Fabrication of Nanocomposites Composed of Carbon Nanotubes and Silica-coated Pt-based Alloy Nanoparticles

Sakae Takenaka,*[1] Yoshiki Orita,[1] Takafumi Arike,[1] Hideki Matsune,[1] Eishi Tanabe,[2] and Masahiro Kishida*[1]
[1]*Department of Chemical Engineering, Graduate School of Engineering, Kyushu University,*
744 Moto-oka, Nishi-ku, Fukuoka 819-0395
[2]*Western Hiroshima Prefecture Industrial Institute, Kagamiyama, Higashi-Hiroshima 739-0046*

(Received August 8, 2007; CL-070846; E-mail: takenaka@chem-eng.kyushu-u.ac.jp)

Silica-coated Pt-based alloys (Pt–Co and Pt–Pd alloys) were prepared using a water-in-oil-type microemulsion. The silica-coated Pt-based alloys decomposed ethylene to form composites composed of the catalysts and carbon nanotubes.

Highly dispersed precious metals supported on carriers such as carbon, silica, and alumina are frequently utilized as catalysts for many catalytic reactions. For example, highly dispersed Pt metal particles supported on carbons are used as the electrocatalysts in proton-exchanged-membrane fuel cells (PEMFCs). The supported metal catalysts are conventionally prepared by impregnation methods. However, the metal particles are easily aggregated to form large particles, because they are supported on the outer surface of the carriers. Thus, the inhibition of the sintering of metal particles supported on the carriers is a general problem to be solved.

We have studied the preparation of silica-supported metal catalysts using microemulsion.[1] By this method, metal particles such as Ni, Rh, and Pt are uniformly covered with silica layers. The metal particles in the catalysts show a high sustainability to sintering, because each particle is covered with silica layers. In addition, the silica-coated metal particles show peculiar catalytic performances, because the active sites in the catalysts are covered with silica layers with a porous structure.[2] In the present study, silica-coated Pt-based alloys were prepared using microemulsion. Pt metal is utilized as a catalytically active component for many reactions. The catalytic performance of Pt metal is frequently modified by the addition of another metal species. For example, the tolerance to CO and the durability of the Pt electrocatalysts in the PEMFCs are improved by the addition of metal species such as Ni, Co, Mo, and Pd.[3] Thus, we prepared Pt–Co and Pt–Pd alloys covered with silica layers. In the present study, the silica-coated Pt-based alloys were used as the catalysts for ethylene decomposition to form carbon nanotubes (CNTs).

Silica-coated Pt–Co alloys (denoted as coated Pt–Co) and silica-coated Pt–Pd alloys (denoted as coated Pt–Pd) were prepared in a water-in-oil-type microemulsion. Mixed aqueous solutions of H_2PtCl_6 and $Co(NO_3)_2$ and of H_2PtCl_6 and $PdCl_2$ were used for the preparation of coated Pt–Co and coated Pt–Pd, respectively. The microemulsion system was prepared by adding aqueous solutions containing the metal cations described above into a surfactant solution in cyclohexane. Polyoxyethylene ($n = 15$) cetyl ether was used as a surfactant. Nanoparticles containing the metal species were formed by addition of aqueous NH_3 into the microemlusion. Hydrolysis of tetraethoxysilane (TEOS) was performed in the microemulsion by the addition of TEOS and aqueous NH_3. After the filtration, the samples were calcined at 773 K for 2 h in air. The calcined samples were washed with aqua regia at room temperature in order to remove metal species that were not covered with silica layers. The loading amounts of metals were evaluated by XRF spectra to be 2.6 wt % of Pt and 1.2 wt % of Co for coated Pt–Co and to be 3.2 wt % of Pt and 1.6 wt % of Pd for coated Pt–Pd.

Ethylene decomposition to form carbon nanotubes was performed at 973 K with a conventional gas-flow system with a fixed catalyst bed. Prior to the ethylene decomposition and the measurements of TEM and EXAFS, the catalysts were reduced with hydrogen at 973 K. TEM images of the samples before and after ethylene decomposition were measured with a JEOL JEM-3000F. X-ray absorption spectra for the samples were measured at the Photon Factory in the Institute of Materials Structure Science for High Energy Accelerator Research Organization, Tsukuba, Japan. Pt L_{III}-edge EXAFS was measured at the beam line BL-9C equipped with Si(111) in a transmission mode at room temperature (Proposal No. 2005G194). The analysis of EXAFS data was performed using an EXAFS analysis program, REX (Rigaku Co.). Inversely Fourier-transformed data for Fourier peaks were analyzed by a curve-fitting method, using phase-shift and amplitude functions derived from FEFF 8.0.[4]

Figure 1 shows TEM images for coated Pt–Co and coated Pt–Pd. In both the TEM images, particles with diameters of ca. 80 nm were observed. Judging from the contrast of the TEM images, the particles are mainly composed of silica. In addition, small particles with diameters of a few nanometers were observed in these TEM images. It should be noted that the small particles were not observed on the surfaces of silica particles but in the bodies of the particles. These results strongly suggest that the small particles are uniformly covered with silica layers.

Figure 2 shows Fourier transforms of Pt L_{III}-edge k^3-weighted EXAFS spectra (RSFs; radial structural functions) for coated Pt–Co and coated Pt–Pd as well as for Pt foil. In a RSF for Pt foil, a strong peak due to Pt–Pt bonds is observed at around 2.8 Å. In contrast, two peaks were observed in the R range from 1.5 to 3.0 Å in the RSFs for coated Pt–Co and coated Pt–Pd, suggesting the formation of alloys between Pt and Co or Pt and Pd. The

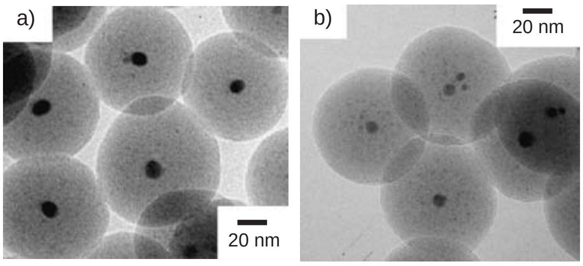

Figure 1. TEM images of coated Pt–Co (a) and coated Pt–Pd (b).

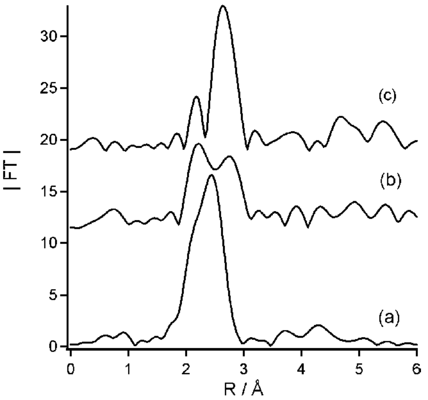

Figure 2. Fourier transforms of Pt L_{III}-edge k^3-weighted EXAFS for coated Pt–Co (a), coated Pt–Pd (b) and Pt foil (c). The intensity of the peak for Pt foil was halved.

peaks in the R range of 1.5 to 3.0 Å for coated Pt–Pd and coated Pt–Co were analyzed by the curve-fitting methods. The structural parameters evaluated by the curve-fitting are summarized in Table 1. The peaks for coated Pt–Co and coated Pt–Pd were fitted by Pt–Pt and Pt–Co bonds and by Pt–Pt and Pt–Pd bonds, respectively. The interatomic distances for these bonds in the samples were very similar to those of the corresponding alloys in the previous reports.[5] Thus, metal species in coated Pt–Co and coated Pt–Pd were present as alloys.

Figure 3 shows TEM images for coated Pt–Co and coated Pt–Pd after ethylene decomposition at 973 K. Ethylene decomposition was also carried out over silica-coated Pt catalyst at 973 K. However, the formation of nanoscaled carbons on the catalyst was not observed in TEM images (the result is not shown). In contrast, both the silica-coated Pt-based alloys formed CNTs through ethylene decomposition at 973 K, as shown in Figure 3.[6] The amounts of carbons deposited on coated Pt–Co and coated Pt–Pd were estimated to be 6 and 23 wt %, respectively. Thus, nanocomposites composed of silica-coated Pt-based alloys and CNTs could be obtained by the hydrocarbon decomposition over the catalysts. It is well accepted that Pd and Co also decompose hydrocarbons to form carbon nanotubes.[6] However, Co or Pd species in silica-coated Pt-based alloys were mainly present as the corresponding alloys. Thus, we consider that Pt–Co and Pt–Pd alloys decompose ethylene to form carbon nanotubes. No metal particles were found at the tip or in the body of CNTs in the TEM images of coated Pt–Co or coated Pt–Pd after ethylene decomposition. Thus, Pt-based alloy particles stabilized on the silica layers decompose ethylene to form CNTs, i.e., the base-growth model of CNTs. The diameters of CNTs for coated Pt–Co and coated Pt–Pd were estimated to ca. 8 and 15 nm, respectively. HRTEM images (b) and (d) show that the structure of graphene that formed the walls of CNTs was different for the two samples, i.e., the graphitization degree of CNTs on coated Pt–Co was higher than that on coated Pt–Pd.

Table 1. Structural parameters estimated by the curve-fitting for the EXAFS spectra of coated Pt–Co and coated Pt–Pd

Sample	Shell	C.N.[a]	R/Å[b]	D.W./Å[c]
coated Pt–Co	Pt–Co	5.0 ± 0.5	2.59 ± 0.01	0.066
	Pt–Pt	4.3 ± 0.5	2.68 ± 0.01	0.078
coated Pt–Pd	Pt–Pd	4.4 ± 0.3	2.71 ± 0.01	0.070
	Pt–Pt	4.5 ± 0.3	2.72 ± 0.01	0.060

[a]C.N., coordination number. [b]R, interatomic distance. [c]D.W., Debye–Waller factor.

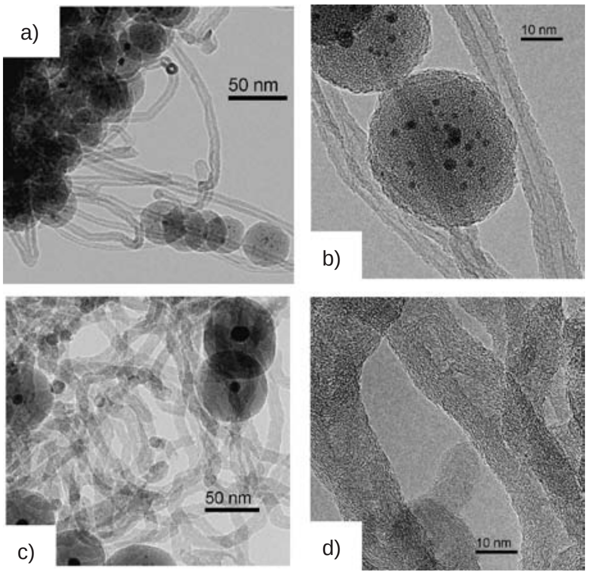

Figure 3. TEM images of coated Pt–Co (a) and (b) and coated Pt–Pd (c) and (d) after ethylene decomposition.

As described earlier, silica-coated Pt-based alloy catalysts could be prepared using microemulsion. The catalysts decomposed ethylene to form the composites composed of CNTs and the catalysts, whereas silica-coated Pt did not show the catalytic activity for ethylene decomposition. The Pt-based alloy nanoparticles in the nanocomposites should be directly interacted with CNTs, because the alloy particles grew the CNTs. Therefore, the composites are expected to show peculiar catalytic performances due to remarkable electronic, mechanical, and chemical properties of CNTs as well as silica-coated Pt-based alloy nanoparticles. We would apply these nanocomposites to catalytic reactions and PEMFCs.

This study was supported by the Industrial Technology Research Grant Program in 2005 from the New Energy and Industrial Technology Development Organization (NEDO) of Japan.

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Published on the web (Advance View) September 15, 2007; doi:10.1246/cl.2007.1250