Synthesis of Si and Ti-Si-MCM-48 mesoporous materials with controlled pore sizes in the absence of polar organic additives and alkali metal ions

Avelino Corma,* Qiubin Kan and Fernando Rey

Instituto de Tecnologia Química, UPV-CSIC, Universidad Politécnica, Avda. de los Naranjos, S/N, 46022 Valencia, Spain

A new route for the synthesis of Si- and Si-Ti-MCM-48 has been developed which allows these materials to be obtained without using polar organic additives and alkali metal ions; this procedure not only produces more active and selective Ti-MCM-48 oxidation catalysts than those reported before, but also permits the synthesis of MCM-48 with controlled pore diameters.

The development of ordered mesoporous materials (M41S) containing different atoms in the pore walls has opened up new possibilities for the use of mesoporous molecular sieve materials in the field of catalysis.[1–7] These materials have large channels with regular pores which can be varied in some cases from 1.5 to 7.0 nm, and which are ordered in a hexagonal (MCM-41), cubic (MCM-48), or laminar (MCM-50) array. All these materials are characterised by extremely narrow pore size distributions in the mesoporous region, long range order, high surface areas (> 700 m^2 g^{-1}) and are stable after calcination. From the point of view of catalytic activity the most interesting materials are the MCM-48 array, because its pore structure is built up of two independent tridirectional channel systems.[8] However, little research has been carried out on MCM-48, probably due to the difficulty of its synthesis compared with the more studied MCM-41, and also the difficulty of controlling its pore size. In general, MCM-48 is prepared with high surfactant to silicon ratios (0.65–1.5),[9] and the presence of polar organic additives in the reaction mixture is believed to be essential for a successful synthesis of MCM-48[10,11] when cetyltrimethylammonium ion (CTA$^+$) surfactant is used as the structure-directing agent. To achieve the latter, tetraethylorthosilicate (TEOS) is usually used as the silicon source for preparation of MCM-48 since in this case the ethanol produced from the hydrolysis of TEOS acts as the required polar organic additive. When sodium silicate or other silica sources were used without addition of polar organics, MCM-41 was produced instead.[10,12] Furthermore, in most of the reported syntheses of pure siliceous MCM-48 materials and their metal derivates, NaOH was introduced in the synthesis gel.[9,12–14] It is known however, that there is a detrimental effect of alkali metal ions on the catalytic properties of titanium silicate molecular sieves.[15,16] We have found only one report in which pure siliceous and titanium-containing MCM-48 were prepared in absence of sodium ions by using TEOS as the silicon source.[17] Unfortunately, the synthesis was poorly reproducible due to the ill defined and critical ethanol evaporation step, which is required for the synthesis. While MCM-41 can be prepared with a large range of pore diameters, even in the absence of added organics,[18] this is not the case for the MCM-48 structure where relatively small changes in the pore diameter could only be achieved by using surfactants with different chain length, and pore sizes larger than *ca.* 2.8 nm have not been reported.

It is possible to overcome the above synthetic shortcomings and to produce high quality MCM-48 samples in the absence of polar organics and alkali metal ions, as well as enabling the pore diameter to be increased to *ca.* 3.8 nm. These achievements certainly open more possibilities for the use of MCM-48 as catalysts as is illustrated for Ti-MCM-48.

The hydrothermal synthesis of Si-MCM-48 was carried out with the following molar composition: 1.0 $SiO_2 : x$ CTAOH/Br : 32.0 H_2O, $x = 0.18–0.35$; the source of silicon was amorphous silica (Aerosil 200, Degussa) and an aqueous solution of CTAOH/Br with a OH/Br ratio of 90/10 was used. The homogenous gel was sealed in Teflon-lined stainless steel autoclaves and heated at 60–150 °C under static conditions. The time of synthesis was varied from 1 to 7 days depending on the temperature of synthesis and the pore size to be obtained. The resulting solid products were recovered by filtration, washed and dried at 60 °C for 24 h. The occluded organic was removed by heating the samples at 540 °C under a continuous flow of N_2 for 2 h, followed by calcination in a flow of air at 540 °C for 6 h.

From the XRD patterns presented in Fig. 1 it can be seen that highly ordered MCM-48 mesoporous materials consistent with an *Ia*3*d* cubic symmetry were obtained. In our procedure we succeeded in synthesising the MCM-48 structure at low surfactant to silicon ratios (0.20–0.28), unlike in the synthesis reported by Mobil Researchers where higher ratios seem to be mandatory to obtain the cubic structure.[9] However, following our synthesis procedure it is critical to stay in between the limits given above for the surfactant/silicon ratio, since when this ratio reached 0.35, a lamellar phase (MCM-50) was formed under the same reaction conditions, and MCM-41 was produced when the ratio was lower than 0.18. The reaction temperature and crystallisation time were the key variables to control the pore diameter of the resultant samples. For instance, two different MCM-48 samples with cell parameters $a_0 = 92.8$ Å and $a_0 = 98.6$ Å were obtained after 24 h crystallization at 135 °C and 150 °C, respectively. Longer reaction times at 150 °C, *e.g.* 3 or 5 days, resulted in the swelling of the unit cell volume of the MCM-48 to $a_0 = 112.7$ and 116.8 Å, respectively. Moreover, after 5 days of crystallization a lamellar structure starts to appear due to a phase transition of MCM-48 (Fig. 1), producing a pure lamellar phase after 7 days of synthesis. The nitrogen

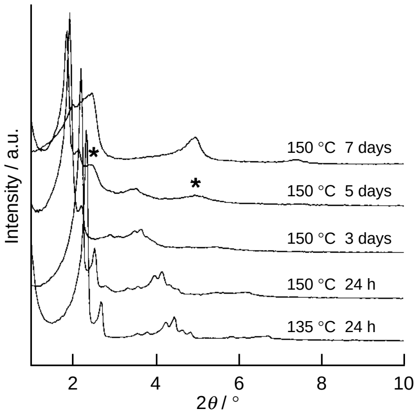

Fig. 1 X-Ray diffraction patterns of mesophases (MCM-48) synthesised at various temperatures and different reaction times. The phase transition from MCM-48 to the lamellar structure (*) upon extended synthesis times can be clearly seen.

Table 1 Unit cell parameter a_0 upon calcination at 540 °C, pore diameter, BET surface area and pore volume of MCM-48

	Synthesis conditions		Unit cell, a_0/Å					
Sample	T/°C	t/h	as[a]	ca[a]	Unit cell contraction/ Å	Pore diameter, d/Å	Surface area, s/m^2 g^{-1}	Pore volume, v/cm^3 g^{-1}
1	135	24	92.8	84.6	8.2	24	1121	0.87
2	150	24	98.6	92.1	5.5	28	1026	1.00
3	150	72	112.7	110.9	1.8	36	961	1.09
4[b]	150	120	116.8	115.4	1.4	38	800	0.93

[a] as = as-synthesized, ca = calcined. [b] Containing lamellar phase (see Fig. 1).

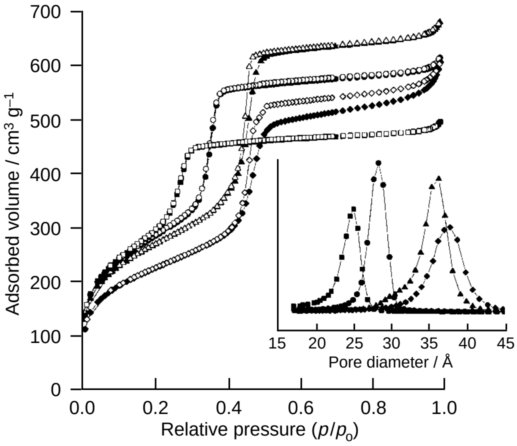

Fig. 2 Nitrogen adsorption–desorption isotherms of calcined MCM-48 materials with unit cell a_0 = 84.6 Å (■), a_0 = 92.1 Å (●), a_0 = 110.9 Å (▲) and a_0 = 115.4 Å (◆); inset: pore distribution of calcined MCM-48 materials with different unit cell parameters (calculated from N_2 adsorption isotherm branch)

adsorption–desorption isotherms of the corresponding calcined samples and the pore size distribution deduced from them are illustrated in Fig. 2. Table 1 lists the physicochemical characteristics of the as-synthesised and calcined samples, showing that swelling of the pore diameter occurs when the unit cell parameter increases.

If lower reaction temperatures are used the formation of MCM-41 is favoured. For instance, mesoporous materials with the MCM-41 structure were generated at 60 and 100 °C after 3 days when the synthesis gel composition given above was used. The effect of temperature on the structure of the mesoporous products is probably associated with the modification of the packing parameter g ($g = V/A_0 l$) of the surfactant organisation,[19,20] where V is the surfactant tail volume, l is the length of surfactant chain and A_0 is the effective head group area at the micelle surface. At lower temperatures, *e.g.* at 60 or 100 °C, where MCM-41 is produced, the effective g value for CTA$^+$ ions is smaller[21] than that at 135 to 150 °C when MCM-48 is generated.

By following the above procedure for the synthesis of Si-MCM-48, Ti-MCM-48 with Si/Ti = 100 has been successfully obtained. UV–VIS spectra for the as-synthesised and calcined Ti-MCM-48 show a main band at *ca.* 200–210 nm assigned to isolated framework titanium in tetrahedral coordination. The catalytic reactions for epoxidation of cyclohexene with *tert*-butyl hydroperoxide (TBHP) over the Ti-MCM-48 was carried out at 60 °C with an alkene/TBHP ratio of 4.0 and 5 mass% of catalyst and following the reaction and analytical procedure described previously.[4] The Ti-MCM-48 prepared here in the absence of alkali metal ions shows an initial reaction rate of 1.642 mol g^{-1} h^{-1}. The sample with the same Si/Ti ratio obtained in the presence of sodium ions using the method described in ref. 15 gives an initial reaction rate four times lower (0.448 mol g^{-1} h^{-1}) than that over the Ti-MCM-48 reported here, illustrating the beneficial effect of the novel synthesis procedure presented here.

In conclusion, it has been proven that it is possible to carry out the synthesis of mesoporous materials having the MCM-48 structure without using polar organics and alkali metal cations in the synthesis mixture. When the synthesis is carried out in the absence of alkali metal ions, the Ti-MCM-48 produced is a more active epoxidation catalyst than the Ti-MCM-48 synthesised following the conventional procedure in the presence of Na$^+$. Finally, by precisely controlling the synthesis conditions, *i.e.* composition of the gel, synthesis temperature and time, it was possible to produce MCM-48 samples with different pore diameters up to 3.8 nm.

The authors thank CICYT for financial support (MAT97-1207-C03-01).

Notes and References

* E-mail: itq@upvnet.upv.es

1 C. T. Kresge, M. E. Leonowicz, W. J. Roth, J. C. Vartuli and J. S. Beck, *Nature*, 1992, **359**, 710.
2 C. Y. Chen, S. L. Burkett, H. X. Li and M. E. Davis, *Microporous Mater.*, 1993, **2**, 27.
3 A. Corma, V. Fornes, M. T. Navarro and J. Perez-Pariente, *J. Catal.*, 1994, **148**, 569.
4 A. Corma, M. T. Navarro and J. Perez-Pariente, *J. Chem. Soc., Chem. Commun.*, 1994, 147; T. Blasco, A. Corma, M. T. Navarro and J. P. Pariente, *J. Catal.*, 1995, **156**, 65.
5 K. M. Reddy, I. L. Moudrakouski and A. Sayari, *J. Chem. Soc., Chem. Commun.*, 1995, 973.
6 F. Rey, G. Sankar, T. Maschmeyer, J. M. Thomas and R. G. Bell, *Top. Catal.*, 1996, **3**, 121.
7 A. Corma, *Chem. Rev.*, 1997, **97**, 2373.
8 A. Monnier, F. Schuth, Q. Huo, D. Kumar, D. Margolese, R. S. Maxwell, G. D. Stucky, M. Krishnamurty, P. Petroff, A. Firouzi, M. Janicke and B. F. Chmelka, *Science*, 1993, **261**, 1299.
9 J. C. Vartuli, K. D. Schmitt, C. T. Kresge, W. J. Roth, M. E. Leonowicz, S. B. McCullen, S. D. Hellring, J. S. Beck, J. L. Schlenker, D. H. Olson and E. W. Sheppard, *Chem. Mater.*, 1994, **6**, 2317.
10 Q. Huo, D. Y. Margolese and G. D. Stucky, *Chem. Mater.*, 1996, **8**, 1147.
11 K. W. Gallis and C. C. Landry, *Chem. Mater.*, 1997, **9**, 2035.
12 D. Zhao and D. Goldfarb, *J. Chem. Soc., Chem. Commun.*, 1995, 875.
13 M. Morey, A. Davidson and G. Stucky, *Microporous Mater.*, 1996, **6**, 99.
14 W. Zhang and T. J. Pinnavaia, *Catal. Lett.*, 1966, **38**, 261.
15 C. B. Khouw and M. E. Davis, *J. Catal.*, 1995, **151**, 77.
16 M. A. Camblor, A. Corma and J. Pérez-Pariente, *Zeolites*, 1993, **13**, 82.
17 K. A. Koyano and t. Tatsumi, *Chem. Commun.*, 1996, 145.
18 A. Corma, Q. Kan, M. T. Navarro, J. Perez-Pariente and F. Rey, *Chem. Mater.*, 1997, **9**, 2123.
19 J. Chavrolin and J. F. Srdoc, *J. Phys.*, 1987, **48**, 189.
20 S. M. Grunner, *J. Phys. Chem.*, 1989, **93**, 7562.
21 G. D. Stucky, A. Monnier, F. Schüth, Q. Huo, D. Margolese, D. Kumar, M. Krishnamurty, P. Petroff, A. Firouzi, M. Janicke and B. F. Chmelka, *Mol. Cryst. Liq. Cryst.*, 1994, **240**, 187.

Received in Bath, UK, 18th December 1997; 7/09093E