Morphological Control of MCM-41 by Pseudomorphic Synthesis

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The development of micelle-templated silicas (MTS) has represented one of the most original fields of materials research since the seminal papers from the Kresge and Beck groups on MCM-41 and MCM-48.[1, 2] The self-assembly of surfactant aggregates and mineral species can be controlled to provide stable mesoporous materials with extremely narrow pore-size distributions. Several recent reviews show the advances in the preparation of ordered porous oxides,[3–5] as well as their applications in catalysis.[6–8]

Adsorbents with narrow pore-size distribution at the nanometer scale allow new applications to be devised for the separation of large organic molecules. MCM-41 silicas have been proposed as possible stationary phases for size-exclusion chromatography,[9] normal-phase HPLC,[10] capillary gas chromatography,[11] and enantioselective HPLC.[12, 13]

The control of the size and shape of the adsorbent particles is an essential condition for any chromatographic application: particle-size scattering affects separation and plate height. Indeed, the preparation of spheres of MTS with predetermined monodispersed size has been the target of several research groups. Positive results have been obtained by introducing surfactant templates in classical preparations of silica gel with controlled grain size. In this way, spheres of MTS have been prepared from water–alcohol systems,[14, 15] by controlled hydrolysis,[16, 17] or by spray-drying techniques.[18] A frequent drawback of these methods is the need to simultaneously optimize the conditions for the synthesis of the desired silica–surfactant mesophase and for the successful formation of monodispersed spheres. This situation restrains the experimental conditions and makes a fine tuning of the properties of MTS, such as, pore size and topology, wall thickness, and aluminum content, difficult. It would be expedient to independently optimize the properties of the particles and the properties of the micelle-templated phase. Herein, a method to achieve this result by transformation of preformed spheres of silica gel into MTS is proposed.

The synthesis procedure is directly adapted from the synthesis of MCM-41,[1, 2] by using commercial spheres of silica gel as the source of silica. Lichrosphere 100 (Merck) was stirred in an alkaline solution of cetyltrimethylammonium bromide (CTAB), the molar composition of the system being 1 SiO_2/0.25 NaOH/0.1 CTAB/20 H_2O. After 30 min stirring at room temperature, the system was put in an autoclave at 388 K for 24 h. The parent silica (Lichrosphere 100) and the recovered solid share the same spherical morphology and granulometric distribution (Figure 1). However, while the parent silica is amorphous, the CTAB-treated solid presents the characteristic X-ray powder diffraction pattern of MCM-41.

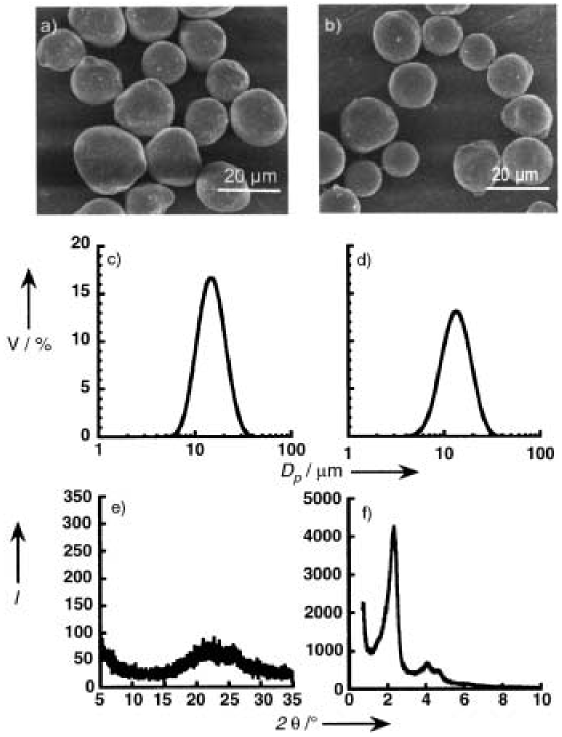

Figure 1. Pseudomorphic transformation of silica gel to MCM-41. Micrographs (a, b), granulometric distributions; the distribution is given in volume V as a function of particle diameter D_p (c, d), and powder diffraction patterns (e, f) for Lichrosphere 100 (Merck) before (e) and after (f) treatment with CTAB solution.

This transformation corresponds to the definition of pseudomorphism from mineralogy: a pseudomorph is an altered mineral the form of which has the outward appearance of another mineral species. In our case, the MCM-41 grains are pseudomorphs of the silica gel grains.

The pattern of the pseudomorphic transformation can be monitored by X-ray diffraction and nitrogen sorption experiments (Table 1). The adsorption pattern of the parent silica (BK385), which corresponds to a broad pore-diameter distribution centered around 8.5 nm, is completely lost after 15 min at 388 K (Figure 2). This latter material presents a

Table 1. Properties of cetyltrimethylammonium (CTA) treated silica BK385 (Akzo-Nobel).

Time at 388 K [h]	CTA/SiO_2[a] (w/w)	Y_{CTA}[b]	Y_{Si}[c]	V_{mp}[d] [$cm^3 g^{-1}$]	S_{BET}[e] [$m^2 g^{-1}$]	a_c[f] [nm]	D[g] [nm]	t[h] [nm]
0.25	0.66	0.92	0.66	0.63	890	5.4	3.7	1.3
1	0.72	0.95	0.62	0.75	980	4.8	3.7	1.0
168	0.81	0.98	0.57	0.89	1078	4.4	3.7	0.8

[a] Composition. [b] Yield of CTA (from thermogravimetric weight loss). [c] Yield of silica (from thermogravimetric weight loss). [d] Structural pore volume. [e] BET surface area. [f] Cell parameter. [g] Pore diameter. [h] Wall thickness at different treatment times.

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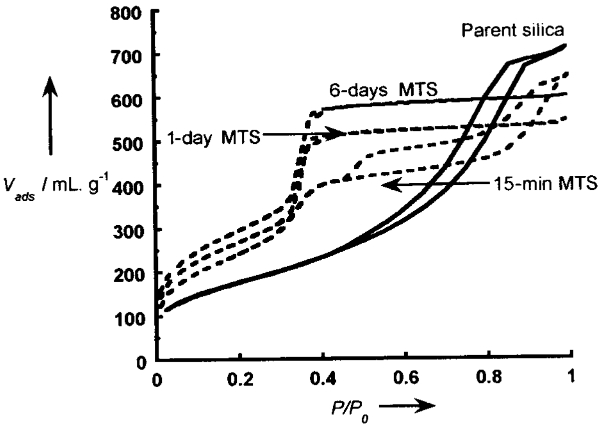

Figure 2. Evolution of the N_2 adsorption/desorption isotherms during the transformation of silica BK385 (Akzo-Nobel) into MCM-41 upon treatment at 388 K for the indicated time. Molar composition 1 SiO_2/0.25 NaOH/0.1 CTAB/20 H_2O. Samples calcined at 823 K in air.

reversible type IV isotherm with a sharp step around p/p^0 0.37, typical of the structural mesoporosity of MCM-41, and a secondary porosity corresponding to a broad distribution of mesopores with a diameter larger than 20 nm. The desorption around p/p^0 0.45 indicates that a part of the secondary mesoporosity is accessible through the smaller structural mesopores. The sample incorporates 92% of the available surfactant (Table 1) and presents two broad X-ray diffraction peaks, which correspond to an MCM-41 with poor long-range order[19] (or/and thick walls on short-range order) and could be indexed according to a hexagonal cell with $a = 5.4$ nm (Table 1).

The amount of incorporated surfactant and the loss of the adsorption pattern of the parent silica suggest that nearly the whole silica is transformed into MCM-41 after 15 min. The secondary porosity corresponds to the volume between the small grains of MCM-41 with poor long-range order formed by nucleation at the pore–silica interface of the parent material. Heterogeneous nucleation of MCM-41 has been reported.[20] Nevertheless, even if MCM-41 formation is initiated on the surface, the mechanism here is different because MCM-41 is formed by the dissolution of the particles themselves. These intermediates evolve to ordered MCM-41 at longer treatment times by internal reorganization, which is often the case in such material synthesis.[21] In the process, the lattice parameter decreases whereas the pore size remains constant, in agreement with a decrease of the wall thickness (Table 1). Thinner-wall materials present a higher surfactant/silica ratio, as shown by the increase of the yield of surfactant, which is virtually nominal at the end of the treatment.

The conservation of the shape and size of the initial system suggests that further transfer of silica from the parent phase to the micelle-templated phase takes place inside the pores of the grains. Each grain behaves like a microreactor in which silica is dissolved by the alkaline solution and silicate species interact with the surfactant to form MTS. In the initial phases of the synthesis, the silica/surfactant ratio inside the grain is higher than the overall composition of the system, which accounts for the formation of a micelle-templated phase with thick silica walls and poor long-range order. Further equilibration with the surfactant-rich and the silica-poor outer solution results in the formation of more-ordered MCM-41 which occupies a larger pore volume and proportionally decreases the secondary mesoporosity.

Starting from parent silica BK385, nearly the whole mesopore volume has the structural porosity of MCM-41 and virtually no secondary mesoporosity is left after seven days. This is not the case for all possible parent silica. In the Table 2, the properties of MCM-41 formed from different parent silica by using the same composition and amount of treatment solution are reported. The grain morphology of the parent silica is always conserved, whereas the structural properties of the final MCM-41 only depend on the composition of the synthesis system and are not affected by the different sources of silica. The secondary mesoporosity does depend on the pore volume of the parent silica. For sources of silica with a pore volume larger than the porosity of the final MCM-41, some secondary porosity is left among the crystallites of MCM-41.

On the contrary, for parent silica with a low initial pore volume, the grain cannot accommodate the forming MCM-41 and bursts during the treatment. Fragmentation of the grain takes place by spalling of the fast-reacting outer rim (Figure 3a). Another instance of grain fragmentation is induced by the use of very alkaline treatment solutions. In this case the dissolution of the parent silica is faster than the diffusion of surfactant inside the grain, and the core of the grain becomes mechanically unstable. Another kind of change of morphology can occur with very long synthesis time (treatments for up to one month have been tested). When the final MCM-41 is left in the mother solution, Ostwald ripening occurs between the MCM-41 crystallites which form the macroscopic grain. Some crystals grow at the expense of others, protrude out of the particles and form spaghetti-like fibers with, in most cases, a hexagonal section (Figure 3b).

Table 2. Properties of calcined MCM-41 synthesized from different silica sources.

Silica source	Average grain size [µm]	Morphology	V_{mp}[a] [cm^3 g^{-1}]	V_p[b] [cm^3 g^{-1}]	a_c[c] [nm]	D[d] [nm]
Nucleosil (Macherey-Nagel)	5	spheres	0.78	0.93	4.5	3.9
Lichrosphere 60 (Merck)	10	spheres	0.86	0.91	4.7	3.8
Lichrosphere 100 (Merck)	15	spheres	0.82	1.00	4.7	3.6
sylopol (Grace)	50	spheroids	0.76	0.80	4.8	3.9
silica gel (Fluka 60)	130	splinters	0.74	0.80	4.7	3.8
BK385 (Akzo-Nobel)	1	dendrites	0.89	0.93	4.4	3.7
sipernat	<1	dendrites	0.79	1.08	4.4	3.8

[a] Structural pore volume. [b] Total pore volume ($p/p^0 = 0.98$). [c] Cell parameter. [d] Pore diameter.

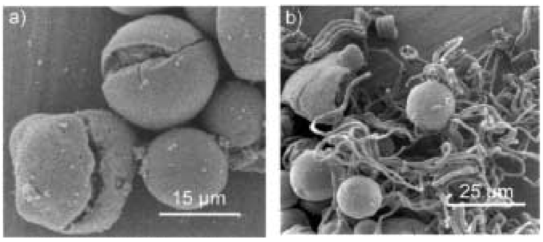

Figure 3. Examples of loss of morphology in unfavorable conditions. a) Blasted grains as a result of low porous volume of the parent silica. b) Long treatment time, Ostwald ripening occurs and spaghetti-like nanocrystallites grow out from the particles.

Pseudomorphic synthesis is a good method to separately optimize the morphology of the grain and the structural properties of MCM-41. The experimental conditions for the treatment with the surfactant solution can be varied widely. The thickness of the MTS walls can be adjusted by changing the alkalinity of the synthesis mixture.[22] The aluminum content, relevant for catalytic applications, can be controlled by either using a silica aluminum oxide as the silica source or by adding the desired amount of sodium aluminate to the reaction mixture. Quite ordered materials were formed with a Si:Al ratio down to 7:1 in the reaction mixture (5.5:1 in the solid formed). The pore size was varied up to 12 nm by adding a swelling agent (1,3,5-trimethyl benzene) to the reaction mixture, as described elsewhere.[23]

Pseudomorphic synthesis was successfully applied to a wide range of particle sizes and morphologies (Table 2) which makes this procedure suitable for the preparation of materials with specific morphological requirements. Besides, for chromatographic applications, this procedure was successfully applied to the large-scale preparation of monodispersed spheres of MCM-41. This method could eventually be applied to macroscopic objets such as membranes or films. However, the stress generated during synthesis can lead to mechanical instability and should be taken into account while choosing the porosity of the parent silica and the experimental conditions.

Experimental Section

MTS materials were prepared in a steel autoclave where reactants were mixed in the following proportions 1 SiO_2/0.1 – 0.4 NaOH/0.05 – 0.1 cetyltrimethylammonium bromide/0 – 1.3 1,3,5-trimethyl benzene/0 – 0.1 $NaAlO_2$/20 – 80 H_2O. Reactants were mechanically stirred (400 rpm) for half an hour at room temperature and put carefully in autoclave and left at 388 K for between 15 min to 1 month. (Therefore, heating rate was not monitored and it is expected that the 15-min synthesis does not reach the target temperature). The resulting solids were recovered by filtration, washed with water, and dried at 353 K overnight. Materials were then calcined under air flow at 823 K for 8 h. Materials were then characterized by powder X-ray diffraction ($Cu_{K\alpha}$ radiation, CGR Theta 60 diffractometer with Inel drive), N_2 sorption at 77 K (Micromeritics ASAP 2000), thermogravimetric analyses (Setaram 90C) and scanning electron microscopy (Hitachi). Pore diameters have been evaluated from adsorption data according to Broekhoff and De Boer[24] and wall thicknesses from diffraction and adsorption data according to Galarneau et al.[25] The volume of the structural porosity has been measured above the pore-filling step of the MCM-41 isotherm and the total mesopore volume includes all pores with diameter lower than 50 nm. The authors gladly acknowledge the contribution of D. Cot for electron microscopy.

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