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Ligand-Free Platinum Nanoparticles Encapsulated in a Hollow Porous Carbon Shell as a Highly Active Heterogeneous Hydrogenation Catalyst**

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Studies on the synthesis of metal nanoparticles (MNPs) and their catalytic activity have become increasingly common because their specific properties, which are often distinct from those of bulk metals, lead to the induction of unique organic reactions.[1–7] These MNP-based catalysts are usually preserved by organic ligands, such as polymers,[2–4] surfactants,[5] and phosphines[6] to prevent coalescence and are used in homogeneous systems similar to those in which metal-complex catalysts are used. Current interest in the design of high-performance practical catalysts is directed towards the heterogenization of MNPs by fixing them on organic and inorganic solid surfaces. Thus, numerous supported MNPs have been studied as catalysts for a variety of reactions.[8] However, since these supported MNPs still have a propensity to coalesce, they are used in the presence of organic stabilizing and/or capping agents in most cases. Our research interest is therefore focused on the evaluation of the catalytic properties of ligand-free MNPs heterogenized on a solid support.

The creation of a core–shell structure is one technique to stabilize MNP cores in a solid shell without the use of organic

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ligands.[9] A promising structure for a catalyst in such a core–shell approach is a core MNP encapsulated by a hollow porous shell whose size is larger than that of the core particle. This "rattle-type" nanostructure enables stabilization of the core MNP without any ligands even under severe reaction conditions in a catalytic system. Although various examples of rattle-type nanostructures have been reported,[10] their catalytic properties have not been demonstrated owing to the difficulty of obtaining a core particle of sufficiently small size for use as a catalyst. Herein we fabricate a ligand-free platinum nanoparticle 2.2 nm in diameter as a typical catalyst which is encapsulated in a hollow porous carbon shell 30–40 nm in diameter (Pt@*hm*C). Since the carbon shell acts as a barrier that prevents the coalescence of Pt nanoparticles and also provides a void space where organic transformation occurs on the surface of the ligand-free Pt nanoparticle, the Pt@*hm*C particle was found to work as a robust and reusable heterogeneous catalyst for hydrogenation reactions.

Fabrication of Pt@*hm*C was performed using the procedure for fabrication of a hollow-core/mesoporous-shell carbon containing a gold nanoparticle about 20 nm in diameter.[10d] This procedure is based on the successive coating of a silica layer and a mesoporous silica layer on the surface of an MNP, subsequent growth of a carbon shell inside the mesoporous silica shell, and removal of the siliceous components by treatment with aqueous HF. When applying the procedure to much smaller Pt nanoparticles, we modified both the silica-coating and carbon-grafting steps of the above procedure (see Experimental Section). We employed Pt nanoparticles stabilized by poly(*N*-vinyl-2-pyrrolidone) (Pt–PVP) with an average particle size of 1.8 nm as a starting material (Figure 1 a). As confirmed by the TEM image shown in Figure 1 b, the Pt nanoparticles retain the size and size distribution of the original Pt–PVP after being covered with a double layer of silica and mesoporous silica (Pt@SiO_2–*m*SiO_2), while some Pt@SiO_2–*m*SiO_2 particles contain more than one Pt nanoparticle in each silica shell.

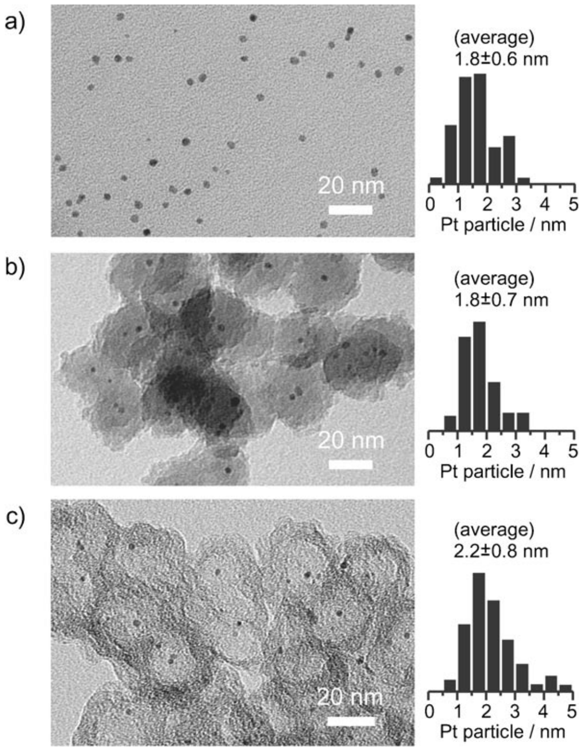


Figure 1. TEM images and Pt particle size distributions of a) Pt–PVP, b) Pt@SiO_2–*m*SiO_2, and c) Pt@*hm*C.

Figure 1 c shows a TEM image of Pt@*hm*C obtained from the Pt@SiO_2–*m*SiO_2 and the size distribution of the Pt nanoparticles in this material. The Pt@*hm*C particle consists of a hollow carbon cage (30–40 nm in diameter with a shell thickness of 15 nm) and a central Pt nanoparticle with an average particle size of 2.2 nm. This value is consistent with the crystallite size determined by X-ray diffraction (XRD) analysis and implies the single crystalline nature of each Pt nanoparticle.[11] The increase (0.3 nm) of the Pt particle size relative to that in Pt@SiO_2–*m*SiO_2 is probably due to the coalescence of the Pt particles originally included in the same silica shell. The XP spectrum of Pt@*hm*C (Pt 4f region) is typical for Pt^0 with a small contribution from Pt^{2+}. The fact that almost no peak for expected impurities, such as Cl and F, is observed within the sensitivity of this measurement indicates that the surface of the Pt nanoparticle is free from any ligand but is partially oxidized.[11] The content of Pt in Pt@*hm*C, as measured by inductively coupled plasma (ICP) analysis, is 2.1 wt % under these reaction conditions.[11]

The N_2 adsorption–desorption isotherm of Pt@*hm*C measured at 77 K shows a significant hysteresis loop enclosed by a sudden drop in the adsorbed volume for the desorption isotherm at a relative pressure (P/P_0) of 0.42–0.46. Since this phenomenon is typically observed in materials having a large mesopore encapsulated by a pore system of relatively small pore size,[12] the carbon shell of Pt@*hm*C is likely to consist of a porous wall structure. In practice, micropore and mesopore analyses of the adsorption branch by an α_s-plot and the BJH method revealed that the carbon shell has both micro- (< 0.9 nm) and nanosized (1–4 nm) pore systems.[11] It is also notable that the BET surface area calculated from the isotherm at a relative pressure of 0.05–0.09 reaches 1830 $m^2 g^{-1}$, which is an extremely high value that is comparable to representative activated carbons.

Figure 2 shows the catalytic performance of Pt@*hm*C for hydrogenation of nitrobenzene compared with that of the original Pt–PVP, a commercial Pt catalyst supported on activated carbon (Pt/AC),[13] and Pt@SiO_2–*m*SiO_2. It is clear that remarkable activity is achieved with Pt@*hm*C: all of the

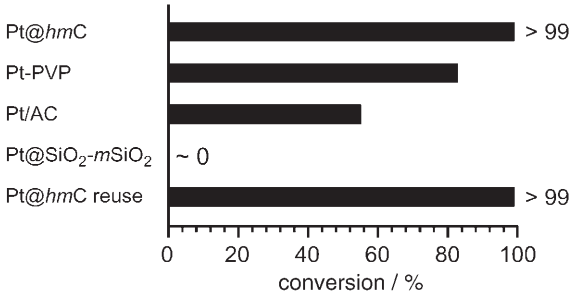
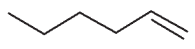
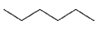
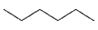
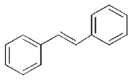
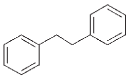


Figure 2. Liquid-phase hydrogenation of nitrobenzene into aniline by various Pt catalysts at 303 K.

nitrobenzene is converted into aniline by Pt@*hm*C, whereas the reaction does not go to completion with Pt–PVP and Pt/AC.[14] The Pt@SiO_2–*m*SiO_2 particle shows no activity, thus indicating that the presence of voids in Pt@*hm*C is indispensable for induction of the reaction. Although the original Pt–PVP exhibits a higher level of activity than Pt/AC, it cannot be recovered and reused efficiently. However, the Pt@*hm*C catalyst can be recovered simply by centrifugation and recycled for further reaction. A TEM image of Pt@*hm*C taken after the reaction revealed that there is no change in the structure of the catalyst.[11]

As summarized in Table 1, Pt@*hm*C also shows a high level of catalytic activity for the hydrogenation of primary, secondary, and cyclic olefins in comparison with Pt–PVP and Pt/AC catalysts. The corresponding turnover frequency TOF (h^{-1}) for Pt was calculated to be more than 20000, which is much larger than that obtained with the platinum-nanoparticle-based system reported recently.[7] It is notable that the Pt@*hm*C catalyst also gives higher conversion for the hydrogenation of *trans*-stilbene (*trans*-1,2-diphenylethylene) into 1,2-diphenylethane than Pt–PVP or Pt/AC, which suggests that there is no significant effect of the porous carbon shell on the mass transfer of such a bulky substrate. Thus, we have demonstrated that Pt@*hm*C has high potential as a heterogeneous hydrogenation catalyst.

Table 1: Hydrogenation of various olefins by Pt@*hm*C, Pt/AC, and Pt-PVP catalysts.[a]

Substrate	Catalyst	Product	*t* [h][b]	Conv. [%][c]
	Pt@*hm*C		2	>99
	Pt–PVP		2	91
	Pt/AC		2	7
	Pt@*hm*C		2	96
	Pt–PVP		2	70
	Pt/AC		2	16
	Pt@*hm*C		1	91
	Pt–PVP		1	42
	Pt/AC		1	3
	Pt@*hm*C		15	72
	Pt–PVP		15	46
	Pt/AC		15	16

[a] All reactions were carried out with 0.1 μmol of catalyst (Pt) and 0.5 mmol of substrate under H_2 (0.2 MPa in absolute pressure) at 348 K. [b] Reaction time. [c] Conversion of substrate.

All of the results described above are consistent with our prediction that a metal nanoparticle that is not bound to anything should be able to catalyze a chemical reaction efficiently. We have employed only Pt nanoparticles as hydrogenation catalysts in the present study. However, the basic concept of the system should be applicable to the selective oxidation of various organic compounds and C–C bond-formation reactions when other MNPs, such as Pd[1,2a,3b,c,8b,d,e] and Au,[2b] are used. Studies along these lines are now in progress.

Experimental Section

Poly(*N*-vinyl-2-pyrrolidone) (PVP)-stabilized Pt (Pt–PVP) was synthesized as reported elsewhere.[4b] Typically, PVP (66 mg) was added to a solution of hexachloroplatinic acid ($H_2PtCl_6 \cdot 6H_2O$; 0.03 mmol, 15.5 mg) in water (5 mL) and ethanol (45 mL) and the mixture was heated under reflux for 3 h. After adding acetone (160 mL) to 16 mL of the solution, the mixture was centrifuged (23000 g, 20 min) to collect the Pt–PVP precipitate. A mixture of ethanol (30.7 mL), aqueous NH_3 (0.28%, 1.28 mL), and tetraethylorthosilicate (TEOS, 0.1 mL, 0.45 mmol) was then added to the Pt–PVP precipitate and the mixture was stirred at room temperature for 16 h. The resulting precipitate of silica-covered Pt nanoparticles (Pt@SiO_2) was isolated by centrifugation (23000 g, 20 min). A mixture of ethanol (30.7 mL), aqueous NH_3 (0.28%, 1.38 mL), TEOS (0.1 mL, 0.45 mmol), and *n*-octadecyltrichlorosilane (ODTS, 0.04 mL, 0.09 mmol) was then added to this Pt@SiO_2 precipitate. After stirring the suspension at room temperature for 2 h, the precipitate was isolated by centrifugation (23000 g, 20 min), washed with ethanol, and calcined at 823 K for 6 h in air to produce Pt@SiO_2 coated with a mesoporous silica shell (Pt@SiO_2–*m*SiO_2).

The typical procedure for obtaining Pt@*hm*C: The carbon source used was resol-type phenol-formaldehyde resin (PF), which was prepared by the reaction of phenol (90 mmol, 8.46 g) and formaldehyde (110 mmol, 4 mL) in water (5.6 mL) in the presence of aqueous NH_3 (28%, 0.75 mL) at 363 K for 2 h. Pt@SiO_2–*m*SiO_2 (60 mg) was added to an ethanolic solution (2 mL) of PF (60 mg) and the solution was stirred overnight at room temperature to yield a PF–Pt@SiO_2–*m*SiO_2 composite. This composite was heated at 1173 K under vacuum for 2 h to carbonize the PF. Dissolution of the SiO_2–*m*SiO_2 shell with 10% aqueous HF generated Pt@*hm*C, which was characterized by TEM, XRD, XPS, N_2 adsorption–desorption measurements, and ICP analysis (see Supporting Information).

Catalytic hydrogenation of nitrobenzene was performed at 303 K whilst bubbling H_2 through the reaction vessel. Thus, 0.1 μmol of Pt catalyst (1.0 mg of Pt@*hm*C) and ethanol (5 mL) were placed in a cylindrical Schlenk flask (30 mL) and, after addition of substrate (0.5 mmol) under argon, the mixture was vigorously stirred (1200 rpm) at 303 K under H_2 bubbling (20 mL$\,$min^{-1}) for 1.5 h. For the hydrogenation of olefins, the reactions were conducted in a stainless-steel autoclave equipped with a glass reactor (50 mL). Typically, Pt@*hm*C (1.0 mg) and acetone (5 mL) were put into the glass vessel under N_2. After addition of substrate (0.5 mmol), the reactor was purged with H_2, pressurized with H_2 at 0.2 MPa (in absolute pressure), and heated to 348 K whilst stirring (1200 rpm). Catalytic activities were evaluated by determining the conversion of substrate with a Shimadzu GC-2010 gas chromatograph equipped with a flame ionization detector and a TC-FFAP capillary column.

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