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Application of Microwave-Assisted Deposition for the Synthesis of Noble Metal Particles on Ti-Containing Mesoporous Silica

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Abstract A facile and unique methodology to synthesize the nano-sized and uniform noble metal (Pt and Au) particles has been developed using mesoporous silica support including single-site titanium oxide moieties (Ti-HMS) under microwave irradiation. Characterization by CO adsorption, XAFS, and TEM analysis revealed that the size of metal particles depends on the preparation methods and that the smaller sizes of metal particles were formed on the microwave-assisted metal catalysts compared to the conventionally prepared impregnated catalysts. These nano-sized metal catalysts are useful as efficient catalysts for the various reactions such as the hydrogenation of nitrobenzene and oxidation of CO. This method is also successfully applicable to the deposition of Au metal with smaller size on the Ti-HMS.

Keywords Microwave-assisted deposition · Single-site titanium oxide moieties · Nano-sized metal

1 Introduction

Nanometer-sized transition metal particles have been intensively pursued due to their technological and fundamental importance. These potentially advanced materials often exhibit unique electronic, optic, and magnetic properties as well as catalytic functions, which cannot be achieved by their bulk counterparts [1]. Attaining the precise control of particle size and overall particle size distribution is one of the most important goals to provide unique chemical and physical properties. Until now, various approaches for nanoparticle synthesis based on chemical reduction, sonication, γ-ray radiolysis, UV-light irradiation, thermal decomposition, vapor deposition, and electrochemical synthesis, have been investigated [2–4]. These methods, however, are in principle more useful to produce colloids and clusters in the nanoscale. The conventional preparation method of the supported metal catalysts is based on impregnation-reduction process, which does not provide satisfactory control of particle size. The novel strategy to design nano-sized metals with well-controlled size on solid supports has been desired in order to develop the efficient and practical catalysts [5].

Recently, microwave dielectric heating has attracted a great deal of attention as a new promising method in the organic and inorganic synthesis fields [6]. It is widely accepted that the microwave irradiation enables rapid, uniform, and energy efficient heating, which also applicable to the simple preparation of metallic nanostructured materials [7]. For example, Ru, Ag, Pt, PtNi, Cu nanoparticles, ZrO_2, Ag nanowire, and zeolite have been prepared [8–14]. As a supported system, only carbon-supported and polymer stabilized colloids have been synthesised [15–18]. Although much studies dealing with the preparation of metal colloids and clusters are reported, the microwave-assisted synthesis of metal particles supported on silica based porous materials is unexplored so far.

Mesoporous silica and zeolite materials have been attracted to control the photocatalytic and photochemical processes. Especially, the isolated and tetrahedrally coordinated Ti-oxide moieties included within mesoporous silica and zeolite materials can exhibit the unique and

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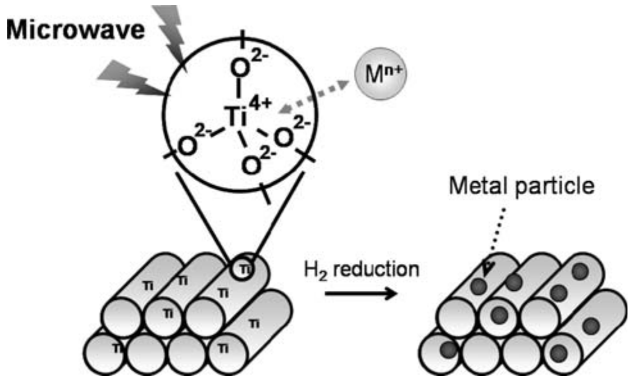

Scheme 1 Microwave-assisted deposition method on single-site

effective photocatalysis under UV-light irradiation and named as "single-site photocatalyst" [19–26]. We have previously developed a novel technique to synthesize nano-sized metal particles on the isolated and tetrahedrally coordinated Ti-oxide moieties. The excited state of Ti-oxide moieties under UV-light irradiation act as anchor to deposit metal precursor such as Pt, Pd and Ag [27, 28]. Along this line, we have found and herein wish to report that the Ti-containing mesoporous silica also act as a promising platform to deposit uniform and small metal particles under microwave irradiation (Scheme 1).

2 Experimental

The synthesis of the Ti-containing mesoporous silica (Ti-HMS) was carried out by using tetraethoxysilane (TEOS: $Si(OEt)_4$) as a silica source, titane tetraisopropoxide (TPOT: $Ti(OiPr)_4$) as a titanium source of precursor materials, and dodecylamine (DDA: $CH_3(CH_2)_{11}NH_2$) as template (Ti/Si = 0.01). The above reagents were mixed with ethanol, 2-propanol, and water, and then stirred at room temperature for 24 h, followed by filtration, drying at 383 K, and calcined at 823 K for 5 h [29]. A mixture of Ti-HMS and an aqueous solution of H_2PtCl_6 (Ti/Pt = 1.0) were irradiated by microwave (500 W, 2,450 ± 30 MHz, MWO-1000S, Tokyo Rikakikai Co. Ltd) for 15 min with stirring. After the filtration, the sample was dried at 383 K for 12 h, calcined at 723 K for 5 h and reduced by H_2 (20 mL min^{-1}) at 473 K for 2 h, giving a Mw-Pt/Ti-HMS (Pt: 0.8 wt%). In comparison, the Pt deposition on Ti-HMS was also performed by the conventional impregnation method (imp-Pt/Ti-HMS).

Inductively coupled plasma measurements were performed using a Nippon Jarrell-Ash ICAP-575 Mark II. Powder X-ray diffraction patterns were recorded using a Rigaku RINT2500 diffractometer with Cu Kα radiation ($\lambda = 1.5406$ Å) operated with 40 kV and 200 mA at 295 K. The specific surface area and pore distribution measurements were carried out BELSORP-max (BEL JAPAN, Inc.) at 77 K. The sample was degassed under vacuum at 473 K prior to data collection. CO pulse adsorption was performed to measure Pt surface area by BEL-CAT (BEL JAPAN, INC). TEM images were recorded with Hitachi H-800 operated at 200 kV. The Pt L_{III}-edge spectra of these catalysts were measured in fluorescence mode at the SPring-8 BL01B1 station.

Hydrogenation of nitrobenzene was performed as follows. Into a reaction vessel (50 cc) with a reflux condenser were placed catalyst (15 mg), nitrobenzene (2 mmol), and methonol (10 mL). The resulting mixture was reacted at 323 K for 4 h under 1 atm of H_2 with magnetic stirring. Analytical GC was performed by an internal standard technique using a Shimadzu GC-14B (TC-1).

CO oxidation was carried out using a fixed-bet reactor enclosed in a quartz-tube placed in an electronic furnace. The catalyst (80 mg) was placed in a quartz-tube reactor and heated at desired temperature in a gaseous mixture of CO (0.16%), O_2 (0.33%), and He (balance) (total flow rate: 30 mL/min, SV = 2,400 h^{-1}). The CO conversion was continuously monitored by a Shimadzu GC-14B GC (Molecular Sieve 5A).

3 Results and Discussion

From the elemental analysis of samples, it was found that the precursor of Pt metal can be successfully deposited on the Ti-HMS under microwave irradiation of the slurry of Ti-HMS in an aqueous H_2PtCl_6 solution. On the other hand, Pt metal precursor could not be deposited on HMS support without Ti-oxide moieties under the identical conditions. Without microwave irradiation conditions, the deposition hardly occurred on the Ti-HMS support. These results suggested that the existence of the tetrahedrally coordinated Ti-oxide moieties and microwave irradiation were indispensable for attaining the deposition of Pt precursors. It was found that color of samples turned from white into gray and color density increased with increasing irradiation time. The change in color shows the deposition of Pt particles on the Ti-HMS support and indicates that amount of Pt increased. The XRD peaks attributable to the Pt metal or oxide could not be confirmed because of the smaller size of nanoparticles dispersed on the silica surface. Nitrogen physisorption experiments showed the type IV isotherm profile, typical of mesoporous materials. The pore size and surface area of Ti-HMS were 2.4 nm and 1,187 m^2 g^{-1}, respectively. Even after Pt deposition, the pore size and high surface area were remained.

The X-ray absorption fine structure (XAFS) measurement was performed to confirm the state of Pt. The white line at the Pt L_{III}-edge is an absorption threshold resonance attributed to the electronic transitions from 2p3/2 to unoccupied states above the Fermi level and is intensified with an increase in the d-band vacancies as a result of oxidation [30]. The XANES spectrum of the Pt deposited on Ti-HMS is similar to that of Pt foil, suggesting the presence of a metal state of Pt. In the Fourier transforms Pt L_{III}-edge EXAFS spectra, the Mw-Pt/Ti-HMS and imp-Pt/Ti-HMS exhibited a peak at approximately 2.7 Å due to the contiguous Pt–Pt bond in the metallic form nanoparticles (Fig. 1). The peak intensity of the Mw-Pt/Ti-HMS is significantly lower than that of the imp-Pt/Ti-HMS, which is due to the smaller particle size of the Pt. Evidently, curve-fitting analysis revealed that coordination number (CN) and interatomic distance (R) in the Mw-Pt/Ti-HMS are 6.3 and 2.74 Å, in the imp-Pt/Ti-HMS are 10.2 and 2.78 Å, respectively.

In an effort to compare the catalytic activity of the Mw-Pt/Ti-HMS with that of the imp-Pt/Ti-HMS, hydrogenation of nitrobenzene to aniline was carried out under an atmospheric H_2 pressure, as shown in Table 1. The Mw-Pt/Ti-HMS catalyst exhibits higher activity than the imp-Pt/Ti-HMS one. In CO oxidation, the catalytic activity of the Mw-Pt/Ti-HMS catalyst is six times higher than the imp-Pt/Ti-HMS one (Table 2). Therefore, it is suggested that microwave-assisted method is very useful for preparation of efficient Pt nanoparticles under these catalytic reactions. The dispersion, surface area, and average particle size of Pt metals were estimated by the pulsed CO adsorption measurement, as summarized in Table 3. These results are in good correspondence with FT-EXAFS measurements. Moreover, TEM observation carried out to confirm Pt particles size and size distribution. As shown in Fig. 2, the Pt nanoparticles with a mean diameter of 3.1 nm having a narrow size distribution were formed on the Mw-Pt/Ti-HMS catalyst. This result is in agreement with CO adsorption measurement, where the Mw-Pt/Ti-HMS catalyst exhibited higher dispersion and the smaller size of Pt metal compared to that of the imp-Pt/Ti-

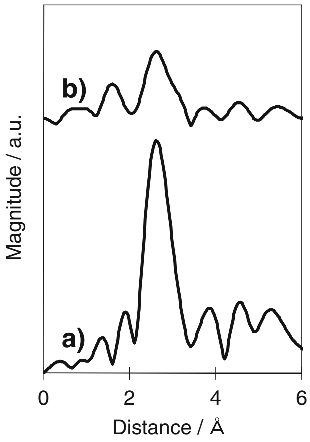

Fig. 1 Pt L_{III}-edge FT-EXAFS spectra of **a** imp-Pt/Ti-HMS and **b** Mw-Pt/Ti-HMS

Table 1 Result of nitrobenzene hydrogenation

Sample	Reaction rate/mmol min^{-1} g^{-1}	Reaction rate/mmol min^{-1} g-Pt^{-1}	TOF/h^{-1}
Mw-Pt/Ti-HMS	0.49	63.8	697
imp-Pt/Ti-HMS	0.11	22.9	291

Conditions: nitrobenzene (2 mmol), ethanol (10 mL), catalyst (15 mg), 323 K, 1 atm of H_2. Analysis was performed by GC (TC-1) using an internal standard technique

Table 2 Results of CO oxidation

Sample	Reaction rate/mmol min^{-1} g^{-1}	Reaction rate/mmol min^{-1} g-Pt^{-1}
Mw-Pt/Ti-HMS	6.17	812
imp-Pt/Ti-HMS	1.00	199

Conditions: CO 0.16%, O_2 0.33%, He balance, catalyst 80 mg, SV 2,400 h^{-1}, total flow rate 30 mL min^{-1}. Analysis was performed by GC (Molecular Sieve 5A)

Table 3 The summarized results of metal dispersion measurement using CO adsorption

Sample	Dispersion/%	Surface area/m^2 g^{-1}	Particle size/nm
Mw-Pt/Ti-HMS	36.1	89.2	3.13
imp-Pt/Ti-HMS	10.7	26.5	10.5
Mw-Au/Ti-HMS	78.0	207	1.50
imp-Au/Ti-HMS	3.83	10.2	30.5

The samples were pretreated under O_2 folw at 673 K for 15 min, and subsequently H_2 flow at 673 K for 15 min. The adsorption was measured at 323 K and CO flow rate was 20 mL min^{-1}

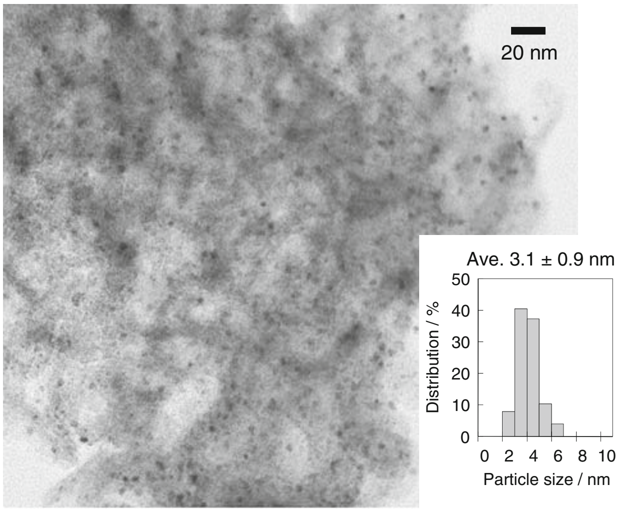

Fig. 2 TEM image and size distribution of Mw-Pt/Ti-HMS

HMS. The particle size and dispersion of Pt metal particles play important role for the above catalytic reactions.

By the microwave-assisted method, Au nanoparticles were also successfully deposited on Ti-HMS. The $HAuCl_4$ aqueous solution and Ti-HMS were mixed and stirred under microwave irradiation for 15 min, giving a Mw-Au/Ti-HMS as a bright pink powder. From the results of pulsed CO adsorption measurement, the Au metal particles of the Mw-Au/Ti-HMS were found to be highly dispersed with a smaller average particle size compared to those of the conventionally prepared imp-Au/Ti-HMS (Table 3).

The mechanism of the formation of the noble metal particles on the Ti-containing support is still under investigation. It has been reported that the incorporation of Ti or Zr atoms within the silica framework creates new adsorption site and the adsorption strength increases in the order $Si-OH < Zr-OH < Ti-OH$ [31–33]. Therefore titanol groups in the Ti-HMS has great impact on microwave irradiation and led to local heating that promote the deposition of Pt precursor. The direct interaction between the precursor species of the nano-sized metal and the activated Ti-oxide moieties has possibility to design the unique and active nano-sized metal catalysts.

4 Conclusions

It is clarified that single-site photocatalyst enables high dispersion of Pt and Au precursor on the activated Ti-oxide moieties using the microwave-assisted deposition method. The Pt and Au nanoparticles showed higher dispersion and smaller particle size than those of impregnation method. In hydrogenation of nitrobenzene and CO oxidation reactions, the Mw-Pt/Ti-HMS catalyst exhibited higher activity than the imp-Pt/Ti-HMS catalyst. This method using microwave and single-site catalysts is facile and useful for preparation of nano-sized metal particles, and can be further applicable in various fields to design unique functional materials.

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