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Ship-in-bottle synthesis and catalytic performances of platinum carbonyl clusters, nanowires, and nanoparticles in micro- and mesoporous materials

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Abstract

Ship-in-bottle synthesis of platinum carbonyl clusters, nanowires, and nanoparticles in micro- and mesoporous materials is described. Reductive carbonylation of Pt ions impregnated on NaY zeolite or on mesoporous silica FSM-16 leads to the selective formation of the Chini-type Pt carbonyl clusters. Decarbonylation of the resulting clusters yields naked Pt nanoparticles (diameter 1.0–1.5 nm) in NaY or in FSM-16. Similar Pt nanoparticles in FSM-16 are prepared by the direct hydrogen reduction of H_2PtCl_6/FSM-16 at 673 K, and in this case Pt particles in size of 2.5 nm are formed in the mesopores of FSM-16 (pore size 2.7 nm). In contrast, Pt nanowires (diameter 2.5 nm, length 50–300 nm) are obtained by the photoreduction of H_2PtCl_6/FSM-16 in the presence of vapors of water and 2-propanol. The Pt nanowires exhibit unique properties in CO chemisorption and magnetism due to their morphology in the mesoporous channels of FSM-16. In the water-gas-shift reaction, Pt nanowire/FSM-16 shows a higher catalytic activity than that of Pt nanoparticle/FSM-16. The Pt nanowires are chemically extracted from the mesopores using $[NBu_4]Cl$ in a mixture of benzene and ethanol.

Keywords: Ship-in-bottle synthesis; Platinum carbonyl cluster; Nanowire; Nanoparticle; FSM-16

1. Introduction

Porous materials such as zeolites, MCM-41, and FSM-16 have tiny channels and windows in size of nanometer, and these porous materials show unique properties in adsorption and catalytic conversion of guest molecules [1–3].[1] Owing to the molecular sieving effect as well as solid acidity, the zeolites are widely used in industry, e.g., catalytic cracking of petroleum. Supported metal catalysts in zeolites are a class of important heterogeneous catalysts for industrial-scale processes, and they have been prepared by impregnation of metal salts into the pores with subsequent calcination (oxidation) and/or hydrogen reduction treatments [5]. However, these conventional preparative methods comprising impregnation of metal salts, calcination, and hydrogen reduction often give rise to ill-organized metal particles of various sizes and shapes both in internal pores and on external surfaces of the porous materials, thus rendering catalytic activity and selectivity low. Therefore, for the rational design of supported metal catalysts in the porous materials, careful consideration is required

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[1] See recent reviews [4,24–26].

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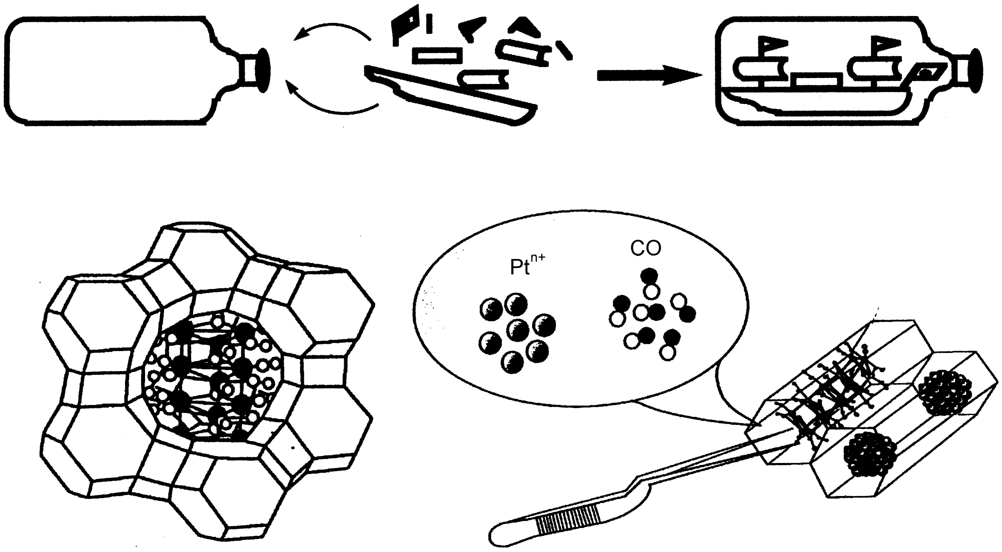

Fig. 1. Ship-in-bottle synthesis of platinum carbonyl clusters.

in choosing precursors and treatments in the so-called catalyst preparation.

Immobilization of molecular metal complexes in porous materials would be a promising method for the preparation of supported metal catalysts, because fine tuning of the metal complexes in terms of electronic states and steric environment is substantially easier than using metal salts in the conventional catalyst preparation.[2] Such metal complexes occluded in the porous materials might be used as precursors of naked metal particles dispersed in the pores by removing coordinated ligands. Based on this principle, we have developed the “ship-in-bottle” synthesis of metal complexes utilizing the pore space as a template of preparation of the complexes (Fig. 1). Here, the pores can be regarded as hosts and the active metal sites as guests like in the host–guest chemistry, and the host pores work not only as ligands of the metal centers but also as reaction vessels of catalytic transformations. So far, the ship-in-bottle synthesis has been established for several metal carbonyl clusters such as $Rh_6(CO)_{16}$ [7,29], $Rh_{6-x}Ir_x(CO)_{16}$ [8], $[Pt_3(CO)_6]_n^{2-}$ $(n = 3, 4)$ [9–11,30–34] and metal phthalocyanines [12] in NaY and/or FSM-16. Moreover, metal nanoparticles highly dispersed in the porous materials can be prepared from the occluded metal complexes by careful removal of coordinated ligands in the thermal activation of the original complexes. The occluded metal complexes and nanoparticles show high catalytic activity and selectivity in CO-related reactions, hydrogenations and oxidations [13,35–38].

In 1990s a new group of mesoporous silicas such as MCM-41, MCM-48, and FSM-16 were discovered. They have large pores (2–10 nm) with a narrow pore size distribution and high surface area (up to $1000\,m^2\,g^{-1}$), thus providing a great opportunity to immobilize large metal complexes such as metalloporphyrins and high nuclearity metal carbonyl clusters. Moreover, the diffusion of bulky organic substrates into the internal active sites would be easier than in the microporous zeolites (pore size <2.0 nm). This prospect again stimulates chemists to investigate the ship-in-bottle synthesis and the occlusion of metal complexes such as $[Mn(bpy)_2]^{2-}$ [14] and Ru and RuCu clusters [15,39,40] in MCM-41.

One-dimensional metal wires and particles would offer interesting physical and chemical properties [16–18,41,42]. We have preliminary report that Pt nanowires are densely formed in the mesoporous channels of FSM-16 by photoreduction of H_2PtCl_6 impregnated in FSM-16 [18,42]. On the other hand, Pt

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[2] See recent reviews [6,27,28].

nanoparticles were formed by the hydrogen reduction of H_2PtCl_6/FSM-16.

In this article, we will show our recent results of the ship-in-bottle synthesis and catalytic performances of platinum carbonyl clusters, nanowires, and particles in NaY and FSM-16.

2. Ship-in-bottle synthesis of platinum carbonyl clusters

2.1. Pt carbonyl clusters in microporous NaY

Many research papers have reported the synthesis of transition metal carbonyls, phthalocyanines, porphyrins, and amine-ligated complexes in microporous zeolites. Here, we exemplify the ship-in-bottle synthesis of platinum carbonyl clusters and the preparation of nanoparticles from the carbonyl clusters. Our goal is to control particle size and shape of platinum nanoparticles using well-defined organometallic complexes [19]. Supported Pt catalysts play a key role in important industrial processes such as naphtha-reforming, $deNO_x$, and combustion [20].

It was demonstrated by Chini and coworkers [21,43] that the reaction of Pt(VI) or Pt(II) ions with CO in methanol in the presence of strong bases such as NaOH and KOH resulted in the formation of triangular prismatic clusters $[Pt_3(CO)_6]_n^{2-}$ ($n = 2$–6). These cluster molecules are attractive precursors to prepare supported Pt catalysts [9,10,22,30–34]. In this series of clusters, the synthesis and isolation of Pt_9, Pt_{12}, and Pt_{15} is easy, but it is difficult to push the Pt_9–Pt_{15} cluster molecules (ca. 0.7–1.2 nm in size) into the micropores (1.3 nm) of NaY zeolite due to the limited window size of NaY micropores (0.7 nm). Therefore, we tried to prepare the Pt clusters in the NaY micropores after introducing Pt ions inside, i.e., ship-in-bottle synthesis [9,30–32]. Thus, NaY was impregnated with Pt(II or VI) salts such as H_2PtCl_6 and $[Pt(NH_3)_4]Cl_2$, and treatment of the sample with $CO + H_2O$ vapor at elevated temperature led to the water-gas-shift reaction ($CO + H_2O \rightarrow CO_2 + H_2$). At the same time, the reductive carbonylation of the Pt ions proceeded to give $[Pt_3(CO)_6]_n^{2-}$ in the micropores of NaY (Fig. 1, bottom left). $[Pt_{12}(CO)_{24}]^{2-}$ was formed from $H_2Pt^{VI}Cl_6$ as a precursor, while further reduction occurred for $[Pt^{II}(NH_3)_4]Cl_2$ to give $[Pt_9(CO)_{18}]^{2-}$ in NaY. IR study of this transformation revealed that mononuclear Pt carbonyl species such as $[Pt(CO)_2Cl_2]$ and $[Pt(CO)Cl_3]^-$ were initially formed. The mononuclear species underwent further reductive carbonylation to form stable Pt carbonyl clusters as an almost single product. Hence, the yield of the Pt clusters is higher than those in solution reactions. The catalytic performances of Pt_9 and Pt_{12}/NaY were tested in the water-gas-shift reaction and the $CO + NO$ reaction.

On the other hand, Gates et al. used MgO having basic OH groups as a support to prepare the Pt carbonyl clusters. MgO was impregnated with Na_2PtCl_6, and the resulting sample was reacted with $CO + H_2$ to give a mixture of $[Pt_9(CO)_{12}]^{2-}$ and $[Pt_{12}(CO)_{24}]^{2-}$ on MgO. This is one of the surface-mediated cluster synthesis, but the above result implies that the selective formation of cluster is not easy by using MgO as a base. NaY has no basic OH groups, but either Pt_9 or Pt_{12} can be prepared by the reductive carbonylation of Pt(II) or Pt(IV) ions utilizing the water-gas-shift reaction, which is presumably due to the steric restriction of NaY micropores.

2.2. Pt carbonyl clusters in mesoporous FSM-16

The Chini-type Pt carbonyl clusters were similarly prepared in mesoporous silica FSM-16 [10,33,34]. Treatment of H_2PtCl_6/FSM-16 (pore size 2.7 nm) in CO at 363 K led to the similar reductive carbonylation of Pt(IV) to $[Pt(CO)_2Cl_2]$ and $[Pt(CO)Cl_3]^-$. Then the sample was exposed to water vapor, and the water-gas-shift reaction took place at 363 K, resulting in further reductive carbonylation of Pt(II) to Pt(0) to form $[Pt_{15}(CO)_{30}]^{2-}$. The IR spectral change in this reaction is shown in Fig. 2. As described above, the Chini clusters $[Pt_3(CO)_6]_n^{2-}$ ($n = 3, 4, 5$) were easily prepared and isolated in the solution synthesis, and Pt_9 and Pt_{12} clusters were synthesized in NaY. In contrast, Pt_{15} cluster was selectively formed in FSM-16. These results indicate that the micropore of NaY (1.3 nm) is not large enough to stabilize $[Pt_{15}(CO)_{30}]^{2-}$ (ca. 1.2 nm in size), but the mesopore of FSM-16 (2.7 nm) has sufficient room to occlude the Pt_{15} cluster stabilized as a major product.

When $[Pt_{15}(CO)_{30}]^{2-}$/FSM-16 was evacuated at elevated temperature, the carbonyl ligands were dissociated stepwise. TEM and EXAFS demonstrated

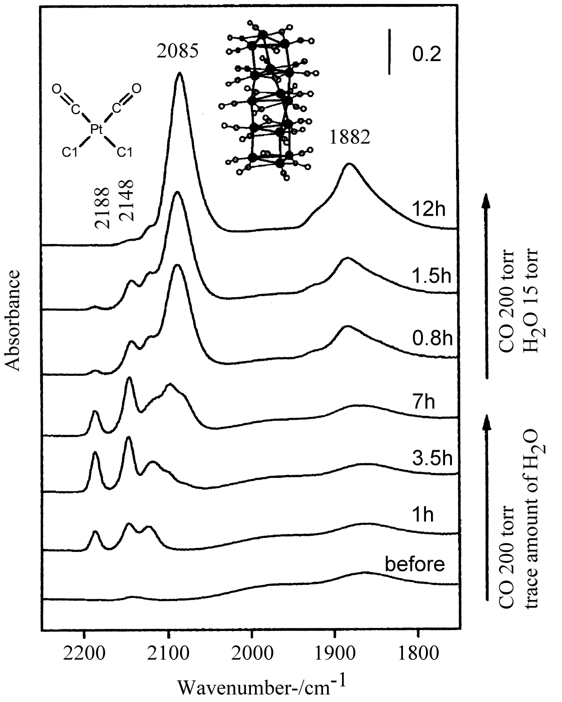

Fig. 2. IR spectral change for the ship-in-bottle synthesis of $[Pt_{15}(CO)_{30}]^{2-}$ in FSM-16 at 363 K.

that at 473 K, Pt nanoparticles with a diameter of ca. 1.5 nm (50–60 Pt metals) were formed, homogeneously dispersed in FSM-16 (Fig. 1, bottom right). Thus, the Pt particles with well-controlled size and high dispersion can be obtained by the decarbonylation of the cluster molecules once prepared in FSM-16. The Pt_{15} carbonyl cluster is similarly prepared in TiO_2- or ZrO_2-modified FSM-16 [34]. The Pt nanoparticle/FSM-16 thus obtained by the decarbonylation catalyzes the water-gas-shift reaction, the NO+CO reaction, and the hydrogenation of butadiene.

3. Preparation, characterization, and catalysis of Pt nanowires and particles in mesoporous FSM-16

In the study of the preparation of Pt nanoparticles by the decarbonylation of Pt carbonyl clusters, we had a question of what happened in the direct reduction of H_2PtCl_6/FSM-16 without the intermediacy of $[Pt_{15}(CO)_{30}]^{2-}$/FSM-16. Accordingly, when

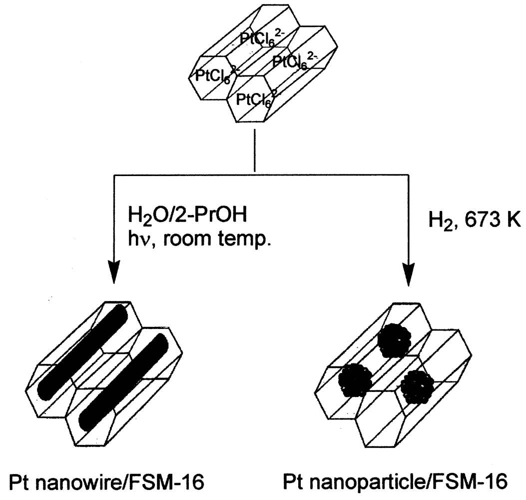

Fig. 3. Schematic representation of preparation of Pt nanowires and nanoparticle in FSM-16.

H_2PtCl_6/FSM-16 (5 wt.% Pt) was reduced in flowing hydrogen at 673 K for 2 h, we found that Pt nanoparticles (ca. 2.5 nm diameter) were formed in FSM-16. In contrast, we tested the photoreduction of H_2PtCl_6/FSM-16 by the UV–Vis light in the presence of water and 2-propanol at room temperature. It was surprising to find that Pt nanowires were formed along the one-dimensional channels of FSM-16 [18,42]. Therefore, Pt nanowires or particles can be prepared by choosing reduction methods of H_2PtCl_6/FSM-16 (Fig. 3). The diameter of the Pt wires is about 2.5 nm in agreement with the pore size of FSM-16 (2.7 nm), and the length of the wires range from 50 to 300 nm (Fig. 4). To our knowledge, this is one of the thinnest wires of transition metals obtained on a preparative scale.

HRTEM and electron diffraction of the Pt nanowires/FSM-16 gave clear lattice fringes and diffraction spots, indicating that the wires are crystalline Pt. However, XAFS and XPS showed that the Pt wires are slightly electron deficient compared to Pt particle/FSM-16 and Pt foil. Moreover, Pt wire/FSM-16 gave a small CO band at 2080 cm^{-1} in IR of CO chemisorption and Pt particle/FSM-16 at 2060 cm^{-1}. This high-frequency shift may also reflect the electron deficiency of the Pt wires, which is due to the stronger interaction of the nanowires with the acidic sites of internal surface of FSM-16 pores.

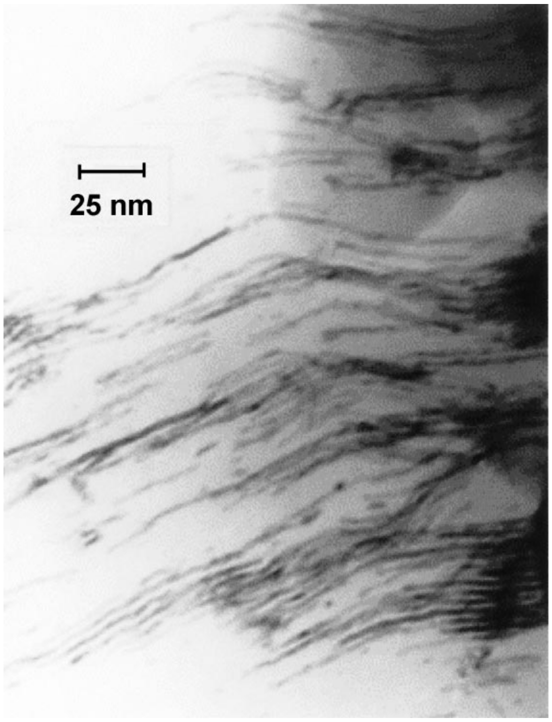

Fig. 4. A TEM image of Pt nanowire in FSM-16 (2.7 nm).

In the formation mechanism of Pt nanowires, small nanoparticles are initially formed in the FSM-16, and $[PtCl_6]^{2-}$ ions are successively reduced on the particles to grow to wires under the UV-irradiation. Pt nanowires with a size of ca. 4.0 nm were also formed in FSM-15 (pore size 4.7 nm) by the similar photoreduction of H_2PtCl_6/FSM-16 (4.7 nm) in the presence of water/2-propanol vapors.

Ryoo [16,41] previously reported similar Pt nanowires in MCM-41 by the sequential impregnation of Pt salts and calcination/H_2 reduction. In this case, they suggested that small Pt particles initially formed work as the core of the formation of nanowires in MCM-41, which is similar to our proposed mechanism for the photoreduction. We have tried to make Pt nanowires in FSM-16 according to the Pt wire/MCM-41 method. The short Pt wires were certainly formed, but big Pt particles were also deposited on the external surface of FSM-16.

Magnetic susceptibility of Pt nanowires and particles in FSM-16 was measured by varying the temperature from 5 to 300 K at 30 kOe. The magnetization of FSM-16 without Pt was used as a background, which was subtracted from measured values of both the samples. The temperature dependence of inverse susceptibility is represented in Fig. 5. The Pt wire/FSM-16 exhibited paramagnetic behavior and obeyed the Curie–Weiss law. On the other hand, the Pt wire/FSM-16 obeyed the Curie–Weiss law below 70 K, but there appeared a deviation from the normal paramagnetic behavior over 70 K for the Pt wire/FSM-16, where the magnetic moment was 0.084 μb and the Nèel temperature was 41.1 K. This deviation might be due to the anisotropic morphology of the Pt nanowires in FSM-16. Another possible origin of the unique temperature dependence of the magnetism is associated with the interaction of the Pt wires with the inner surface of FSM-16.

Catalytic performances of Pt wire/FSM-16 and Pt particle/FSM-16 were explored using the water-gas-shift reaction as a test reaction. The formation of CO_2 was followed with reaction time at 373 K (Fig. 6), where the initial rate for Pt wire/FSM-16 was higher than that for Pt particle/FSM-16 in spite of fewer surface Pt atoms (Table 1). Turnover frequency (TOF) was evaluated from the initial rate based on the surface of Pt atoms using the H/Pt value in the hydrogen uptake: 0.058 for Pt wire/FSM-16 and 0.17 for Pt particle/FSM-16. The TOF was $1.01\,h^{-1}$ for Pt wire/FSM-16 and $0.126\,h^{-1}$ for Pt particle/FSM-16 at 373 K, respectively, and the former was higher than the latter by a factor of 8. We infer that the surface Pt atoms of the wires are highly active for the water-gas-shift reaction compared to those of the particles in FSM-16. This can be explained by the enhancement of nucleophilic attack of H_2O to CO adsorbed on Pt for Pt wire/FSM-16, in which the back bonding from Pt to CO is weaker owing to electron deficiency of Pt atoms than for Pt particle/FSM-16 as suggested in the IR spectra of CO adsorption (vide supra).

Separation of the Pt nanowires from FSM-16 was attempted by using aqueous HF or NaOH solution (ca. 25% each) to dissolve FSM-16, but the nanowires also decomposed to form big Pt aggregates. In contrast, the Pt nanowires were successfully extracted from the mesopores using $[NBu_4]Cl$ in a benzene/ethanol mixture to give supernatant brown–black solution (Fig. 7), though the yield of extracted Pt was low. In the TEM image of the extracted wires, the wires seem to be

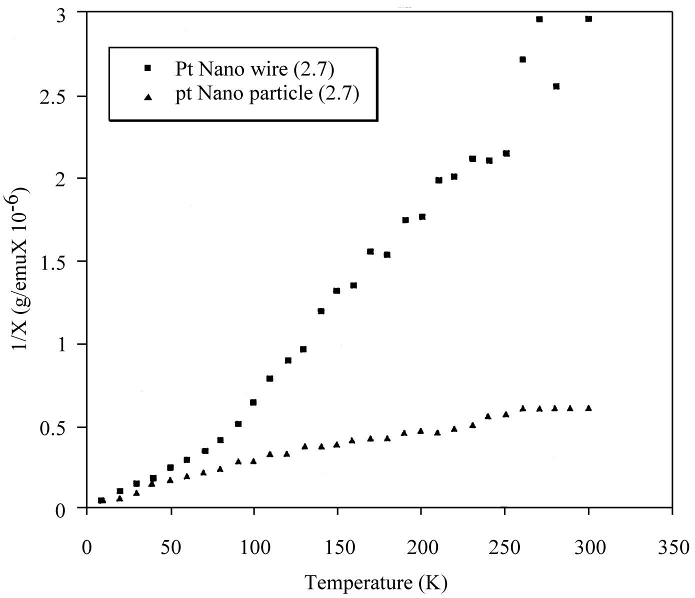

Fig. 5. Temperature dependence of $1/\chi$ (magnetization) for Pt nanowire/FSM-16 and Pt nanoparticle/FSM-16.

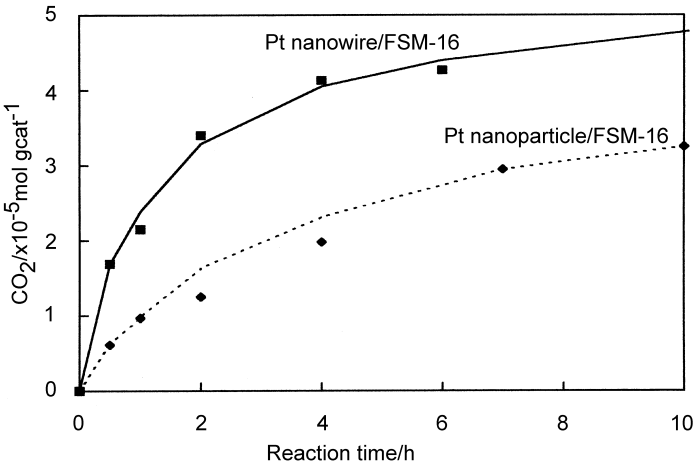

Fig. 6. Formation of CO_2 in the water-gas-shift reaction by Pt wire/FSM-16 and Pt particle/FSM-16.

Table 1
Water-gas-shift reaction by Pt nanowire/FSM-16 and Pt nanoparticle/FSM-16[a]

Catalyst	H/Pt	TOF $(h^{-1})^b$
Pt nanowire/FSM-16	0.058	1.01
Pt nanoparticle/FSM-16	0.17	0.126

[a] Conditions: catalyst 300 mg (5 wt.% Pt), 373 K, initial $P(CO) = 200$ Torr and $P(H_2O) = 20$ Torr.
[b] (mol of CO_2) × (mol of surface Pt)$^{-1}$ × h^{-1}.

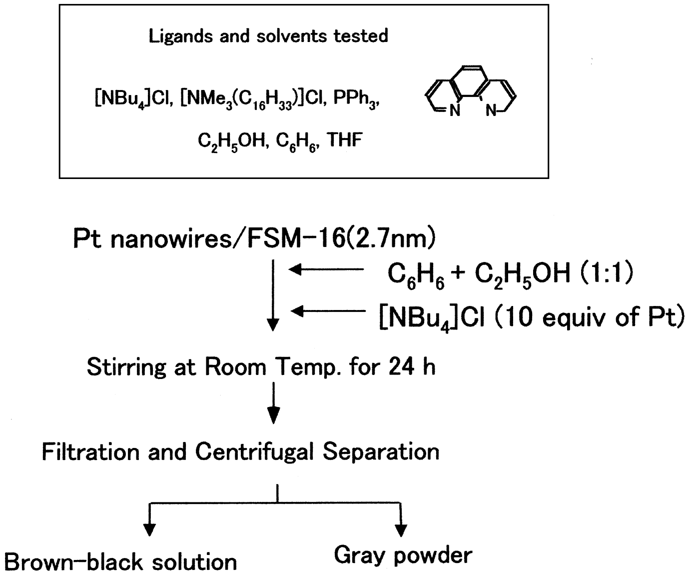

Fig. 7. A procedure for extraction of Pt nanowires from FSM-16.

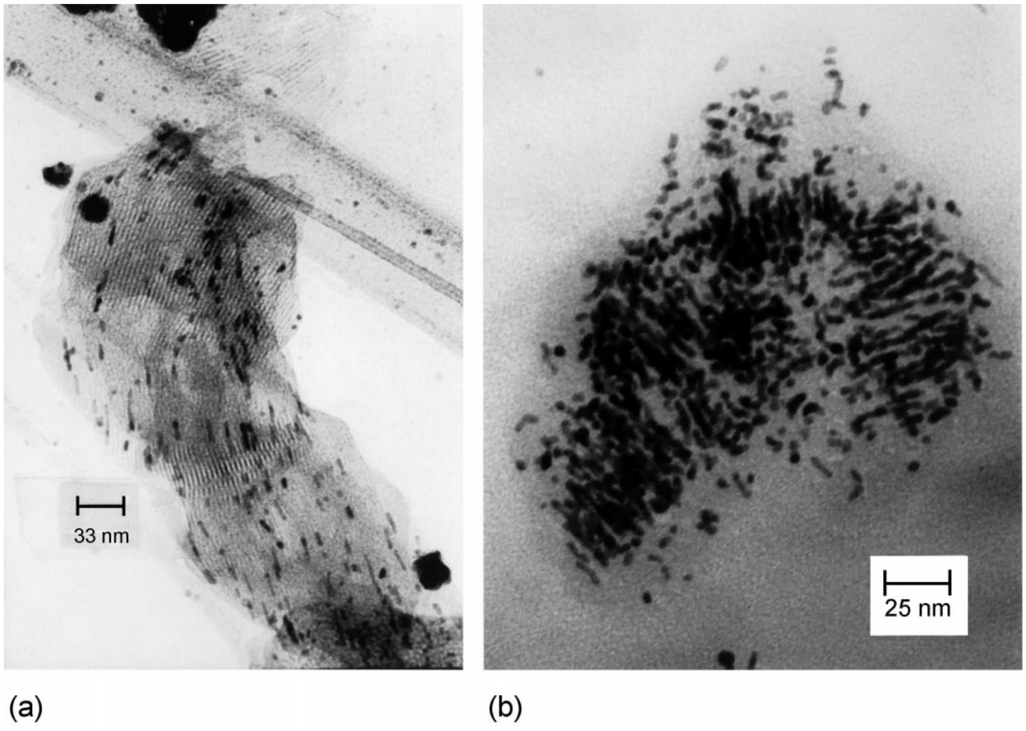

Fig. 8. TEM images of Pt nanowires: (a) before and (b) after extraction from FSM-16 with [NBu$_4$]Cl.

protected by $[NBu_4]Cl$ (or Cl^-) (Fig. 8). In fact, the TEM–EDX analysis of the extracted wires gave peaks of Pt (60–100 wt.%) and Cl (ca. 30 wt.%) without Si (0 wt.%), while Pt nanowire/FSM-16 before extraction showed the presence of Si (60–70 wt.%) and Pt (30–40 wt.%) without Cl (0 wt.%). The absence of Si after extraction clearly indicates that the nanowires are separated from FSM-16 support. Probably, the wires are extruded by forming adducts with $[NBu_4]Cl$ (or Cl^-) that covers the surface of the wires. Presumably, the surface of wires is slightly polarized to have interaction with $[NBu_4]Cl$ (or Cl^-), and the wires are stabilized as organosols [23]. The length of extracted wires was shorter than that before extraction, which suggests that long wires were divided into smaller parts with the interaction of $[NBu_4]Cl$. Pt nanoparticles were also extracted from FSM-16 by the same procedures. Triphenylphosphine, 1,10-phenanthroline, and dodecyl(trimethyl)ammonium chloride were not effective for the extraction of the nanowires/particles. The characterization and reactivity of the extracted wires is now in progress.

4. Conclusion

We have demonstrated that the ship-in-bottle technique has the benefit of selective formation of Pt carbonyl clusters in micro- and mesoporous materials. The carbonyl clusters gave Pt nanoparticles by the decarbonylation reaction. We have also revealed that Pt nanowires or particles can be produced by the photo- or hydrogen reduction of Pt(IV) ions impregnated in FSM-16. The Pt nanowires show a unique magnetic property and a high catalytic activity in the water-gas-shift reaction. Chemical extraction of the Pt nanowires and particles from FSM-16 is also possible, which would promote the utilization of mesoporous materials as a template of synthesis and isolation of metal nanocomposites. We are now studying the preparation and isolation of bimetallic nanowires.

Acknowledgements

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