The syntheses of mesoporous molecular sieves in fluoride medium

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The MCM-41 molecular sieve, a member of the M41S family, is prepared for the first time in the presence of fluoride ions; the mesophase obtained from surfactant : silicon molar ratios in the range 0.2–2 : 1 is always hexagonal.

The discovery of mesoporous aluminosilicates molecular sieves by Mobil Oil researchers[1] broadened the field of reactions that may be catalysed by molecular sieves, a breakthrough long awaited for.

These new materials can be obtained in the presence of a range of surfactant molecules of the type $Me_3C_nH_{2n-1}N^+$,[1–4] (n = 8, 10, 12, 14, 16), yielding monodimensional channels whose diameter depends not only upon the value of n but also on the presence or absence of organic additives.[2,3] Even though the silicon and aluminium sources could be of varied nature, the use of sodium silicate is usually accompanied by the addition of sulfuric acid.[2,4] Also, according to the surfactant : silicon molar ratio, one obtains[2,5] a hexagonal phase (surf : Si < 1 : 1, MCM-41), cubic phase (surf : Si = 1.0–1.5 : 1, MCM-48), the thermally unstable lamellar material (surf : Si = 1.2–2.0 : 1) or the cubic octamer {surf : Si > 2 : 1, $[\{(CTMASiO)_{2.5}\}_8]$ (CTMA = cetyltrimethylammonium)}.

However, until now, no study has been reported on the possibility of synthesizing these mesoporous materials in the presence of fluoride ions, which can modify several physical characteristics of these molecular sieves, in particular the mesophase formed. Also, ageing of the reaction mixture has not yet been examined. These modifications can influence the nature of the structure bonding and degree of polymerization in the final product.

Seven samples were prepared with the following gel composition; $SiO_2 : x$ $CTMA_2O : 100$ H_2O. The amount of CTMABr was varied in such a way as to obtain molar ratios $CTMA^+ : Si^{4+}$, in the gel, of 0.2 (sample 46), 0.33 (sample 48), 0.5 (sample 49), 0.66 (sample 50), 1.0 (sample 52), 1.5 (sample 60) and 2.0 : 1 (sample 53). The reaction mixture was prepared by mixing sodium silicate (62.8 mass% SiO_2, 17.5 mass% Na_2O, 19.7 mass% H_2O, Vetec) with half the water required for the reaction. To this clear solution, a 50 mass% dense solution of CTMABr (Aldrich) in distilled water, aged for 24 h, was added. The viscous solution was stirred for 30 min and 48 mass% HF (Aldrich) was added until the pH reached 10.8–10.9. The suspension was then aged for 4 h at 78–80 °C and transferred to an autoclave. A portion of each batch of reaction mixture was filtered, washed and air dried, and is herein referred to as precursor. After hydrothermal treatment (66 h, 150 °C), the samples were filtered using a Buchner funnel and washed with at least 3 l of distilled water. All samples were air dried. The pH change during the hydrothermal treatment varied between 0.15 and 1.13; the pH of the mother liquor was always higher after hydrothermal treatment.

Fig. 1 shows the powder X-ray profiles obtained for some of the samples prepared as described above (Shimadzu 3A, Cu-Kα radiation, 35 kV, 25 mA, 2° min^{-1}). The as-prepared samples show the typical four-peak profile of MCM-41.[2] Except for samples 48 and 50, the precursor also had a four-peak profile, after just 4 h ageing at 78–80 °C. Sample 50 displayed a better resolved X-ray profile after extraction of $CTMA^+$ with an ethanol–heptane (1 : 1) solution containing 0.15 mol dm^{-3} HCl.[6]

The d-spacing values for these samples varied from 40 to 44 Å, 4 Å above the value reported for materials obtained in the sulfuric acid syntheses (39.8 Å).[5] All samples showed BET surface areas in the range 1000–1100 m^2 g^{-1}.

It is interesting to observe that the peaks corresponding to Miller indices (110), (200) and (210) are more intense in the fluoride system than in the profiles reported in the literature for the sulfate system (see refs. 1 and 2). This indicates a higher organization of the pores when fluoride ions are present. This is not totally unexpected since Guth *et al.*[7] have shown that the use

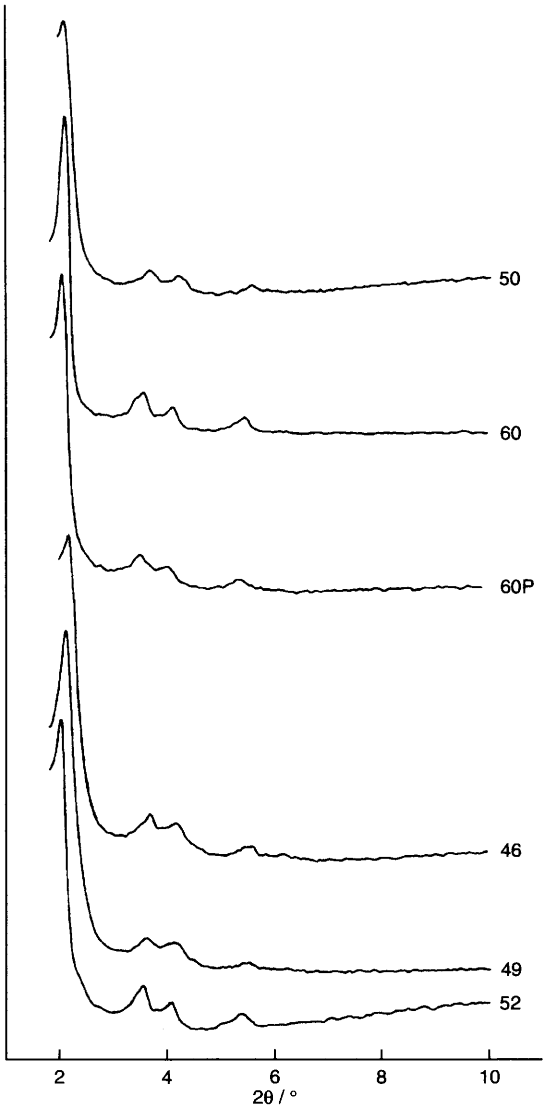

Fig. 1 Powder X-ray profiles of the samples synthesized in the presence of fluoride ions. The numbers refer to the samples described in the text, 60P is the precursor of sample 60.

of this mineralizing agent, between pH 2–12, acts to diminish the number of defects in the framework. The lower the quantity of defects in the material, even when amorphous as is the case for MCM-41, the lower the possibility of distortions on the pore wall.

Generally, the precursor samples show slightly higher *d*-spacing values, indicating that upon hydrothermal treatment, condensation of silanol groups occurs which lowers the *d*-spacing values.

For the extracted samples two different behaviours were observed: samples prepared with $CTMA^+ : Si^{4+} \leqslant 0.5 : 1$, on losing $CTMA^+$ have higher *d*-spacing values, and samples with $CTMA^+ : Si^{4+} \geqslant 0.66 : 1$ have lower *d*-spacings.

The behaviour of the SiO_2–CTA^+–F^- system is significantly different from that for initial reports on the mesophases. Beck and coworkers[1,2] and Vartuli *et al.*[5] were emphatic about the nature of phases formed at each surfactant : silicon molar ratio, leading to the belief that the polymerizing capacity of the silicon precursor was the factor that determined the mesophase formed and that the activity and capacity of the silicon precursor to polymerize depended only on their concentration relative to $CTMA^+$. However, other agents can influence the activity of the silica precursors to alter their activity towards polymerization and therefore affect the mesophase formed.

The fact that the hexagonal mesophase is detected immediately after pH equilibration leads us to think that a lamellar-to-hexagonal transition of the surfactant–silica system does not take place, as proposed by Monnier *et al.*[9]

There are, so far, two proposed general mechanisms for the formation of mesophases.[2] One of these proposes the previous existence of an array of micellar rods hexagonally organized or in the form of lamellae, around which the silica precursors polymerize. The formation of a hexagonal or lamellar arrangement depends on the nature of the surfactant, concentration, and on the solution temperature. The second mechanism proposes that the nature of the array formed is induced by the presence of silicate. In this case, the type of arrangement formed depends on the above conditions as well as the relative concentrations of $CTMA^+$ and Si^{4+}, *i.e.* the $CTMA^+ : Si^{4+}$ molar ratio.

The first mechanism can be influenced by the presence of fluoride if a competition is established between Br^- and F^- for $CTMA^+$, in the sense that CTMAF may not form rods that arrange themselves hexagonally to form the desired mesophase. In this case, samples 46, 48 and 49, in which there are more than one F^- per $CTMA^+$, should show a behaviour different from the others, which is not observed. Similarly, for the second proposed mechanism, fluoride should have the same influence.

However, fluoride ions do influence the nature, activity and polymerizing capacity of the silica precursors. F^- catalyses the gelation of silicates, thus favouring the growth of silica units[8] to larger dimensions than would be expected at this pH, if only the OH^- mineralizing agent was present. Therefore, the units that displace water from the rods, according to the first mechanism, to form the silica wall are much more condensed. These silica units are in the form of multidentate ligands necessary for hexagonal mesophase formation,[9] and are obtained at the beginning of the reaction; therefore, less polymerization is needed to close the pore walls. This could well be why we do not see a lamellar-to-hexagonal transition in the systems reported here. Also, Cheng *et al.*[10] have elegantly shown that less supersaturated and more homogeneous gels lead to better formed crystals and more organized materials and it has been established that F^- provides such conditions.[7]

The formation of the mesophases by the second mechanism would be influenced by the different organizing capacities of the fluoride-generated silicate units. One should also bear in mind that a fluorided silica surface is much more hydrophobic[11] than a silanol silica surface. Klinowski *et al.*[12] also pointed out that the presence of OH^- as counter ions for micellar polar groups catalyse the hydrolysis of tetraethylorthosilicate, therefore accelerating the formation of the hexagonal mesophase. F^- in high concentrations may compete with Br^- and OH^- for these positions and make the hexagonal mesophase the only viable one in this system, regardless of the $CTMA^+ : Si^{4+}$ ratio. This aspect is under study, as well as the influence of lower and higher pH (varying $OH^- : F^-$ ratios), of other sources of F^-, besides hydrofluoric acid, and of the possibility of other mesophase syntheses, in the presence of F^-.

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References

1 J. S. Beck, *US Pat.*, 5 057 296, 1991; C. T. Kresge, M. E. Leonowicz, W. J. Roth and J. C. Vartuli, *US Pat.*, 5 098 684, 1992; 5 102 643, 1992; J. S. Beck, C. T. W. Chu, I. D. Johnson, C. T. Kresge, M. E. Leonowicz, W. J. Roth and J. C. Vartuli, *US Pat.*, 5 108 725, 1992.

2 J. S. Beck, J. C. Vartuli, W. J. Roth, M. E. Leonowicz, C. T. Kresge, K. D. Schmitt, C. T. W. Chu, D. H. Olson, E. W. Sheppard, S. B. McCullen, J. B. Higgins and J. L. Schlenker, *J. Am. Chem. Soc.*, 1992, **114**, 10834.

3 C. T. Kresge, M. E. Leonowicz, W. J. Roth, J. C. Vartuli and J. S. Beck, *Nature*, 1992, **359**, 710.

4 R. Schmidt, D. Akporiaye, M. Stöcker and O. H. Ellestad, *Stud. Surf. Sci. Catal.*, 1994, **84**, 61.

5 J. C. Vartuli, K. D. Schmidt, 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, *Stud. Surf. Sci. Catal.*, 1994, **84**, 53.

6 D. D. Whitehurst, *US Pat.*, 5 143 879, 1992.

7 J. L. Guth, H. Kessler and R. Wey, *Stud. Surf. Sci. Catal.*, 1986, **28**, 121.

8 C. J. Brinker and G. W. Scherer, *Sol-Gel Science*, Academic Press, London, 1990, p. 107.

9 A. Monnier, F. Schüth, 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.

10 C.-F. Cheng, H. He, W. Zhou and J. Klinowski, *Chem. Phys. Lett.*, 1995, **244**, 117.

11 C. J. Brinker and G. W. Scherer, *Sol-Gel Science*, Academic Press, London, 1990, p. 644.

12 C.-F. Cheng, Z. Luan and J. Klinowski, *Langmuir*, 1995, **11**, 2815.

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