Room-temperature synthesis of silicate mesoporous materials. An *in situ* study of the lamellar to hexagonal phase transition

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A study of the lamellar to hexagonal phase transition, in the synthesis of a mesoporous silicate phase, by *in situ* XRD is reported.

Recently a new family of mesoporous molecular sieves with regular and constant pore diameters in the range 15–100 Å, designated as M41S, has been synthesized by scientists at Mobil Oil Corporation.[1] The solids were prepared by hydrothermal transformation of alkaline silicate or aluminosilicate gels in the presence of quaternary ammonium surfactants $C_nH_{2n+1}Me_3N^+$ with different alkyl chain length (n = 8–18). One of the mechanisms proposed by these workers for their construction is based on the surfactant micelles aggregating into rods, which form a hexagonal arrangement in solution. Subsequently the silicates condense around this arrangement to produce an inorganic structure reflecting the hexagonal micellar array. An alternative process is that inorganic species induce formation of the hexagonal phase.

This latter process was then developed by Chen *et al.*[2] in which silicate species interact with micellar rods to form two or three monolayers around the external surface of the micelles; these composites pack spontaneously into a hexagonal array, characteristic of the MCM-41 material.

Finally, Monnier *et al.*[3] propose that the hexagonal phase forms *via* a lamellar phase. Initially silicate oligomers act as multidentate ligands with a high charge density which provides a lamellar organization of the surfactant. As polymerization of the silica proceeds, the diminished charge density of larger silica polyanions increases the average head-group area of the surfactant assembly, driving the transformation towards the hexagonal mesophase.

The objective of this work was an *in situ* study of the transformation of the lamellar phase into the hexagonal phase. According to the literature,[3,4] such a transition is very sensitive to pH, therefore the product obtained after washing or only filtration and air drying is probably not the same as that obtained by suspension in the mother-liquor.

The composition of the mixture was: 2 SiO_2 : 1.34 Na_2O : 0.43 CTMABr : 255 H_2O and was obtained by the complete dissolution of CTMABr ($C_{19}H_{42}BrN$, Fluka) in NaOH solution (after gentle heating). Then a sodium silicate solution (29.25% SiO_2 : 8.86% Na_2O : 61.88% H_2O, Crosfield Chemical) was added under stirring, leading to the formation of a white precipitate. Next the solution was acidified stepwise with 1 mol dm^{-3} HCl under stirring. During each step of the acidification, part of the slurry (precipitate and mother-liquor) was removed and divided into two samples, one for *in situ* XRD and optical microscopy while the other was filtered and air-dried without washing before characterization.

For the *in situ* XRD analysis, a capillary tube (diameter 0.3 mm) was filled with the suspension and sealed with paste to avoid any further evolution of the precipitate. In both cases, the XRD patterns were obtained with Cu-Kα_1 radiation on a STOE STADI-P diffractometer equipped with a curved germanium (111) primary monochromator and a linear position-sensitive detector. The crystal size and the morphology of the precipitate in suspension in the mother-liquor were checked by optical microscopy.

Before acidification (pH ≈ 13), a lamellar phase was observed [Figs. 1 and 2(*a*)] with a d_{100} spacing of 32 Å. This phase is not pure, since, according to the XRD pattern, amorphous material is also present (Fig. 1). The crystals (thin platelets) display a quasi-hexagonal morphology with sizes ranging from 20 to 100 μm (Fig. 3). Larger platelets were obtained when the surfactant was not completely dissolved in the starting solution.

During acidification (pH ≈ 12.4) this lamellar phase disappeared and only a very small amount of tiny particles remained in the resulting solution which could not be characterized by XRD analysis. When this suspension was kept at a slightly lower temperature, a denser precipitate was obtained and the XRD pattern corresponds to CTMABr [Fig. 2(*b*)]. In no case was a lamellar or a hexagonal phase observed. At this stage, we may conclude that the transition is not a direct transformation of the lamellar phase into the hexagonal mesophase. The decrease of the charge density of the silicate-based species with decreasing pH leads to the dissolution of the lamellar phase. The XRD pattern of the corresponding filtered and air-dried sample also corresponds only to CTMABr and displays two peaks at 26 and 13 Å in the range 2θ 1–8° [Fig. 4(*a*)].

Under the experimental conditions used, the presence of CTMABr can be explained by the fact that the Krafft temperature[5] of the surfactant is close to 25 °C. Above this temperature, the formation of the micelles leads to an increase of the solubility, whereas below 25 °C monomers are mainly present. Therefore the solubility is lower and CTMABr recrystallizes.

When the pH of the mixture was close to 11.6, the hexagonal phase appeared. The XRD pattern displays a main component at

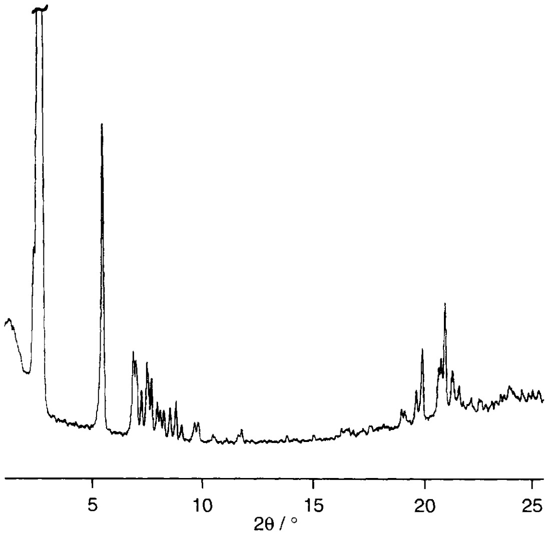

Fig. 1 XRD pattern of the lamellar phase obtained at pH ≈ 13

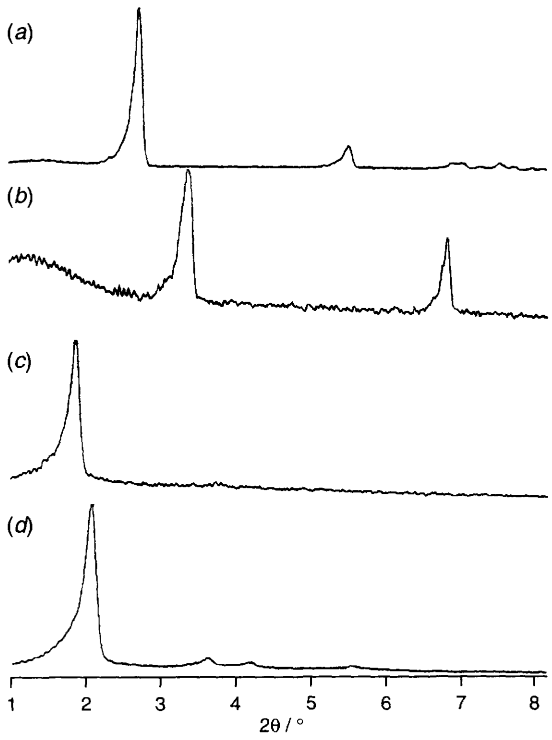

Fig. 2 Lamellar to hexagonal phase transition during acidification, XRD patterns of the suspension in the mother liquor at (*a*) pH ≈ 13, (*b*) ≈ 12.4, (*c*) ≈ 11.6 and (*d*) ≈ 10.7

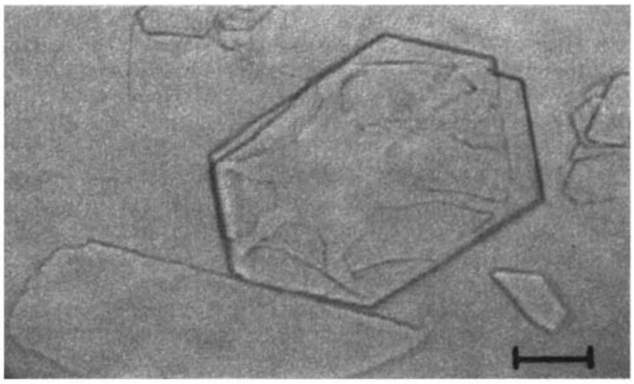

Fig. 3 Typical optical micrograph of lamellar phase at pH ≈ 13 (scale bar = 30 μm)

46.7 Å [Fig. 2(*c*)]. A well ordered hexagonal phase crystallized when the final pH value was 10.7 [Fig. 2(*d*)].

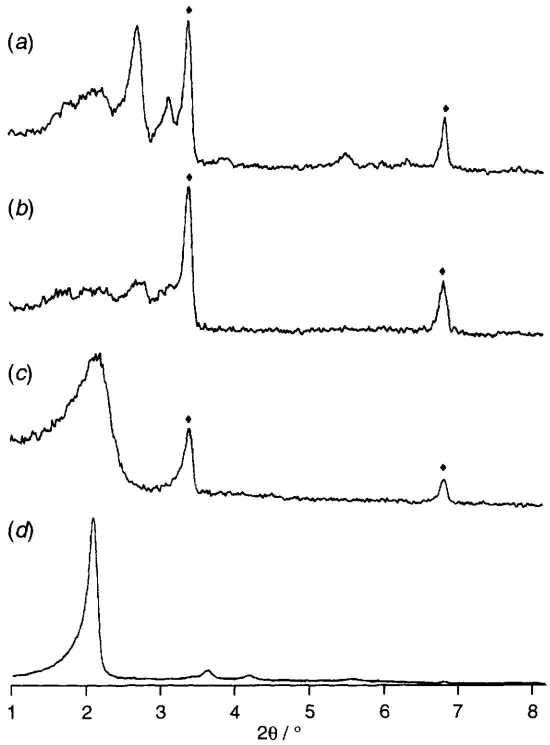

Fig. 4 Lamellar to hexagonal phase transition during acidification, on the filtered and air-dried precipitate. XRD patterns of the precipitate obtained at (*a*) pH ≈ 12.8, (*b*) ≈ 12.4; (*c*) ≈ 11.6 and (*d*) ≈ 10.7; (♦) peaks corresponding to CTMABr.

The results obtained when the precipitate was filtered and air-dried were quite different, since even at high pH, lamellar, hexagonal and CTMABr phases are present on the XRD pattern [Fig. 4(*a*)], the latter two resulting from evaporation and decrease in pH by carbonation on drying. At pH 10.7, a pure hexagonal phase is obtained [Fig. 4(*d*)]. The reaction is more complete and a stoichiometric amount of the surfactant (0.215 CTMA per Si) is completely trapped in the hexagonal mesophase. Moreover, d_{100} of the filtered and air-dried hexagonal phase (d = 42 Å) is slightly lower than that of the corresponding material present in the mother-liquor (d = 42.4 Å); hydration of the organic cations in the latter case might explain this difference.

In conclusion, this study shows clearly that the lamellar–hexagonal phase transition in the synthesis of mesoporous silicate materials at room temperature depends on the pH of the reaction mixture. Such a transformation is not a direct transformation but proceeds *via* a dissolution of the lamellar phase followed by crystallization of the hexagonal phase.

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