Formation of Silica–Surfactant Mesophases studied by Real-time *in situ* X-Ray Powder Diffraction

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Real-time *in situ* energy dispersive synchrotron X-ray powder diffraction data provides evidence for the formation of an intermediate lamellar silica–surfactant intercalate during the synthesis of the hexagonal mesophase derived from the layered polysilicate kanemite, whereas no intermediate phases are observed during the formation of the silica–surfactant mesophase that leads to the mesoporous material MCM-41.

Since the role of surfactants in the formation of ordered mesoporous materials has been disclosed,[1] there have been many attempts to make such materials, and to elucidate the mechanisms associated with the synthesis of highly ordered mesoporous materials including MCM-41.[2] The first report[1] shows that the reaction of a crystalline single-layered polysilicate kanemite ($NaHSi_2O_5{\cdot}3H_2O$) with aqueous solutions of alkyltrimethylammonium (ATMA) ions yields silicate–organic complexes and that the complexes can be converted to mesoporous silica with narrow pore size distributions by calcination.[1,3] A hexagonal mesophase can also be prepared from the same starting materials by changing the reaction conditions, and it can be converted into highly ordered hexagonal mesoporous materials such as FSM-16 by calcination.[4]

The proposed formation mechanism reported previously involves the intercalation of ATMA ions into the interlayer space of kanemite *via* the ion-exchange of interlayer sodium ions and subsequent folding and condensation of thin silicate layers.[4,5] Chen *et al.*[6] have recently claimed that the layered structure of kanemite is locally rearranged by the reaction with ATMA ions and that a hexagonal phase formed by condensation of the fragmented layered silicates after wrapping around rodlike micelles, although the conditions employed by Inagaki *et al.*[4] to form a hexagonal phase are too drastic to retain local environments of the layered nature. Because the hexagonal structure of FSM-16 is very similar to that of MCM-41,[2,4] the formation mechanism of the hexagonal mesophase derived from kanemite has become an interesting problem to be solved.

In order to clarify the formation mechanisms, it is necessary to follow the reaction processes *in situ*. The conversion of kanemite to various silicate–organic mesostructured materials is the key issue in understanding the nature of the porous materials derived from kanemite. However, no *in situ* measurements relating to the formation processes from kanemite with ATMA ions have been reported. O'Hare and coworkers have already shown that real-time *in situ* X-ray diffraction is a powerful technique for investigating the kinetics of intercalation reactions.[7] A detailed description of the reaction cell and the energy-dispersive X-ray diffraction experiment have been reported elsewhere.[8] In this study we report our investigations into the mechanism of the formation of the silica-surfactant mesophases leading to FSM-16 and MCM-41 using *in situ* diffraction techniques.

Fig. 1 shows the time-resolved energy dispersive X-ray powder diffraction spectra of an aqueous solution of hexadecyltrimethylammonium chloride ($C_{16}H_{33}NMe_3{}^+Cl^-$ = C_{16}TMACl) and kanemite at 70 °C.† As the reaction proceeds a new crystalline phase with a *d*-spacing of *ca.* 30 Å appears. This *d*-spacing increases gradually throughout the course of the reaction reaching a constant value of *ca.* 33 Å. Our preliminary investigations of this intermediate phase strongly suggest it has a lamellar structure due to its swelling properties in organic solvents, we also believe it has a somewhat condensed silica network because of the presence of a large amount of Q^4 units.[9] Subsequently, a second phase with a *d*-spacing of *ca.* 36 Å grows in with time. Although this phase cannot be definitely assigned at present, the value of the *d*-spacing suggests that it is either another disordered lamellar phase or a partly condensed silicate phase.

At longer reaction times we observed the growth of a set of peaks which can be indexed as the (100), (110) and (200) Bragg reflections corresponding to a 41 Å hexagonal phase [although in Fig. 1 only the (100) reflection is visible]. This hexagonal phase is the silica–surfactant mesophase which, after pH adjustment and filtration, gives FSM-16 on calcination. The growth of this hexagonal mesophase can be correlated to a corresponding decrease in the intensity of the initial (33 Å) lamellar phase. The diffraction data shown in Fig. 1 clearly indicates that the hexagonal (41 Å) silica mesophase forms before dissolution of all the crystalline silicates. Vartuli *et al.* have reported the formation of intercalation compounds from kanemite and ATMA ions.[10] However, the Na content of the kanemite ($Na_{0.4}H_{1.6}Si_2O_5{\cdot}nH_2O$) is much lower than that of conventional kanemite, thus the findings cannot be related to the present results.

Recent developments have clarified that molecular assemblies of surfactants can work as templates for the preparation of inorganic–organic mesophase materials which yield highly ordered mesoporous materials such as the M41S family

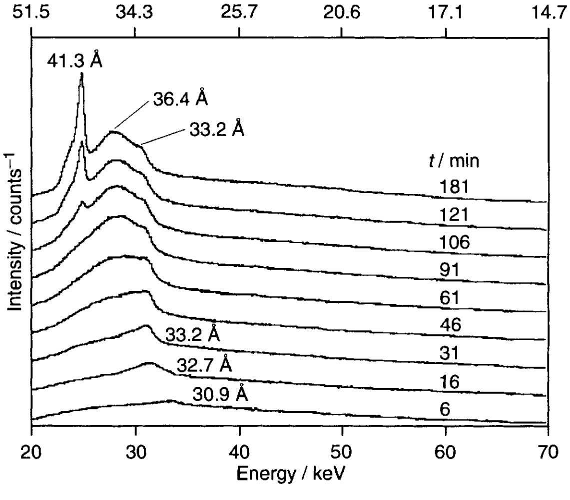

Fig. 1 Time-resolved energy dispersive X-ray diffraction spectra of C_{16} TMACl and kanemite in water at 70 °C, showing the development of three distinct crystalline silicate phases

including hexagonal MCM-41. Currently, there is much debate as to whether the FSM and MCM familes of mesoporous silicates are formed *via* similar mechanisms. Fig. 2 shows the time-resolved *in situ* energy dispersive X-ray powder diffraction data for the synthesis of silica–surfactant mesophase which on calcination yields MCM-41 using the conditions described by Kresge *et al.*[2]‡ The diffraction data shows the smooth growth of the intensity of the (100) and (110) Bragg reflections of the silica–surfactant hexagonal mesophase precursor to MCM-41, no peaks assignable to any intermediate crystalline silicates are observed. This data is consistent with the results reported by Chen *et al.*,[6] and those by Anderson and coworkers[11] based on ^{14}N NMR spectroscopy, although Monnier *et al.*[12] have proposed the transformation of a lamellar phase to a hexagonal phase.

In conclusion, the time-resolved X-ray diffraction data indicate that the silica–surfactant mesophase precursor to FSM-16 forms from a medium containing a number of intercalated silicate phases. In contrast, the hexagonal mesophase precursor to MCM-41 forms from a medium containing no other crystalline silicate species.

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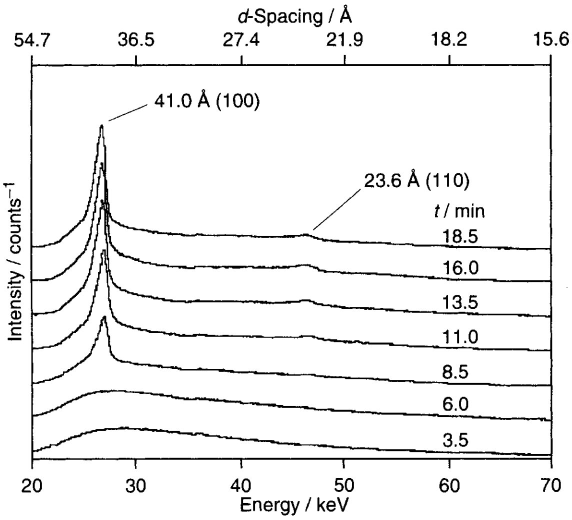

Fig. 2 Time-resolved energy dispersive X-ray diffraction spectra of the silicate–surfactant mixture, in a sealed vessel at 150 °C, from which MCM-41 is derived

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Footnotes

† The reaction mixture consisted of a mixture of 5 ml of 0.1 mol dm^{-3} $C_{16}TMACl$ solution and previously prepared kanemite ($NaHSi_2O_5{\cdot}3H_2O$) in a kanemite : $C_{16}TMACl$ molar ratio of 2.2 in water at 70 °C.

‡ The preparation of silica–surfactant mesophase derived from MCM-41 was precisely the procedure described by Kresge *et al.*[2] 0.004 mol C_{16} TMACl/OH (30% hydroxide), 4.9×10^{-4} mol Al_2O_3, 0.014 mol SiO_2, 0.004 mol tetramethylammonium hydroxide, 0.1 mol H_2O. The subsequent gel was aged for 1 hour prior to placing in the heating block at 150 °C in a sealed ampoule and the recording of the *in situ* diffraction data.

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