COMMUNICATION

ChemComm
www.rsc.org/chemcomm

Silica-based powders and monoliths with bimodal pore systems†

Jamal El Haskouri,[a] David Ortiz de Zárate,[a] Carmen Guillem,[a] Julio Latorre,[a] Maite Caldés,[b] Aurelio Beltrán,[a] Daniel Beltrán,[a] Ana B. Descalzo,[c] Gertrudis Rodríguez-López,[c] Ramón Martínez-Máñez,[c] M. Dolores Marcos*[c] and Pedro Amorós*[a]

[a] *Institut de Ciència dels Materials (ICMUV), Universitat de València, P.O. Box 2085 46071-València, Spain. E-mail: pedro.amoros@uv.es*

[b] *Institut des Materiaux Jean Rouxel, Laboratoire de Chimie des Solides, UMR CNRS 110, Université de Nantes, P.O. Box 32229 44322-Nantes Cedex, France*

[c] *GDDS, Departamento de Química, Universidad Politécnica de Valencia, Camino de Vera s/n 46071-València, Spain. E-mail: mmarcos@qim.upv.es*

Received (in Cambridge, UK) 28th November 2001, Accepted 11th January 2002
First published as an Advance Article on the web 5th February 2002

Porous pure and doped silicas with pore sizes at two length scales (meso/macroporous) have been prepared and shaped both as powders and monoliths through a one-pot surfactant assisted procedure by using a simple template agent and starting from atrane complexes as inorganic precursors.

High surface porous materials showing tailor-made pore sizes and shapes are especially interesting in a variety of applications where molecular recognition is needed.[1] The discovery of the M41S family of mesoporous silicas was a breakthrough finding in this field by opening a new way towards ordered uniform mesoporous systems, which in turn implied an opportunity for expanding the available pore sizes typical of zeolites.[2] Once the preparation of MCM-41 related solids began to be controlled, a new key objective was to achieve the incorporation of different elements to the silica materials to modulate their catalytic properties.[3] Among the many problems associated to this goal, those related with accessibility to the active sites have meant, in some cases, non-attainment of the catalytic performances which could be *a priori* expected on the basis of the intimate nature of a given material. Several strategies have been developed to overcome such a limitation. Thus, the site accessibility (and, therefore, the catalytic response) can be enhanced through insertion of active elements in mesoporous solids having relatively small particle sizes (HMS solids)[4] or displaying interconnected 3-D channel systems (MCM-48).[5] In some cases, this goal can be simply achieved by expansion of the pore sizes.[6] Recently, it has been reported on the preparation of bimodal (meso–macro or micro–macro) porous materials having enhanced site accessibility.[7] In this last case, the synthesis strategy includes the use of additional templates (besides the proper surfactant), such as latex spheres and microemulsions. This is a polished successful approach. However, besides its apparent singularity, it necessarily implies previous somewhat cumbersome processes of preparation and stabilisation of the large-scale template.

We report here on a new direct and reproducible one-pot surfactant-assisted procedure that has allowed us to prepare silica-based materials, both as powders and monoliths (denoted UVM-7 and M-UVM-7), having bimodal pore systems (meso–large mesoporous or meso–macroporous) and containing a diversity of dopant elements (M = Al, Ti, V, Zr).[8] Modulation of pore sizes depends on both the surfactant (small pores) and the procedural (synthesis and ageing) conditions (large pores).

The procedure is based on the use of a simple structural directing agent (CTABr = cetyltrimethylammonium bromide) and a complexing polyalcohol (2,2′,2″-nitrilotriethanol, TEAH3) able to adequately regulate the rates of the hydrolysis and condensation processes involving the different inorganic components (or heteroelements) of the final material.[9] In fact, TEAH3 derivatives have been also used as hydrolytic precursors in the synthesis of mesoporous silicas through non-surfactant-assisted procedures.[10] In a typical synthesis leading to the UVM-7 pure silica, 4.23 g of CTABr were added at 60 °C to a solution of TEAH3 (23 ml) containing 0.045 mol of a silatrane derivative of TEAH3 (*e.g.* in the form of Si(TEA-)(TEAH$_2$), TEA is the fully deprotonated ligand).[9] Then, 180 mL of water were slowly added with vigorous stirring at 50 °C. After a few minutes, a white suspension resulted. This mixture was aged at room temperature for 2 h. The resulting powder was collected by filtration, washed with water and ethanol, and air-dried. To prepare the final porous material, the as-synthesised solid was calcined at 500 °C for 5 h. Heteroelement incorporation is achieved by simply adding variable amounts of the respective metal–atrane complexes[9] to the silatrane containing solution, and following then the same general procedure. Table 1 summarizes the main synthesis variables and physical data. In all cases, the molar ratio of the reagents in the mother-liquor was adjusted to $2\,\mathrm{Si}:x\,\mathrm{M}:7\,\mathrm{TEAH3}:0.52\,\mathrm{CTABr}:130$–

---

† Electronic supplementary information (ESI) available: UV–Vis spectrum of sample **3**. See http://www.rsc.org/suppdata/cc/b1/b110883b/

Table 1 Selected synthetic and physical data for some UVM-7 and M-UVM-7 bimodal porous materials

Sample[a]			Si/M Solution	Si/M[b] Solid	d_{100}/nm	S_{BET}/m^2 g^{-1}	Pore size/nm[e] (small pore)	Pore size/nm (large pore)	Vol./cm^3 g^{-1} (small pore)	Vol./cm^3 g^{-1} (large pore)	Vol./cm^3 g^{-1} (total pore)
1	UVM-7[c]	P	∞	∞	4.19	1095	3.19	43.2	1.06	1.48	2.54
2	UVM-7[d]	P	∞	∞	4.20	1075	2.97	66.5	0.98	1.42	2.40
3	Ti-UVM-7	P	50	40	4.01	1077	3.15	62.5	0.97	1.48	2.45
4	V-UVM-7	P	50	65	4.02	1045	3.17	55.1	1.02	1.46	2.48
5	Al-UVM-7	P	50	40	4.10	1094	2.85	55.0	0.95	1.38	2.33
6	Zr-UVM-7	P	50	50	4.10	1060	2.59	25.2	0.84	1.24	2.08
7	UVM-7[d]	M	∞	∞	4.19	1036	2.70	65.4	0.86	1.06	1.92
8	UVM-7[c]	M	∞	∞	4.20	924	2.77	34.8	0.77	1.25	2.02
9	V-UVM-7	M	70	80	4.13	1070	2.83	70.0	0.85	1.01	1.86

[a] P = powder, M = monoliths. [b] Values averaged from EPMA of *ca.* 50 particles. [c] t = 2 h and water/TEAH3 = 25.7. [d] t = 24 h and water/TEAH3 = 21.4. [e] Pore diameters calculated by using the BJH model on the adsorption branch of the isotherms.

DOI: 10.1039/b110883b

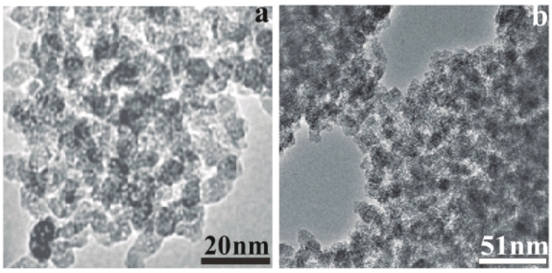

Fig. 1 Representative TEM images of selected UVM-7 and M-UVM-7 materials: (a) sample 1, (b) sample 5.

190 H_2O. Preparation of monoliths was carried out by casting or extrusion of the doughy as-synthesised material (after partial elimination of the solvent by filtration). Surfactant removal from the as-synthesised monoliths was thermally achieved after a prolonged and stepped drying period: 24 h at 110 °C and 5 h at 500 °C (heating rate: 1 °C min^{-1}). All samples were characterised by electron probe microanalysis (EPMA, Philips SEM-515), XRD techniques (Seifert 3000TT diffractometer using Cu-Kα radiation), TEM (Hitachi H9000NAR electron microscope operating at 300 kV) and N_2 adsorption–desorption isotherms (Micromeritics ASAP2010).

Our synthesis strategy has been designed to overcome problems associated to differences in reactivity between the Si source and the other precursor species which contains M cations.[9] The small mesoporous system is generated with the help of the template effect of the surfactant (it very likely might be modulated by changing the length of its chains). The large pores (in the border between the meso- and macro-pore domains) are generated as the nucleation and growth of the primary mesoporous nanoparticles proceeds. Their size can be modulated easily by modifying the water/TEAH3 ratio in the starting solution, as well as varying the ageing time. Relatively high water/TEAH3 molar ratios (*i.e.* in the range 25–28) and short ageing times (t < 6 h) favour the generation of secondary large-mesopores (<50 nm), while low water/TEAH3 ratios (18–23) and prolonged ageing times (12 < t < 48 h) expand the dimension of these large pores to the macropore range.

EPMA shows that all M-UVM-7 samples are chemically homogeneous (monophasic) products with a regular heteroelement distribution.†All materials display low angle XRD patterns with one strong peak and one broad signal of relatively low intensity, which can be associated to the (100) and the overlapped (110) and (200) reflections of a MCM-41-like hexagonal cell, respectively. These patterns are characteristic of hexagonal disordered mesoporous materials, and they only inform us about the existence of the intra-nanoparticle ordered mesopore (small pores) system.

The nature of the non-ordered large pore system in the UVM-7 and M-UVM-7 materials can be understood with the aid of TEM images (Fig. 1). At this level, the most outstanding feature concerning these materials is their unusual architecture: a continuous network constructed from soldered small mesoporous nanoparticles that generates a non-ordered system of large pores (between large-meso and macro). For the UVM-7 pure silicas, the standard dimension of the nanoparticles is very small (12–17 nm); they are slightly larger (30–70 nm) for doped M-UVM-7 materials. The presence of bimodal pore systems in UVM-7 and M-UVM-7 materials is further illustrated by the N_2 adsorption–desorption isotherms (Fig. 2). In all cases, the curves show two well-defined adsorption steps. The first, at an intermediate relative pressure, is related to capillary condensation of nitrogen inside the intra-nanoparticle mesopores. The absence of any hysteresis loop and its sharp curvature suggests the existence of uniform and cylindrical small mesopores. The second step, at a high relative pressure, corresponds to the filling of the large meso- or macro-pores among the primary nanoparticles. In this latter case, the curves show hysteresis and a relatively wide pore size distribution. In short, adsorption–desorption results are consistent with TEM observations. Both UVM-7 and M-UVM-7 materials, as consequence of their very open frameworks, present very high pore volumes. In fact, they are similar to those observed in aerogels[11] and mesocellular silica foams,[12] although slightly lower than those reported for MCM-41AT expanded unimodal porous silicas.[13]

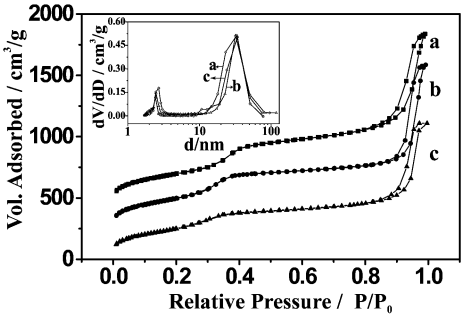

Fig. 2 N_2 adsorption–desorption isotherms (curves are shifted for clarity) for (a) sample 1, (b) sample 5 and (c) sample 8. The inset shows the pore size distributions from the desorption branches.

Fig. 3 UVM-7 monoliths (sample 7) prepared by casting (left) and extrusion (right). Scale values in cm.

Casting or extrusion techniques make it possible to mould mesoporous monoliths of significantly large dimensions (Fig. 3). The so-formed UVM-7 and M-UVM-7 materials maintain the particle and pore morphology of the powders, as well as their adsorptive properties.

In conclusion, we report here on a simple preparative procedure yielding bimodal porous materials admitting variable contents of different heteroelements. The spongy character of these materials results in a enhanced accessibility to their active sites which confers special interest as possible catalysts. On the other hand, there is no doubt that the possibility to shape them at will implies potential advantages for their practical use in other processes involving molecular recognition.

This research was supported by the Spanish MCyT under grants PB98-1424-C02-01 and MAT2000-1387-C02.

Notes and references

1 P. Behrens, *Adv. Mater.*, 1993, **5**, 127.
2 C. T. Kresge, M. E. Leonowicz, W. J. Roth, J. C. Vartuli and J. S. Beck, *Nature*, 1992, **359**, 710.
3 A. Tuel, *Microporous Mesoporous Mater.*, 1999, **27**, 151.
4 T. R. Pauly, Y. Liu, T. J. Pinnavaia, S. J. L. Billinge and T. P. Rieker, *J. Am. Chem. Soc.*, 1999, **121**, 8835.
5 K. A. Koyano and T. Tatsumi, *Chem. Commun.*, 1996, 145.
6 A. Sayari and S. Hamoudi, *Chem. Mater.*, 2001, **13**, 3151.
7 C. F. Blanford, H. Yan, R. C. Schroden, M. Al-Douas and A. Stein, *Adv. Mater.*, 2001, **13**, 401.
8 P. Amorós, A. Beltrán, D. Beltrán, A. B. Descalzo, J. El Haskouri, C. Guillem, J. Latorre, M. D. Marcos and G. Rodríguez-López, *Spanish Pat.*, P200102777.
9 S. Cabrera, J. El Haskouri, C. Guillem, J. Latorre, A. Beltrán, D. Beltrán, M. D. Marcos and P. Amorós, *Solid State Sci.*, 2000, **2**, 405.
10 J. C. Jansen, L. Marchese, W. Zhou, N. v. d. Puil and T. Maschmeyer, *Chem. Commun.*, 2001, 713.
11 J. Frieke, *Aerogel*, Springer Verlag, Berlin, 1986, vol. 149, p.147.
12 P. Schmidt, W. W. Luckens, D. Zhao, P. Yang, B. F. Chmelka and G. D. Stucky, *J. Am. Chem. Soc.*, 1999, **279**, 548.
13 A. Sayari, *Angew. Chem., Int. Ed.*, 2000, **39**, 2920.