SYNTHESIS OF NANOSTRUCTURED PARTICLES/FILMS IN MICRO- AND MESO-POROUS MATERIALS USING SUPERCRITICAL CO_2.

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Nanostructured particles and films are of great interest with respect to their applications as catalysts, and in sensors, optics and electric devices. In this study, supercritical fluids (SCFs) are demonstrated as excellent solvents for loading nanoparticles and coating thin films onto nanoporous materials.

Firstly, SCFs were used for the preparation of size-controlled Pt nanoparticles in micro- and meso-porous silica with uniform pore sizes, FSM-16 series(pore size; 1.6, 2.1, 2.4 and 3.5 nm). Pt precursors, Pt(acac)$_2$ dissolved in supercritical CO_2 with acetone, were loaded on the FSM-16, followed by reduction in flowing in H_2. A TEM investigation revealed that the size-controlled Pt nanoparticles can be prepared in micro- and meso-pores of FSM-16 by impregnation in a supercritical fluid solvent. The particle size increased almost linearly with the increase in the pore diameter of FSM-16. This is not the case for impregnation in a liquid solvent, acetone. Although Pt particles can be introduced into the pores of FSM-16 (3.5 nm), the Pt particles can not be introduced into the pores of FSM-16 (1.6, 2.1, 2.4 nm). The investigation of the influence of particle size on catalytic activity indicates that smaller Pt nanoparticles more efficiently catalyze the CO oxidation reaction.

Secondly, SCFs were used for tailoring the porous structures of FSM-16. Silica precursors, tetraethylorthosilicate (TEOS) dissolved in supercritical CO_2 or in liquid ethanol, were impregnated onto FSM-16. The pore size of all the FSM-16 series decreased after coating in the supercritical solvent. On the other hand, silica was not introduced into pores smaller than 2.4 nm by coating in the liquid solvent.

These two results are elucidated in terms of the penetration difference into the nanoporous structures of supercritical solvents and liquid solvents.

1. INTRODUCTION

Metal or semiconductor nanoparticles and films are of great interest with respect to their applications as catalysts, and in sensors, optics and electric devices. Their properties depend on their nanoscale structures. Thus, the accurate control of their nanoscale structures is very important for these applications. Nanoparticles have been synthesized by the oxidation or reduction of precursors.[1] Micelles[2] and stabilizing polymers[3] have been used to restrict particle aggregation. Porous materials have been used as hosts for the synthesis of nanoparticles.[4-8] The synthesis of nanoparticles using porous materials with uniform pore sizes and high surface area as hosts have attracted interest ever since the sizes of the nanoparticles can be easily directed in well-defined matrices. Mesoporous (2-50nm) silica, FSM-16,[4] MCM-41,[5] SBA-15[6] are used for the synthesis of the nanoparticles of Pt, Pd, Rh, Au and Ag. A

microporous (<2nm) host, zeolite, can also be used for the synthesis of metal carbonyl clusters,[7] which takes a few days for the synthesis in a liquid phase solvent[7] and the reduction process generates larger particles on the external surface. These are due to the limitation of mass transfer in the liquid solvent and difficulty in controlling the growth rate of the nanoparticles from salt-type precursors, even though they are smaller than other types of precursors such as organometallic molecules. The filtration process using the vapor phase such as the CVD process is a very effective method for preparing particles or thin films on a nanometer scale. However, the precursors are limited in terms of high volatility and thermal stability. Conventional methods to prepare nanoparticles in porous matrices often yield nanoparticles of various sizes in the internal pores and on the external surface of the porous matrices.[6, 8] Accurate size control of nanoparticles using porous materials as hosts with a wide range of uniform pore sizes including micropores and the investigation of the relationship between particle size and their properties still remain challenging.

Supercritical fluids (SCFs) have excellent properties of noncohesivity, high diffusivity and controllable solubility. Thus, SCFs are expected to overcome these previously mentioned limitations of conventional solvents. SCFs have been demonstrated as excellent solvents for chemical reactions in nano-sized spaces.[9-12] The templating process using SCFs, denoted as the Nanoscale Casting using Supercritical Fluid (NC-SCF) process has been developed to replicate nanoscale and macroscopic structures of templates in metal[9] or metal oxide[10] replicas.

In this study, SCFs are used for the preparation of size-controlled Pt nanoparticles in micro- and meso-porous silica with uniform pore sizes, $C_nFSM-16$ (n=8, 10, 12, and 16). Pt precursors, $Pt(acac)_2$ dissolved in supercritical CO_2 with acetone, were loaded on the FSM-16, followed by reduction in flowing in H_2. The investigation of the influence of particle size on catalytic activity indicates that smaller Pt nanoparticles more efficiently catalyze the CO oxidation reaction. These results are compared with the samples prepared in the liquid phase. The SCFs were also used for coating onto nanoporous structures. By using micro- and meso-porous silica with a uniform pore size, FSM-16, we verified how small space SCFs can impregnate, compared with those in liquid solvents.

2. EXPERIMENTAL SECTION

2.1 Pt NANOPARTICLES ON FSM-16 The synthesis of the Pt nanoparticles was performed using micro- and meso-porous silica, $C_nFSM-16$ (n=8, 10, 12,and 16), where the value n denotes the carbon number in the alkyl chain of the surfactant template. These FSM-16 series are obtained by the synthesis procedures reported in the literature.[13] Acetone (5mL) along with $Pt(acac)_2$ (0.5g) were placed in a stainless steel autoclave (50mL). A stainless steel basket with 1g of FSM-16 was then fixed in the upper portion of the autoclave. The closed autoclave was filled with CO_2 and heated in an oil bath at 423 K and 32 MPa for 2 hours. After this treatment, the recovered samples were treated while the temperature was gradually increased from room temperature to 673 K for 2 hours and maintained for 1 hour in flowing H_2/N_2 (100/900 mLmin^{-1}.) for reduction of the Pt precursors. For comparison, the samples were prepared without supercritical fluids, in which 1 g of FSM-16 was immersed in 50 mL of liquid acetone with 0.5 g of $Pt(acac)_2$ at 423 K for 2 hours in an autoclave.

2.2 SILICA COATING ON FSM-16 Silica was coated on micro- and meso-porous silica, $C_nFSM-16$ (n=8, 10, 12 and 16). The experimental equipment for silica coating was reported elsewhere[10]. TEOS (30mL) was placed at the bottom of a stainless steel autoclave (1000mL). A

stainless steel cage with 1 g of FSM-16 sealed in a glass ampoule after vacuum degassing was fixed in the upper portion of the autoclave. The closed autoclave was filled with CO_2 and heated by an external electric heater at 343 K and 30 MPa. After a treatment time of 2 h, the pressure was released by venting. The glass ampoule was found to be crushed after these treatments.

For comparison, samples were prepared in a liquid solvent. One g of FSM-16 sealed in a glass ampoule after vacuum degassing was immersed in 970 mL of ethanol with 30 mL of TEOS in a beaker. The glass ampoule was broken in the liquid solution. The samples were stirred using a magnetic stirrer and heated at 343 K for 2 h.

3. RESULTS AND DISCUSSION
3.1 Pt NANOPARTICLES ON FSM-16
A TEM investigation revealed that the average particle size of Pt nanoparticles impregnated on $C_nFSM-16$ (n=8, 10, 12, and 16) in a supercritical fluid solvent before the reduction treatment is 1.5, 1.8, 2.1, and 2.4 nm. The particle size is slightly smaller than the pore diameter of FSM-16 and it increases with an increase in the pore diameter. This would be due to the impregnation of the particles mainly inside the pores of FSM-16. The particles are highly dispersed and have a small distribution. TEM images of the Pt-supported FSM-16 prepared in a supercritical fluid solvent after reduction in flowing H_2 are shown in Figure 1. As shown in Figures 1a-1d, the particles are still inside the pores of FSM-16 even after the reduction treatment. It was found that the particle size of the Pt nanoparticles impregnated on $C_nFSM-16$ (n=8, 10, 12, and 16) is 1.5, 1.7, 2.3, and 2.9 nm. They are highly dispersed and have a small distribution. During the reduction process, the particles did not sinter into larger particles and they did not leave the pores for the external surface. This result would suggest an excellent thermal stability and durability for practical use. The particle sizes are slightly larger than those before the reduction treatment in most cases. The particle size increased with the increase in the pore size of the silica matrix.

For the impregnation in a liquid solvent, particles in the size range of 2-3 nm in diameter aggregate into larger particles (10-30 nm in dia.) on the external surface of the $C_nFSM-16$ (n=8, 10, and 12). No particles can be observed in the TEM images of the Pt-supported $C_{16}FSM-16$ in a liquid solvent. After reduction, the Pt particles in the size slightly smaller than the pore size of $C_{16}FSM-16$ can be observed (Figure 1e). During the impregnation process in a liquid solvent, the Pt particles can be introduced into the pores of only $C_{16}FSM-16$. For $C_nFSM-16$ (n=8, 10, and 12) with smaller pores than those of $C_{16}FSM-16$, the Pt particles can not be introduced into the pores (Figure 1f).

The particle size and standard deviation of the Pt nanoparticles prepared in a supercritical solvent estimated from the TEM image, pore diameter of FSM-16 calculated from the XRD result and N_2 sorption measurement and the temperature for a 50% conversion during the CO oxidation reaction are summarized in Table 1. Figure 2 shows the relationship between the average particle size of the Pt nanoparticles impregnated on FSM-16 in a supercritical solvent and the pore diameter of FSM-16 calculated from the XRD result and N_2 sorption measurement. The particle size increased almost linearly with the increase in the pore diameter of FSM-16.

The CO oxidation reaction as a test reaction is performed by using the samples containing the same Pt weight. For the materials prepared using supercritical fluids, the particle size of the Pt nanoparticles strongly affected the catalytic performance. The least active catalyst was obtained with $C_{16}FSM-16$, corresponding to the relatively large average Pt particle size. A 50% conversion was attained at 724 K. The best performance was achieved over the sample with the smallest Pt

particle size prepared with C_8FSM-16, where this catalyst reached 50% conversion at a temperature as low as 477 K. The temperature for 50% conversion decreased as the Pt particle size decreased. It is possible that the higher catalytic activity should be related to the higher surface area of the smaller Pt nanoparticles. For the materials prepared using liquid impregnation, the most active catalyst was obtained with C_{16}FSM-16. The samples with C_nFSM-16 (n=8, 10 and 12) showed less catalytic activity. These results should be due to the fact that the Pt nanoparticles impregnated on C_{16}FSM-16 have smaller particle size and higher surface area than those of the Pt nanoparticles impregnated on C_nFSM-16 (n=8, 10 and 12).

It was determined that the size-controlled Pt nanoparticles can be prepared in micro- and meso-porous silica with a uniform pore diameter by impregnation in a supercritical fluid solvent. This is the first study to prepare the well-controlled sizes of the nanoparticles in micro- and meso-porous hosts using SCFs and to relate the particle size and catalytic performance. Supercritical fluids were determined to be an excellent solvent for the introduction of nanoparticles into fine spaces on a nanometer scale. This would be due to their properties of noncohesivity, high diffusivity and controllable solubility. This is not the case for impregnation in a liquid solvent. Although Pt particles can be introduced into the pores of C_{16}FSM-16, the Pt particles can not be introduced into the pores of C_nFSM-16 (n=8, 10, and 12). During impregnation in a liquid solvent, the wettability, surface tension and low diffusivity prevent the introduction of Pt precursors into nanospaces smaller than the pore size of the C_{16}FSM-16, 3.5 nm. It was shown that the catalytic activity significantly depends on the particle size of the Pt nanoparticles. SCFs were demonstrated as a possible solvent for preparing high performance catalysts.

3.2 SILICA COATING ON FSM-16 Figure 3 compares the nitrogen sorption isotherms for the C_nFSM-16 (n=8, 10, 12 and 16) before and after coating with silica in the supercritical and liquid solvents. The inset to Fig. 3 shows the BJH pore size distribution curves.

For the C_nFSM-16 (n=8 and 10), the pore volume and the pore size decreased after silica coating only in the supercritical solvent. The uptake at the relative pressure of less than 0.1 for C_8FSM-16 or 0.2 for C_{10}FSM-16 shifted to a lower pressure after coating in the supercritical solvent. As shown in the inset to Fig. 3 (b) for C_{10}FSM-16, the BJH pore size decreased only after coating in the supercritical solvent. On the other hand, the pore volume of C_nFSM-16 (n=8 and 10) did not significantly change at the relative pressure of less than 0.2 and slightly increased at the relative pressure above 0.7 after coating in the liquid solvent. These results suggest that silica was not introduced into the pores of FSM-16 and silica gel was produced on the external surface. The results for C_nFSM-16 (n=8 and 10) demonstrated that silica was introduced into the pores of FSM-16 by the treatment only in the supercritical solvent. For C_nFSM-16 (n=12 and 16), the pore volume and the pore size decreased after coating both in the supercritical solvent and in the liquid solvent, as shown in Figs. 3 (c)-(d). These results show that silica was introduced into the pores of C_nFSM-16 (n=12 and 16) by the treatment both in the supercritical solvent and in the liquid solvent.

The molecule size of the silica precursor, TEOS (ca. 1.2 nm), is smaller than the pore size of C_nFSM-16 (n=8 and 10). However, TEOS was not introduced into the pores of C_nFSM-16 (n=8 and 10) by using the liquid solvent. This is attributed to the low diffusivity, the high viscosity and the disturbance of the wettability and of the surface tension of the liquid solvent. On the other hand, high diffusivity, low viscosity and noncohesivity of the supercritical solvent facilitated the introduction of TEOS into the pores of C_nFSM-16 (n=8, 10, 12 and 16).

(a) — 10nm **(b)** — 10nm

(c) — 10nm **(d)** — 10nm

(e) — 10nm **(f)** — 10nm
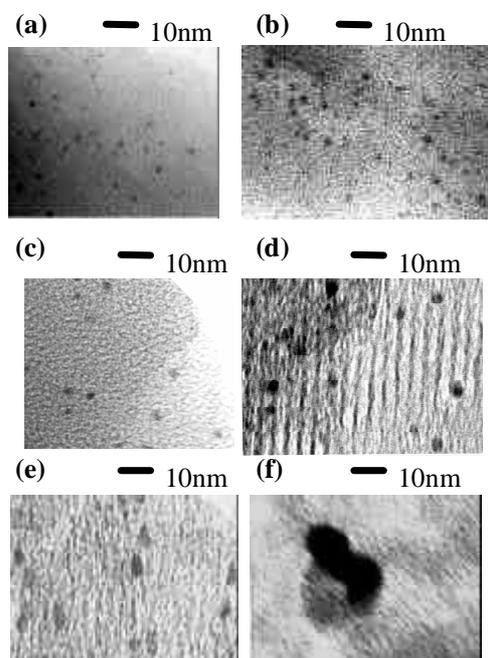
Figure 1. TEM images of Pt-supported FSM-16 in supercritical fluid solvent after reduction in flowing H_2 (a: C_8FSM-16, b: $C_{10}FSM$-16, c: $C_{12}FSM$-16, d: $C_{16}FSM$-16) and of Pt-supported FSM-16 in liquid solvent after reduction in flowing H_2 (e: $C_{16}FSM$-16, f:$C_{10}FSM$-16).
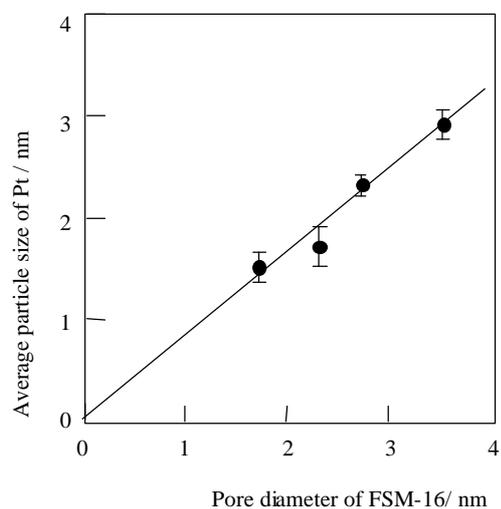
Figure 2. Average particle size of Pt nanoparticles impregnated on FSM-16 in supercritical solvent after reduction plotted as a function of the pore diameter of FSM-16.

Table 1. The particle size and standard deviation of Pt nanoparticles prepared in supercritical solvent estimated from TEM image, pore diameter of FSM-16 calculated from XRD result and N_2 sorption measurement and the temperature for a 50% conversion during the CO oxidation reaction.

silica matrix	Pt particle size /standard deviation [nm/nm]	pore diameter of FSM-16 [nm]	temperature for 50% conversion in CO oxidation [a] [K]	temperature for 50% conversion in CO oxidation [b] [K]
C_8FSM-16	1.5/0.15	1.6	477	825
$C_{10}FSM$-16	1.7/0.19	2.1	495	809
$C_{12}FSM$-16	2.3/0.10	2.4	575	816
$C_{16}FSM$-16	2.9/0.16	3.5	724	743

[a] materials prepared using supercritical fluids
[b] materials prepared using liquid solvents

Figure 3. Nitrogen adsorption isotherms and BJH pore size distributions (inset) of FSM-16 (closed circle), FSM-16 coated in supercritical fluid (open circle) and in liquid solvent (cross). (a: $C_8FSM-16$, b: $C_{10}FSM-16$, c: $C_{12}FSM-16$, and d: $C_{16}FSM-16$)
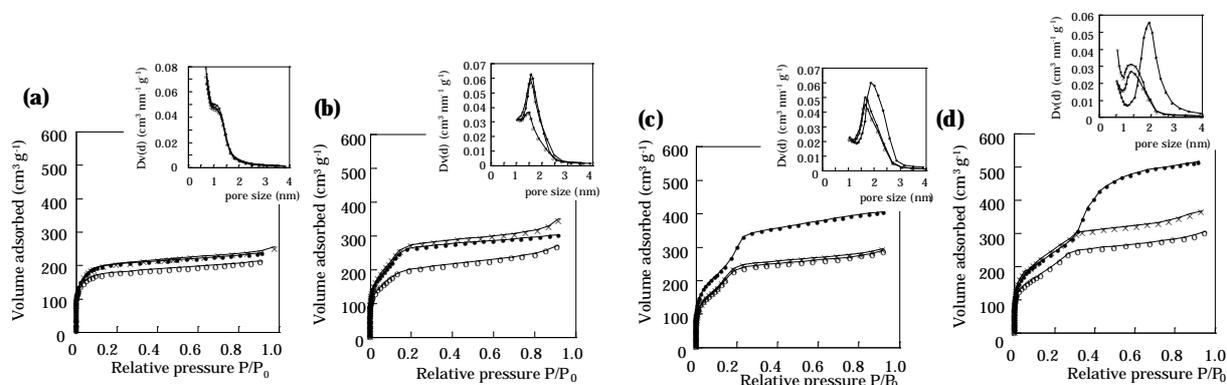
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