Full Paper

In situ preparation of platinum nanoparticles in mesoporous silica using linear polyethyleneimine as a protective agent

Kazuki YAMAMOTO¹, Haruka SUZUKI¹, Masahiro OHASHI¹, Ryohei HAYAMI¹,
Satoru TSUKADA² and Takahiro GUNJI¹,³

1Department of Pure and Applied Chemistry, Tokyo University of Science, 2641 Yamazaki, Noda, Chiba 278-8510, Japan
2Department of Materials Science, Graduate School of Engineering, Chiba University,
1–33 Yayoi-cho, Inage-ku, Chiba 263–8522, Japan

Ordered mesoporous silica SBA-15 with homogeneously dispersed platinum nanoparticles (PtNPs) was prepared via a sol–gel process. The PtNP content in the SBA-15 support as a result of this procedure was estimated to be up to 0.029 wt % using inductively coupled plasma analysis. Small-angle X-ray scattering measurements revealed that SBA-15 with PtNPs possessed regular pores with a two-dimensional hexagonal structure and \( p6mm \) symmetry. Nitrogen adsorption/desorption measurements for SBA-15 revealed an average pore size of 5.8 nm and a Brunauer–Emmett–Teller surface area as high as 1034 \( m^2/g \); this pore size is comparable to those of SBA-15 prepared using the conventional immersion method while the specific surface area is higher. Transmission electron microscopy with energy dispersive X-ray spectrometry revealed that the PtNPs were dispersed in the as-prepared SBA-15 interpore. These results indicate that this method is a new route for preparing SBA-15 with PtNPs that suppresses aggregation between the PtNPs.

Key-words : Mesoporous silica, Platinum nanoparticles, Polyethyleneimine, Protective agents, Aggregation

1. Introduction

Metal nanoparticles, whose particle sizes are smaller than 1 \( \mu \text{m} \), have unique properties like high catalytic activities derived from large specific surface areas and surface plasmon resonances based on the quantum effect, leading to their use in many applications such as optical, electrical, and magnetic materials.¹–³ Many types of metal nanoparticles, including Pt⁴–¹¹ Pd,¹² Ag,¹³ and Au¹⁴ nanoparticles, have been prepared through chemical treatment methods, including reduction, thermal decomposition, and vapor-phase growth from precursors. Metal nanoparticles are generally supported on an inorganic or organic polymer matrix to achieve larger surface areas and to suppress aggregation. In particular, platinum nanoparticles (PtNPs) have received much attention as catalysts for coupling reactions,⁵ oxygen reduction on an electrode,⁶ and hydrogenation of olefins.⁷ As a supporting material, mesoporous silica (MPS) is known as a promising candidate for immobilizing metal nanoparticles in silica channels. MPS is typically prepared via a sol–gel process with alkoxy-silanes in the presence of a surfactant micelle template; the MCM-41 and SBA-15 types with different pore sizes (2–10 nm) and structures (two-dimensional hexagonal and three-dimensional cubic) are fabricated by modifying the preparation conditions such as the concentration, pH, and surfactant template.⁹–¹⁸

PtNPs homogeneously dispersed in MPS interpores exhibit high catalytic activity and durability. It is well known that the preparation procedure significantly affects the catalytic performance of PtNPs. Several methods to immobilize PtNPs in MPS interpores have been presented. Song et al. reported immersion of the precursor in MPS followed by reduction, which causes aggregation between the PtNPs.⁵ To suppress aggregation, Zhang et al. demonstrated that the outer surface of SBA-15 is poisoned with Si–CH₃ groups, and modified SBA-15 interpore channels with Si–H groups and then reduced hexachloroplatinic acid hexahydrate (H₂PtCl₆·6H₂O) in situ, leading to the dispersion of platinum nanoclusters.⁸ Although PtNPs are well dispersed in MPS interpore selectivity without aggregation as a result of this procedure, this route requires complex multi-step modification of the SBA-15 surface before the reduction of the Pt precursor. For the other methods, utilizing PtNPs stabilized by polymer protective agent followed by thermal decomposition of polymer is promising way to fabricate MPS. As protecting polymers covering PtNPs, poly(methacrylic acid), polyvinylpyrrolidone (PVP), and polyamideamine dendrimer have been reported.⁹ Koebel et al. reported that PVP stabilized PtNPs as a hydrophilic ligand polymer, but is restricted to

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neutral or basic conditions owing to its low stability in low pHs. Song et al. also reported the preparation of Pt/SBA-15 using PtNPs stabilized by PVP via a neutral sol-gel process and hydrothermal growth of the MPS precursor with a template polymer to prevent the collapse of the Pt precursor. Considering MPS is usually prepared in a low pH region, it is desired that PtNP precursors are sufficiently stable in low pHs.

In a previous work, we reported the preparation of PtNPs stabilized by an ethyleneimine and N-methyl-ethylenimine copolymer [poly(EI-co-NMEI)] as a protective agent through the reduction of H₂PtCl₆·6H₂O in the presence of the polymer, as shown in Fig. 1. The sizes of the PtNPs were 1.8–3.6 nm and the PtNPs were stable enough to be used in severe acidic or basic sol–gel conditions, in pHs ranging from −1 to 15. In this paper, therefore, we propose a simple method to produce well-dispersed polyethyleneimine-stabilized PtNPs directly using a sol–gel system, namely the “in situ method”. With this method, it is considered that the acid-stable precursor is installed in the MPS interpores, suppressing aggregation between PtNPs. Dispersity and morphology studies of the resulting PtNPs in SBA-15 (Pt/SBA-15), which is a common type of MPS, were conducted by comparing them with Pt/SBA-15 prepared using the “immersion” method to probe the effectiveness of this method.

2. Experimental

Hexachloroplatinic(IV) acid hexahydrate, sodium borohydride, formic acid, and formaldehyde were purchased from Wako Pure Chemical Industries, Ltd. Pluronic P123 and poly(2-ethyl-2-oxazoline) (average molecular weight Mₙ = 5000, polydispersity index ≤ 1.2) were purchased from Sigma-Aldrich Co. LLC. Hydrochloric acid (6 mol/L) and 28% ammonia aqueous solution were purchased from Kanto Chemical Co., Ltd. Tetraethoxysilane (TEOS) was obtained from Shin-Etsu Chemical Co., Ltd. These chemicals were used as received without further purification. Anion-exchange resin Dowex 50WX8 (74–149μm) was purchased from the Dow Chemical Company. Ultrafiltration membrane (ADVANTEC, Polysulfone Q0100076E) was purchased from Toyoh Roshi Kaisha, Ltd.

Inductively coupled plasma (ICP) analysis was performed with a Shimadzu simultaneous ICP atomic emission spectrometer (ICPE-9000). Small-angle X-ray scattering (SAXS) spectra were recorded using an Anton-Paar SAXSess camera with PANalytical W3830 glass using Cu-Kα radiation (wavelength of 0.154 nm). Transmission electron microscopy (TEM) was performed using a JEOL JEM-2100F on an Okensyoji Cu microgrid. Scanning electron microscopy (SEM) was performed using a JEOL NeoScope JCM6000Plus. Nitrogen adsorption/desorption measurements were conducted using a MicrotracBEL BELSORP-max.

PtNPs protected by poly(EI-co-NMEI) were prepared according to the literature. In brief, linear polyethyleneimine (LPEI, Mₙ = 2150) was synthesized from poly-(2-ethyl-2-oxazoline) and hydrochloric acid. Poly(EI-co-NMEI) (52% of NH groups were methylated) was synthesized via the Eschweiler-Clarke reaction of LPEI with formaldehyde and formic acid. Poly(EI-co-NMEI) protected PtNPs (52% methylated) were prepared from chloroplatinic(IV) acid hexahydrate and sodium borohydride and obtained as a brown liquid. The particle diameter of the obtained product was confirmed using TEM to be approximately 3 nm.

SBA-15-supported PtNPs (Pt/SBA-15) were prepared using two procedures, the “in situ” and “immersion” methods, and the products will be referred to as ins-Pt/SBA-15 and imm-Pt/SBA-15, respectively. In the in situ method, to a flask equipped with a reflux condenser, 6 mol/L hydrochloric acid (40 g), deionized water (110 g), and Pluronic P123 (4.0 g) were added, and the mixture was stirred for 0, 3, 6, or 12 h at 35°C. Subsequently, poly(EI-co-NMEI)-protected PtNPs (25 mg) and TEOS (8.5 g) were added to the solution, which was heated at 35°C for 20 h and then at 80°C for 24 h. The solution was cooled to room temperature and filtered. The powder was washed with water and ethanol, and then heated at a rate of 10°C/min to 300°C and kept at that temperature for 6 h to give Pt/SBA-15. Bare SBA-15 was prepared in the same way but without the addition of the PtNPs. In the immersion method, bare SBA-15 (2.5 g) was immersed in an aqueous solution containing PtNPs (25 mg) and ultrasoundated at 30°C for 3 h. After filtration, the powder was poured into ethanol (200 mL) and the solution was heated at 60°C with stirring for 6 h. After filtration, the powder was calcined with the temperature increasing at 60°C/h for 8 h and then at 500°C for 6 h to give Pt/SBA-15.

3. Results and discussion

3.1 Preparation of PtNPs in SBA-15

Two types of Pt/SBA-15 were prepared via different routes, as shown in Fig. 2. In the in situ method, the template surfactant (Pluronic P123) was dissolved in hydrochloric acid. Subsequently, PtNPs protected by poly(EI-co-NMEI) and TEOS [Fig. 2(a)] were added to the solution. After heating at 80°C, the obtained powder was filtered out and calcined at 500°C to decompose the protecting polymer to afford ins-Pt/SBA-15. On the other hand, in the immersion method, preliminarily prepared bare SBA-15 was immersed in poly(EI-co-NMEI)-PtNPs in aqueous solution and subsequently calcined to give imm-Pt/SBA-15 [Fig. 2(b)].

The preparations of Pt/SBA-15 via the in situ and immersion methods are summarized in Table 1. The yields of Pt/SBA-15 from both methods were similar because the modification amounts of the PtNPs were much
lower than the weight of the SBA-15 support. The Pt contents of the Pt/SBA-15 samples were estimated via ICP analysis. With the in situ method, the Pt content increased up to 29% with increasing stirring time of the mixture of Pluronic P123, hydrochloric acid, and the platinum precursor because stirring time affects the homogeneity in the solution owing to the adoption of the silica support to an extent. However, the Pt contents of immobil-Pt/SBA-15 were lower than that of imm-Pt/SBA-15. According to a previous report concerning immobilization of platinum particles on MCM-41 MPS through a similar method, the modified platinum amount can be as high as 0.3 wt%. This phenomenon might be related to silica surface charges. In general, silica surface charges are negative owing to anionic Si–OH groups. However, in acidic conditions, the silica surface becomes neutral because of the protons, preventing interactions with cationic protecting agents. To improve the platinum incorporation on MPS with the in situ method, MPS with a well-defined pore structure must be prepared in basic sol–gel conditions, which is difficult.

### 3.2 Structural analysis of SBA-15

The structural analysis of ins-Pt/SBA-15 was performed using the sample stirred for 12 h during the preparation. SAXS measurements were performed to obtain structural information on the prepared MPS. The SAXS patterns are shown in Fig. 3. The scattering vector (q) is related to the diffraction angle (θ) by the Bragg equation (λ = 2d sin θ) and q = 4π sin θ/λ (λ = 0.15418 nm). The peaks at q = 0.6, 1.1, and 1.3 nm⁻¹ were assigned to (100), (110), and (200), indicating the existence of regular pores with two-dimensional hexagonal p6mm symmetry. However, the intensities of the peaks ascribed to (100) and (200) for imm-Pt/SBA-15 were lower than those of bare SBA-15, indicating that part of the pore was covered by the nanoparticles. The peak of ins-Pt/SBA-15 ascribed to (100) was also weaker than that of bare SBA-15, indicating that skeletal deformation caused by expansion of the protective polymer occurred during calcination. The calculated lattice constants (a) and interplanar spacings (d) are shown in Table 2. The lattice constant (a) was calculated as a = d_{100} × 2 × √3. According to the interplanar spacing ratios, all samples have hexagonal structures (d_{100}:d_{110}:d_{200} = 1:1/√3:1/2). Thus, the pore structures of all SBA-15 products were nearly identical.

The pore structures of Pt/SBA-15 were investigated using TEM, and the results are shown in Figs. 4 and 5. Previously we found that the sizes of Pt particle of the precursor, LP(EI-co-NMEI)-PtNPs, were 2–5 nm. With the immersion method in Figs. 4(a) and 4(a’), the large black dots distributed on the SBA-15 surface of ca. 15 nm
in size was ascribed to the aggregated particle likely generated during preparation process. On the other hand, the in situ method in Fig. 4(b) and 4(b’), the large black dots could not be observed, indicating that the in situ method clearly suppresses the aggregation between the platinum particles. Bright-field (BF) images in Fig. 4(a’’a) is also seemed aggregated PtNPs as white dots distribute on SBA-15. Element mapping with energy dispersive X-ray spectrometry (EDS) mapping image in Fig. 4(a’’b) show that Si and O atoms correspond to SBA-15 framework. Aggregated particles were confirmed in imm-SBA-15, while large particles were not observed in ins-SBA-15 in Fig. 4(b’’b). TEM image of PtNPs in ins-SBA-15 at high magnification is shown in Fig. 5(a). The fine black dots of 2–5 nm enclosed in a round frame corresponded to the PtNPs, whose particle size was almost the same to the precursor, LP(EI-co-NMEI)-PtNPs, as shown in Fig(b). This result also indicates that the in-situ method suppresses aggregation between PtNPs.

TEM line profile was also conducted to investigate interpore elemental information. In Fig. 6(a), line peaks ascribed to Si and O elements corresponded to the silica framework. A white particle ascribed to the Pt atom was

| Table 2. Lattice constants and interplanar spacings of prepared SBA-15 |
|------------------|------------------|------------------|------------------|
|                  | Lattice constant/\( \text{nm} \) |
|                  | \( a_0 \) | \( d_{100} \) | \( d_{110} \) | \( d_{200} \) |
| imm-Pt/SBA-15    | 11.1   | 9.63   | 5.57   | 4.84   |
| bare SBA-15      | 11.2   | 9.72   | 5.56   | 4.83   |
| ins-Pt/SBA-15    | 11.1   | 9.63   | —      | 4.83   |

Fig. 4. (a), (a’) TEM images of imm-Pt/SBA-15 and (a’’) their BF image with EDS mapping, and (b), (b’) TEM image of ins-Pt/SBA-15 and (b’’) BF image with EDS mapping.
larger than silica pore, indicating that the particle is on the SBA-15 surface. The peak in Fig. 6(a’), enlargement of Fig. 6(a), is clearly detecting Pt element and the Pt peak was diminished in dark religion in BF image, indicating SBA-15 framework contains PtNPs. In addition, the comparatively fine particle was observed in Fig. 6(b), suggesting that PtNPs are well dispersed in SBA-15 interpore.

The morphology of the prepared SBA-15 surface was observed by SEM, which is shown in Fig. 7. The bare SBA-15 was observed as needle crystal in overall and imm-SBA 15 was observed as block like crystal compared to bare SBA-15. This might because immersion and calcination process to immobilize PtNPs deformed the surface morphology. On the other hand, SBA-15 by in situ process was observed as rod like structure. In this method, formation of SBA-15 structure was not the same because formation of the SBA-15 in the sol–gel process contains polymer-protected PtNPs.
To determine the pore structure, nitrogen adsorption/desorption measurements of SBA-15 were carried out. The isotherms and pore size distribution curves are shown in Fig. 8, and the Brunauer–Emmett–Teller (BET) surface areas, pore diameters, and pore volumes are summarized in Table 3. As shown in Fig. 8(a), all isotherms showed type-IV(a) adsorption/desorption behavior, as categorized by the International Union of Pure and Applied Chemistry, indicating the existence of meso-sized pores, while the total adsorbed volumes were rather different. As shown in Fig. 8(b), the pore size distributions of the SBA-15 samples were almost identical. Comparison of the calculated BET surface areas of the prepared SBA-15 samples revealed that the in situ method led to the largest values. This result means that poly(EI-co-NMEI)-protected PtNPs increase the surface area, while the immersion method led to the mesopores on SBA-15 being covered.

Comparing the in situ and immersion methods revealed that the in situ method gives Pt/SBA-15 as fine particles with a high specific surface area, but with a lower degree of crystallinity than that of bare SBA-15. On the other hand, the immersion method gave Pt/SBA-15 with a lower specific surface area and high crystallinity using a simple procedure. Therefore, the in situ method would be an effective route for preparing SBA-15 with PtNPs that would suppress PtNP aggregation.

4. Conclusions

Ordered MPS with homogeneously dispersed poly-(ethyleneimine-co-N-methylethyleneimine)-stabilized Pt NPs was prepared successfully under acidic sol–gel conditions. Pt/SBA-15 prepared using this in situ process had mesopores approximately 5.8 nm in size, whose parameters were almost identical to those of bare SBA-15 and Pt/SBA-15 prepared via the immersion method, indicating
that the MPS skeleton had not collapsed. The results of TEM and SAXS measurements supported the generation of SBA-15 without any collapses. This procedure provides a new approach for preparing Pt/SBA-15, although the catalyst activity could not be evaluated. The results of TEM-EDS and line profile indicated that the in situ method clearly suppressed aggregation between the PtNPs in SBA-15 during calcination. This in situ approach will be useful for incorporating other metal nanoparticles into mesoporous supports with any additional treatment of SBA-15, while preparation of polymer-protected platinum nanoparticle is required. Further investigation will be carried out to evaluate the practical applicability.

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| Table 3. Pore sizes and surface areas of prepared SBA-15 |
|-----------------|-----------------|-----------------|
| SBA-15          | $S_{BET}$       | Average          | Pore volume          |
|                 | ($m^2/g$)       | pore size ($nm$) | ($cm^3/g$)          |
| bare SBA-15     | 854             | 5.84             | 0.87               |
| imm-Pt/SBA-15   | 584             | 5.83             | 0.74               |
| ins-Pt/SBA-15   | 1034            | 5.81             | 1.33               |