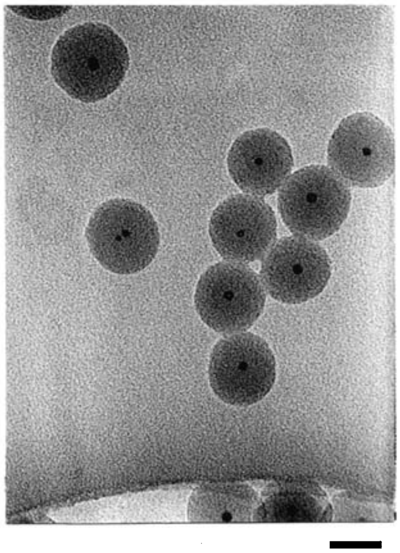

Figure 2. TEM (x250 K) micrograph of silica-coated Rh particles synthesized using polyoxyethylene(15)cetyl ether after air-calcination and H_2-reduction(bar =20 nm).

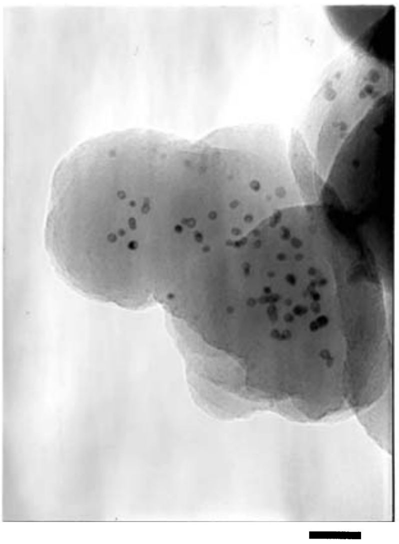

Figure 3. TEM (x250 K) micrograph of Rh-SiO_2 samples prepared using polyoxyethylene(23)lauryl ether after air-calcination and H_2-reduction(bar = 20 nm).

Such structure of the composite particle indicates that the aggregation of rhodium–hydrazine nanoparticles occurred via silica nuclei when silica started to be formed from TEOS. It also indicates that the aggregation was completed at an early stage of the TEOS hydrolysis. Furthermore, from the result of the fixed number of the nanoparticles included, it is considered that the fixed number (it may be 4) of rhodium–hydrazine nanoparticles formed a group and that the group was dispersed in the C-15 microemulsion.

The rhodium–hydrazine nanoparticles had an average diameter of 2.0 nm. On the other hand, the composite silica particles including rhodium–hydrazine nanoparticles were monodispersed and spherical in shape, and their diameters were 35 nm.

The TEM micrograph of the sample after hydrogen reduction was shown in Figure 2. Here, the reduction of rhodium–hydrazine nanoparticles to metallic rhodium ones was confirmed by XRD measurement. The most important feature in this figure is that a single metallic nanoparticle of rhodium was located at the center of a spherical silica particle. The rhodium nanoparticles were monodispersed and 3.8 nm in diameter (4.1 nm by XRD). On the other hand, the entire silica particles including rhodium ones were also monodisperese, and the overall diameters were 31 nm. Therefore, the rhodium nanoparticles coated with silica of 14 nm in thickness was prepared by our simple method.

Finally, the rhodium–silica sample prepared using the L-23 surfactant was observed by TEM after the hydrogen reduction. The TEM micrograph is shown in Figure 3. Although the size of rhodium particles was nearly equal to that in the case of C-15 (see Table 1), silica particles were shapeless and the number of rhodium nanoparticles included in a silica particle was not single. Similar structure was observed in the rhodium–silica samples prepared using the surfactant, NP-5 or AOT. Accordingly, the results suggest that the surfactant C-15 had an important role in the preparation of silica-coated Rh nanoparticles.

We thank the research laboratory of High Voltage Electron Microscope, Kyushu University, for the transmission electron micrographs.

References

1 M. Giersig, T. Ung, L. M. Liz-Marzán, and P. Mulvaney, *Adv. Mater.*, **9**, 570 (1997).

2 T. Li, J. Moon, A. A. Morrone, J. J. Mecholsky, D. R. Talham, and J. H. Adair, *Langmuir*, **15**, 4328 (1999).

3 L. M. Liz-Marzán and A. P. Philipse, *J. Colloid Interface Sci.*, **176**, 459 (1995).

4 L. M. Liz-Marzán, M. Giersig, and P. Mulvaney, *Langmuir*, **12**, 4329 (1996).

5 L. M. Liz-Marzán, M. Giersig, and P. Mulvaney, *Chem. Commun.*, **1996**, 731.

6 P. Mulvaney, M. Giersig, and A. Henglein, *J. Phys. Chem.*, **97**, 7061 (1993).

7 M. A. Correa-Duarte, M. Giersig, N. A. Kotov, and L. M. Liz-Marzán, *Langmuir*, **14**, 6430 (1998).

8 M. Ohmori and E. Matijevic, *J. Colloid Interface Sci.*, **150**, 594 (1992).

9 A. P. Philipse, A.-M. Nechifor, and C. Patmamanoharan, *Langmuir*, **10**, 4451 (1994).

10 M. A. Correa-Duarte, M. Giersig, and L. M. Liz-Marzán, *Chem. Phys. Lett.*, **286**, 497 (1998).