Supramolecular templated synthesis of platinum-supported silica

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The incorporation of Pt onto MSU-1 mesoporous silica by direct inclusion of various precursors in a synthesis gel containing a structure-directing non-ionic surfactant was studied.

The M41S family of mesoporous molecular sieves has aroused enormous interest ever since these materials started to be used as sorbents, catalysts and supports[1] of high thermal stability, pore size uniformity and surface area. Individual noble metals including Pd[2] and Pt,[3,4] and combinations such as Cu–Ru,[5] have been supported on MCM-41 to prepare catalysts that are active in various processes. The metal is incorporated onto the support either by incipient wetness impregnation, ion exchange or direct introduction of platinum during the synthesis of MCM-41. This last procedure ensures uniform dispersion of platinum on the support, with particle sizes in the region of 6 nm that vary with the particular precursor used.[4]

Mesoporous metal oxides, designated MSU-X, can be obtained by assembling electrically neutral polyethylene oxide surfactants and neutral inorganic precursors.[6,7] These surfactants promote framework assembly through hydrogen bonding between the hydrophilic $(EO)_n$ segments and the silanol groups of the neutral inorganic precursor. These materials exhibit wormhole structures that lack regular channel packing order; however, they possess uniform channel diameters over a range comparable to M41S materials. The low cost and ready biodegradation of the surfactant are two major advantages of this synthetic procedure.

Controlled synthesis of colloidal platinum nanoparticles has been accomplished by altering the ratio of the concentration of a capping material (sodium polyacrylate) to that of Pt^{2+} ions.[8] Also, nanostructured mesoporous platinum has been synthesized by using a lyotropic liquid-crystalline phase as reaction medium.[9] This porous material possesses a high surface area, which is of great interest with a view to its catalytic application.

This paper reports the synthesis of platinum nanoparticles supported on mesoporous silica by use of the surfactant Tergitol 15-S-12 [$Me(CH_2)_{14}O(OCH_2CH_2)_{12}OH$] as structure-directing agent.

Unsupported mesostructured silica (solid MSU-1) was synthesized following procedures similar to those reported elsewhere.[6] Platinum-supported silicas were obtained by supplying the starting mixture with 1 mol % Pt (relative to Si), using $(NH_4)_2PtCl_4$, H_2PtCl_6 and $(NH_3)_4PtCl_2$ as precursor salts, which produced the solids denoted MSU-1-1, MSU-1-2 and MSU-1-3, respectively.† A Tergitol 15-S-12 solution (0.1 mol l^{-1}), under stirring, was supplied with the platinum salt at 298 K. Then, TEOS was added and stirring was continued for a further 24 h. The TEOS–Pt–surfactant–H_2O mole proportion in the mixture was 10 : 0.1 : 1 : 560. The mixture was allowed to age for 72 h and the resulting powder was filtered, washed with distilled water and air-dried. Finally, the solid was calcined at 873 K in the air for 3 h.

Solids were characterized by powder X-ray diffraction (XRD), thermogravimetric analysis (TGA), N_2 sorptometry, elemental analysis (for Pt), transmission electron microscopy (TEM), temperature programmed reduction (TPR) and hydrogen chemisorption.

As a rule, the XRD patterns obtained (Fig. 1) exhibited a low angle peak (d_{100}), with a *d*-spacing between 37 and 66 Å (Table 1). The second-order peaks obtained at higher incidence angles were broad and short. These are typical of mesostructured materials with a sponge-like or worm-like pore channel structure, which are devoid of any regular long-range order, as expected for materials assembled using neutral or non-ionic surfactants. All the solids studied were calcined at 873 K in order to ensure removal of the surfactant, which was confirmed by TGA (*e.g.* solid MSU-1-1 exhibited a total weight loss of 52% as a result). In every case, the low angle d_{100} peak was

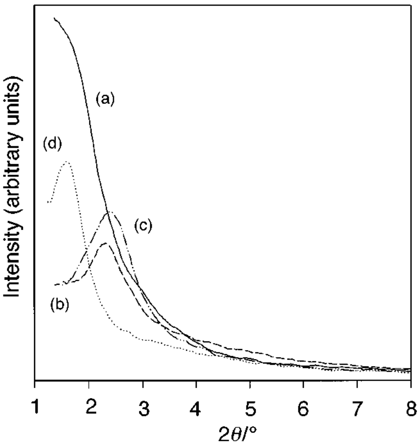

Fig. 1 Powder XRD patterns for solids MSU-1 (*a*), MSU-1-1 (*b*), MSU-1-2 (*c*) and MSU-1-3 (*d*), all calcined at 873 K.

Table 1 Physicochemical properties of Pt-supported and unsupported MSU-1 mesoporous silica

Solid	d_{100} lattice spacing^a/Å	d_{100} lattice spacing^b/Å	BET surface area/m^2 g^{-1}	Pore volume/ ml g^{-1}	BJH pore size/Å	Pt content (wt%)
MSU-1	—	55	644	0.96	37	—
MSU-1-1	41	38	851	0.42	19	2.08
MSU-1-2	43	37	606	0.30	19	0.36
MSU-1-3	66	56	707	0.87	38	0.23

^{a} As synthesized. ^{b} Calcined in air at 873 K for 3 h.

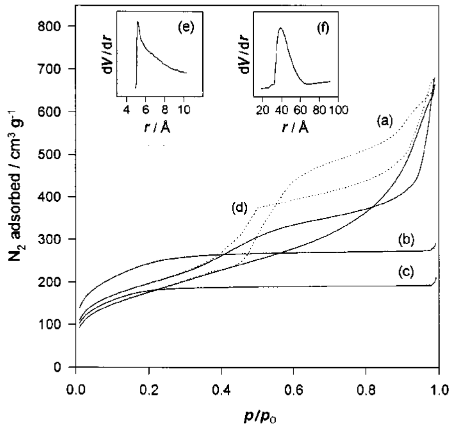

Fig. 2 N_2 adsorption (solid line) and desorption (dotted line) isotherms for calcined MSU-1 (*a*), MSU-1-1 (*b*), MSU-1-2 (*c*) and MSU-1-3 (*d*). Insets: Horvath–Kawazoe pore diameter (*r*) distribution of MSU-1-1 (*e*) and BJH pore diameter distribution of MSU-1 (*f*).

shifted to a higher angle upon calcination, thus indicating gradual contraction of *d*-spacings in the lattice upon removal of the surfactant.

Table 1 also gives the surface areas, pore diameters and pore volumes of the solids. As can be seen, all possess a high specific surface area (>600 m^2 g^{-1}). The N_2 adsorption–desorption isotherms are of type IV (*i.e.* typical of mesoporous solids) for MSU-1 and MSU-1-3 (Fig. 2), pore size in which varies over narrow ranges (35–50 and 32–42 Å), with type H2 and type H4 hysteresis cycles, respectively.[10] Also, MSU-1-1 and MSU-1-2 exhibit a type I isotherm, with the step at a relative pressure around 0.2. Nitrogen isotherms of this kind are typical of pores with sizes in between the micro and meso ranges.[11] The micropore distribution in solid MSU-1-1 as determined by the Horvath–Kawazoe method[12] confirms the presence of pores in this size range, most of size about 7 Å (Fig. 2).

Table 1 lists the Pt content in each solid. As can be seen, the amount of Pt incorporated into the silica was only significant (50% of the amount added) when $(NH_4)_2PtCl_4$ was used as precursor. A temperature programmed reduction (TPR) run for solid MSU-1-1 revealed that virtually the whole deposited metal was present as Pt^0, so the metal ion was reduced during the solid synthesis and calcination, which is consistent with previous findings in MCM-41 as support.[4] Chemisorption tests revealed solid MSU-1-1 to be able to adsorb 60 and 19 µl of H_2 at room temperature and 673 K, respectively; this results in a metal dispersion of 32%, with a metal surface area of 80 m^2 g_{metal}^{-1} and an average particle diameter of 43 Å, all consistent with the TEM results. Fig. 3 shows the particle size distribution as determined by this technique and Fig. 4 shows a typical TEM image.

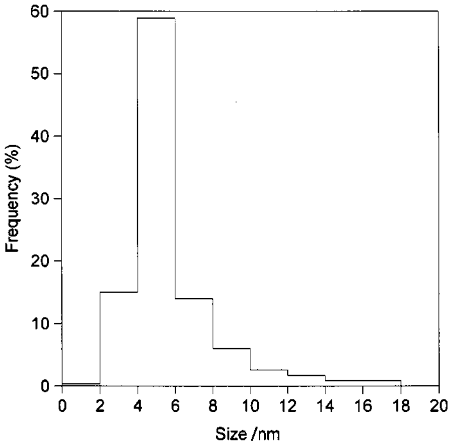

Fig. 3 Size distribution of platinum particles in solid MSU-1-1.

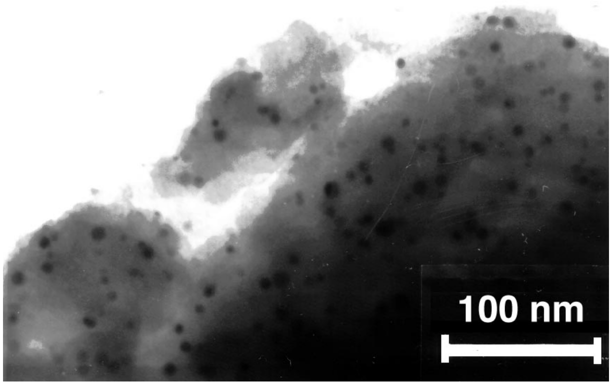

Fig. 4 TEM image of calcined MSU-1-1.

In summary, our results suggest that platinum nanoparticles can be supported onto mesostructured silica by using a non-ionic surfactant assembly involving direct incorporation *via* the synthesis gel. Other experimental variables such as the surfactant used, temperature, concentrations, solvent extraction of the surfactant, *etc.*, can be altered as required. One of the most salient advantages of this procedure is that it allows the incorporation of metal nanoparticles into other mesoporous metal oxides that are inaccessible by electrostatic templating routes, simply by hydrolysing the corresponding alkoxides (*e.g.* titania or tin oxide). These materials can be used as, for example, catalysts, and also in optical, electronic and magnetic devices.

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Notes and references

† *Typical procedure:* solid MSU-1-1 was obtained by adding 10 ml of tetraethylorthosilicate (TEOS) over a solution containing 0.171 g of $(NH_4)_2PtCl_4$ in 46 mL of 0.1 mol l^{-1} Tergitol 15-S-12 at room temperature. After 24 h under stirring, the suspension was allowed to stand for 3 days and the solid was filtered off, air-dried and calcined at 873 K for 3 h.

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