Highly Efficient MCM-48-based Template Synthesis of Osmium and Platinum 3-D Nanonetworks

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Nanostructured materials have attracted a great attention because of their novel size- and shape-dependent electronic, magnetic, optical, and catalytic properties that differ drastically from those of bulk materials.[1] Metals of nanosize, in particular, are expected to find useful applications in catalysis due to high surface area,[2] and some results using nanoparticles as catalysts were reported. Ni/Pd core/shell nanoparticles show good catalytic activities in Sonogashira coupling reactions,[3] and Pd nanoparticles with chiral ligands are good catalysts for asymmetric catalyses.[4] These nanoparticles contain ligands on their surface, thus possessing very good solubilities in organic solvents. The improved solubility of nanoparticles, however, can impede facile recovery of the catalysts after reaction. Hyeon *et al.* reported the preparation of micron-sized hollow palladium spheres composed of bare nanoparticles without surfactants and these materials showed excellent catalytic activities in Suzuki cross coupling reactions and a good recoverability,[5] thus calling for further extensive studies on designed 3-D nanostructures of other metals for efficient catalyses and facile catalyst recovery processes.

Nanomaterials with smaller dimensions (2-10 nm in diameter)[1b,1c,6] could be obtained through template synthesis using mesoporous silicates[7] such as SBA-15, MCM-41, and MCM-48.[8-10] Metal precursors, however, do not readily diffuse into the small pore channels of these mesoporous silicates, and thus efficient methods to load the metal inside the pores need to be developed to prepare porous template-based nanomaterials. Although the insertion of the metal precursors by solution-phase infiltration[8] and thermal vapor infiltration[9] techniques have been successful in the preparation of nanostructured materials, the incorporated metal contents are rather low (3-10 wt % of metal loading based on SiO_2 template). Supercritical fluids with large diffusion coefficients and low viscosity have also been employed to increase the amount of precursors loaded into small mesopores.[10] The required harsh conditions to generate supercritical fluids, however, are very cumbersome. Herein we report a facile preparation of 3-D structured Os and Pt nanonetworks by utilizing the capillary action of mesopores of MCM-48 toward molten organometallic precursors. Some preliminary results of the work described herein have

been previously reported.[11]

A Pyrex glass ampoule (1 × 5 cm, wall thickness = 2 mm) containing C_{16}-MCM-48 (0.2 g)[12] and $Os_3(CO)_{12}$ (0.75 g; Os metal content = 0.47 g) is evacuated by a diffusion pump for 1 h, and then flame-sealed. The ampoule is heated at 265 °C in a silicone oil bath. The color change of MCM-48 from white to brown indicates efficient sorption of brown liquid produced by the melting of thermolysis products of $Os_3(CO)_{12}$, such as $Os_5C(CO)_{15}$, $Os_6(CO)_{18}$, and $Os_7(CO)_{21}$.[13] In order to induce decomposition of the Os cluster compounds into Os metal, the ampoule is heated at 265 °C for 3 days, further heated at 350 °C for 6 h, and finally maintained at 400 °C for 24 h. The black-colored powder thus obtained after ampoule breakage has been treated by H_2 (100 mL/min) at 400 °C for 6 h, which results in complete removal of the carbon contents (Elemental Analysis; C, 0.0%). After subsequent thermal annealing of the black powder at 500 °C under Ar for 12 h, the furnace is cooled down to room temperature, and the Os@MCM-48 sample is exposed to air. In order to obtain template-free Os nanomaterial, the resulting black powder is reacted with 48% HF in H_2O (20 molar excess based on Si content) at room temperature. Centrifugation and drying under vacuum give voluminous black powder (0.51 g). Figure 1 shows the X-ray powder diffraction (XRD) patterns of (a) MCM-48, (b) Os@MCM-48 after thermal annealing at 500 °C, (c) template-free Os nanomaterial. Figure 1d and 1e are the XRD patterns of Pt nanomaterials, which will be discussed later. The free MCM-48 template with a highly ordered structure exhibits a diffraction peak at $2\theta = 2.22°$, which corresponds to (211) reflection (Fig. 1a). Figure 1b shows that the (211) peak is shifted to $2\theta = 2.25°$ after Os impregnation, which suggests that some degree of lattice contraction of the original MCM-48 framework has been induced. The intensity of this peak is decreased to less than 20% of that of free MCM-48. Such a drastic decrease in the intensity of the diffraction peak due to silica framework indicates that large amount of Os has been loaded inside the pores.[14] Similar lattice contraction and intensity loss of XRD peak for material-filled mesoporous silicates has been previously observed.[8,9,10b,15]

XRD analysis (Fig. 1c) of the nanostructured Os network

Notes

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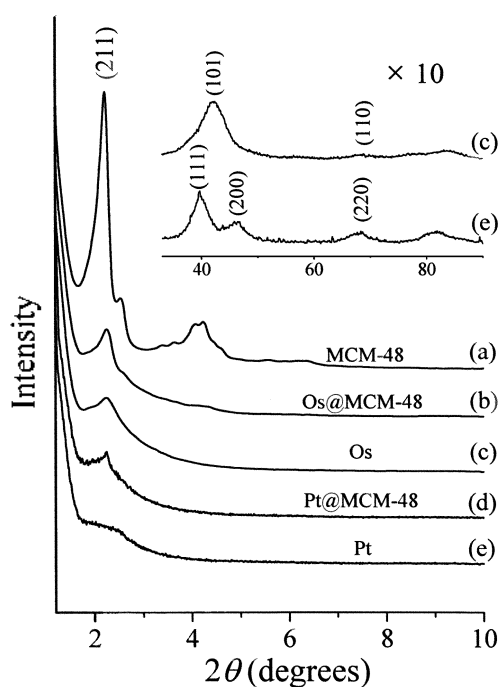
Figure 1. Changes in XRD patterns: (a) MCM-48, (b) Os@MCM-48 after thermal annealing at 500 °C, (c) template-free Os, (d) Pt@MCM-48 after thermal annealing at 500 °C, and (e) template-free Pt.

(N-Os) shows an identical pattern to that of MCM-48 supported Os metal. The XRD pattern of the N-Os shows broad peaks at 43.6° and 68.6°, which correspond to (101) and (110) reflections of hexagonally close-packed (hcp) Os (JCPDS card No: 06-0662), respectively, as shown in the inset of Figure 1c. Sharp XRD peaks at high angles are not observed, indicating that large Os particles are not formed on the outer surface of MCM-48. Figure 1c shows a rather broad peak around 2θ = 2.2°, which is similar to that of MCM-48 template, and suggests that some degree of long-range order transferred from the MCM-48 host still remains. Such a long-range ordered structure is further supported by transmission electron microscope (TEM) images. The TEM images of the template-free Os nanomaterial (Fig. 2a-c) show that it is composed of Os particles with 50-500 nm diameter. These particles have a substructure in which nanoparticles with ~3 nm diameter are regularly networked, with textures similar to those of silica-based MCM-48. Figure 2d shows that the Os nanoparticle aggregates are randomly dispersed, when they are not thermally annealed within MCM-48. Obviously, the final annealing process at 500 °C is an indispensable step for the nano-sized metal within the pore channels of MCM-48 to establish a long-range order. The mobility of molten nanoparticles within the pore channels at 500 °C may explain the facile annealing process at this temperature. A dramatic lowering of melting point for nanowires of noble metals has been previously reported.[8c,9b]

In order to confirm that the facile metal impregnation is in fact due to the capillary action of MCM-48, nanostructured Pt has been prepared from an organometallic precursor
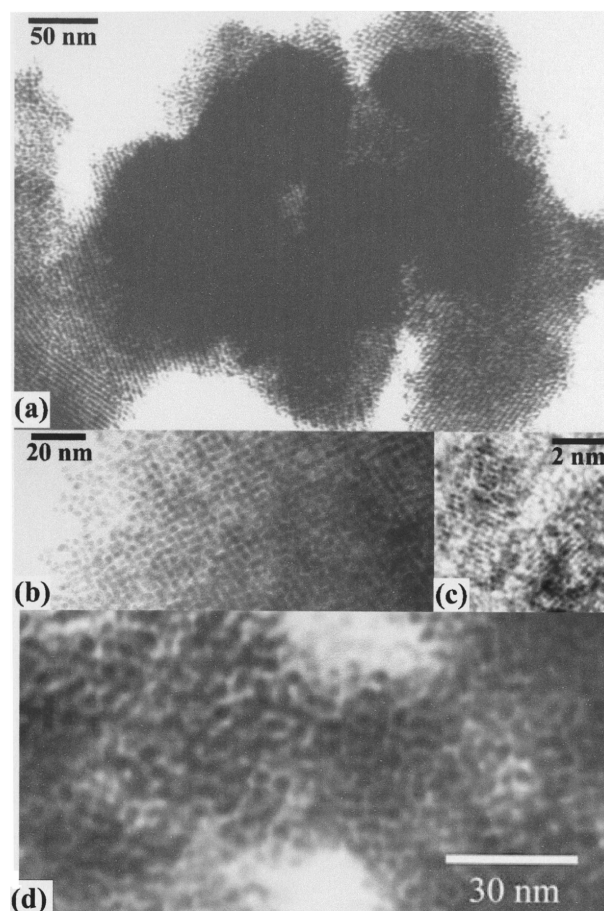
Figure 2. TEM images of template-free nanostructured Os: (a-c) at various magnifications after thermal annealing at 500 °C, and (d) before thermal annealing at 500 °C.

Pt(COD)Cl₂, of which the decomposition behavior is very different from Os₃(CO)₁₂. While Os₃(CO)₁₂ slowly transforms to various long-lived viscous cluster compounds before decomposing to Os metal, Pt(COD)Cl₂ decomposes directly to Pt upon melting (m.p. ~250 °C). If the sorption of the molten precursor due to the capillary action is not very efficient, large Pt particles will form only on the outer surface of MCM-48. When Pt(COD)Cl₂ is thermally decomposed in the presence of MCM-48, and treated by H₂ and subsequently by thermal annealing, a black powder is obtained. The XRD pattern of this Pt@MCM-48 sample shown in Figure 1d exhibits a broad hump around 2θ = 2.2°, which is decreased significantly as compared to the (211) peak of MCM-48. When SiO₂ content of the black powder is removed by HF treatment, template-free nanostructured Pt is prepared (Elemental Analysis; C, 0.0%). TEM image of this material is shown in Figure 3, where the MCM-48-like texture is clearly seen, as suggested by the weak broad hump at 2θ = 2.2° in the XRD pattern (Fig. 1e). The XRD pattern of this sample also exhibits broad peaks at 39.8°, 46.2°, and 67.5° corresponding to (111), (200), and (220) reflections, respectively, of face-centered cubic (fcc) Pt (See the inset of Figure 1e, JCPDS card No: 4-802). Some rather large (~10 nm) Pt particles, presumably formed by sintering of Pt
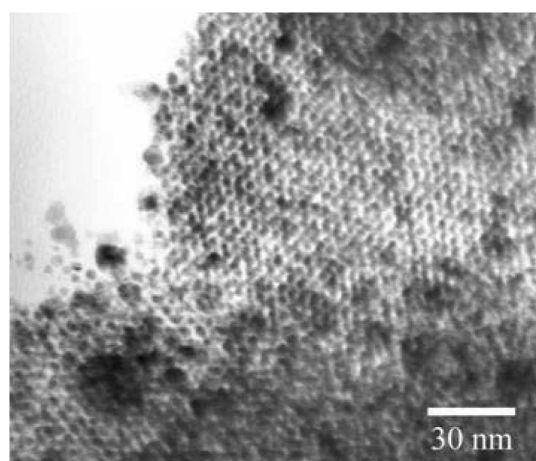
Figure 3. TEM image of template-free nanostructured Pt.

nanoparticles on the outer surface of MCM-48, are also observed on the surface of the fabric-like Pt nano-network. Their content in the whole sample, however, is marginal, as indicated by the absence of sharp peaks in the XRD pattern.

Very high BET surface areas of 126 m²/g and 93 m²/g have been obtained for the nanostructured Os and Pt, respectively, from N_2 adsorption isotherms, suggesting their potential utility as efficient heterogeneous catalysts.

In conclusion, we have utilized the facile capillary action of MCM-48 template toward molten organometallic precursors to prepare networked metal 3-D nanostructures. The simple experimental procedure and availability of numerous organometallic precursors with similar decomposition behaviors would make this capillarity-based template synthesis a very promising method for the preparation of various functional mesoporous metals.

Experimental Section

3-D structured *N*-Pt. The mixture of MCM-48 (0.2 g) and finely ground Pt(COD)Cl₂ (0.5 g, Strem Chemicals, 99%) in a 50 mL Pyrex Schlenk tube connected to a bubbler was heated at 250 °C for 12 h under Ar atmosphere to give a black powder. Additional Pt(COD)Cl₂ (0.5 g; Pt metal content = 0.26 g) powder was introduced to the Schlenk tube against Ar stream and was thermally treated under the same condition. After treatment with H₂ at 400 °C for 6 h to remove C and Cl impurities, thermal annealing at 500 °C under Ar for 12 h, and SiO₂ removal with 48% HF in H₂O (20 molar excess based on Si content), voluminous black powder of nanostructured Pt (0.49 g) was obtained.

Characterization of 3-D structured *N*-Os and *N*-Pt. The prepared materials were characterized by XRD (Rigaku

Miniflex (Cu Kα, 0.5 kW, RT)) and TEM (Philips CM20 operated at 160 kV). Samples for TEM investigations were prepared by putting an aliquot of methanol suspension of *N*-Os and *N*-Pt onto an amorphous carbon substrate supported by copper grid. The BET surface areas were obtained from nitrogen adsorption data. Nitrogen adsorption isotherms were measured on a Micromeritics ASAP 2010 Volumetric adsorption analyzer.

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