JOURNAL OF Materials CHEMISTRY

Transformation of kanemite into silicalite 1: parameters affecting the cation exchange reaction

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Received 12th June 2000, Accepted 16th August 2000
First published as an Advance Article on the web 5th October 2000

The optimum crystallization conditions for the transformation of kanemite into silicalite 1 have been determined by X-ray powder diffraction, thermal analysis and ^{29}Si NMR spectroscopy. The synthesis of silicalite 1 was favored by the use of a TPAOH template, in preference to a TPABr template, highly basic conditions during stirring of the suspension at 70 °C and the adjustment of the pH to 8.5 after stirring. The more the layered structure of kanemite disintegrated after the cation exchange reaction, the higher the amount of incorporated template and the higher the crystallinity of silicalite 1 after the solid-state transformation. The dissolution process that occurs during the cation exchange reaction with short-chain alkylammonium cations was different from that which occurs in the case of long-chain alkylammonium cations which are used for the synthesis of mesoporous materials.

Silicalite 1 is widely used in the petroleum and petrochemical industries as a selective adsorbent.[1] This material can be synthesized *via* a hydrothermal method,[2] however, in order to shape the product into a disk, it is necessary to use binders which affect its crystallinity and sorbent properties. Recently, increasing efforts have been directed towards the preparation of binderless preshaped zeolites *via* solid-state transformation.[3–5] Silicalite 1 can be synthesized in a disk-shaped form through the solid-state transformation of polysilicate kanemite, $NaHSi_2O_5\cdot3H_2O$, by heating at 130 °C 16 h in a closed glass ampoule.[6] It was observed by scanning electron microscopy that silicalite 1 crystals obtained by solid-state transformation at 130 °C from kanemite were more uniform and smaller than the crystals obtained by hydrothermal synthesis at the same temperature from cataloid SI-30 (SiO_2: 30.7; Na_2O: 0.4%), which is of great interest for technical applications. The disks prepared by solid-state transformation presented excellent mechanical strength, enough to keep their shape during sample handling and pretreatment for the usual applications.[7,8] Furthermore, the structure of the disk consisted of intergrown individual crystals forming secondary mesopores, thus providing high gas permeability. In the presence of aluminium (zeolite ZSM-5), high *p*-xylene selectivity was observed in the alkylation of toluene with methanol.[8]

Kanemite is a hydrated layer sodium silicate[9] that can be easily synthesized.[10] The kanemite structure has been studied by ^{1}H, ^{23}Na and ^{29}Si NMR spectroscopy[11–15] and single-crystal X-ray diffraction,[16] however, the structure has not been completely elucidated, as yet. The physical properties of kanemite include a high capacity for ion exchange whereby sodium ions can be replaced by organic moieties, such as alkylammonium cations.[10]

Mesoporous materials have been prepared from kanemite by exchanging sodium cations with long-chain alkylammonium cations and several mechanisms have been proposed. Inagaki *et al.*[17] proposed a "folded sheets" mechanism for the formation of FSM-16. The silicate sheets of kanemite are folded around the ion-exchanged surfactant cations and cross-linked by condensation of silanol groups on adjacent silicate sheets to form the three dimensional framework. Chen *et al.*[18] proposed the dissolution mechanism in the course of which the loss of structural integrity of the kanemite layers in combination with the ability of the surfactant molecules to change from a bilayered structure to a cylindrical micelle-like aggregate drives the reorganization of the organic–inorganic composite material. More recently, Thiesen *et al.*[19] proposed another dissolution mechanism in the course of which partial destruction of the silicate structure by long-chain alkylammonium ions occurs, followed by aggregation of the alkylammonium ions and fragments of the silicate layers leading to the formation of meso- and micro-pore frameworks during calcination.

So far, very little is known about the formation of zeolites from kanemite by exchanging sodium cations with short-chain alkylammonium cations. Unlike the synthesis of mesoporous materials from kanemite, which is carried out in one step, the synthesis of silicalite 1 from kanemite is carried out in two steps:

(1) Cation exchange in a liquid phase at 70 °C for 3 h, followed by adjustment of the pH to 8.5.
(2) Solid-state transformation of the intercalated kanemite into silicalite 1 at 130 °C.

To distinguish it from the hydrothermal synthesis, we call the procedure corresponding to these two steps "solid-state transformation".

For comparison, the transformation of kanemite into silicalite 1 through hydrothermal synthesis at 150 °C, using tetrapropylammonium hydroxide template, takes 3 days, the suspension having an initial pH value of 13.

In this paper, the influence of the parameters affecting the solid-state transformation of silicalite 1 from kanemite is studied by X-ray powder diffraction, thermal analysis and ^{29}Si NMR spectroscopy in order to better understand the process of formation of zeolites from kanemite using short-chain alkylammonium cations.

Experimental

Synthesis

The starting materials for the solid-state transformation from layered silicate were kanemite (Na^+ form) and an aqueous solution containing tetrapropylammonium (TPA) cation acting as a structure directing agent (template). The synthesis of kanemite from waterglass was described in a previous paper.[6]

Silicalite 1 was prepared by dispersing 1 g of kanemite in

DOI: 10.1039/b004664g

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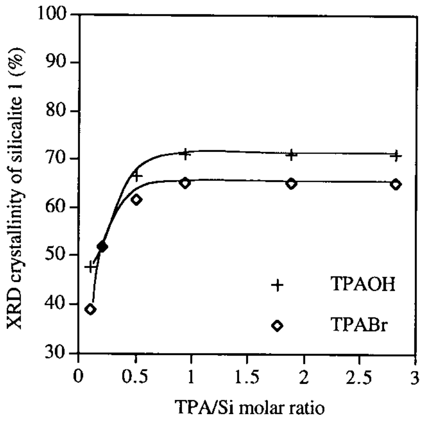

Fig. 1 Change in XRD crystallinity (%) of silicalite 1 *vs.* template/Si molar ratio.

10 ml of an aqueous solution of template. The mixture was heated at 70 °C for 3 h under stirring. After cooling to room temperature, the pH of the suspension was lowered to 8.5. The resulting product was filtered off, washed with deionized water and dried overnight at room temperature to yield kanemite–TPA powder. To shape the kanemite–TPA powder into a disk, a uniaxial compression moulder at a pressure of 400 kg cm^{-2} was used. The disk (prepared from 0.5 g of powder) was 20 mm in diameter and *ca.* 1 mm thick. Silicalite 1 was synthesized in a closed glass ampoule about 5 cm^3 in volume in an oven at 130 °C for 16 h.

The parameters (nature and concentration of the template, pH, temperature, *etc.*) were varied separately in order to study their influence on the synthesis of silicalite 1.

Analysis

X-Ray powder diffraction patterns of the samples were recorded using a MXP 18 diffractometer (Mac Science Co. Ltd.) with monochromatic Cu-Kα radiation. The crystals which were obtained by solid-state transformation from kanemite being smaller than 300 nm, the relative XRD crystallinity was taken as the sum of the (101), (011), (501) and (051) peak areas[20] of the unknown material divided by the sum of the peak areas of a standard silicalite 1 material which was taken to be 100% crystalline.

TG-DTA measurements were carried out with a Mac-Science TG-DTA 2000 analyzer. The template amount was evaluated by heating the samples to 1000 °C in a dry air flow (100 ml min^{-1}) at a heating rate of 10 °C min^{-1}.

^{29}Si MAS NMR spectroscopic characteristics of the samples were determined by a BRUKER AMX500 spectrometer operating at 99.36 MHz, with the samples placed in a 4 mm ZrO_2 rotor spinning at 4 kHz.

Results

The experimental conditions were thoroughly studied and the most important parameters were found to be the type and concentration of template and the pH before and after stirring the template–kanemite mixture at 70 °C.

Two templates were used: tetrapropylammonium hydroxide (TPAOH) and tetrapropylammonium bromide (TPABr). Preliminary experiments showed that, because TPAOH and TPABr templates gave kanemite–TPA solutions of different pH, the structure of the intercalated kanemite was also different after cation exchange. Thus, in order to start with materials of similar structure before solid-state transformation, the study into the influence of the kind and concentration of template was carried out by adjusting the pH to 12 (using HCl in the case of TPAOH template and NaOH in the case of TPABr template) before stirring at 70 °C. Although for both templates the highest crystallinity was obtained when TPA/Si $\geqslant$ 0.94 (Fig. 1), more template was intercalated (Fig. 2) and a higher crystallinity was obtained in the case of TPAOH.

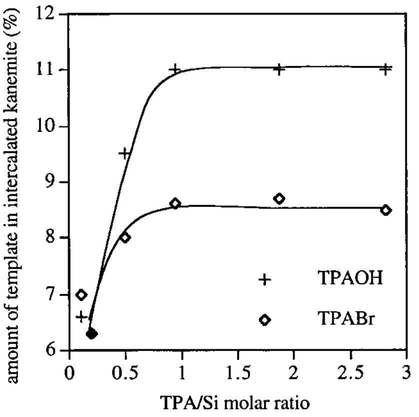

Fig. 2 Change in the amount (%) of intercalated template in kanemite powder *vs.* template/Si molar ratio.

It was observed that, by starting with 1 g of kanemite, about 0.7 g of kanemite–TPA powder was obtained after cation exchange independent of pH. Furthermore, the higher the pH of the kanemite–TPA mixture before stirring at 70 °C, the clearer the mixture was.

Figs. 3, 4 and 5 show that when the pH of the kanemite–TPA mixture before stirring at 70 °C increases, the amount of template which is intercalated increases and the intercalated kanemite progressively loses its initial structure. On the other hand, the crystallinity of silicalite 1 increases. It was observed that the Q_4/Q_3 ^{29}Si ratio increased slightly from pH = 11 to 13 (Q_4/Q_3 ^{29}Si ratio = 0.84; 0.86 and 0.97 for pH = 11; 12 and 13, respectively).

When the pH of the kanemite–TPA mixture after stirring at 70 °C was adjusted to a value smaller or equal to 8.5, a thick gel was obtained. Figs. 6, 7 and 8 show that, when the pH decreases down to 8.5, the amount of template which is intercalated increases, the Q_4/Q_3 ^{29}Si ratio increases and the intercalated kanemite progressively loses its initial structure. At pH = 8.5, a quasi-amorphous product is obtained. For pH $\leqslant$ 7.5, the main peak in the spectrum of the hydrogen-exchanged form of kanemite, $H_2Si_2O_5$,[21] ($2\theta = 24.06°$) is observed. On the other hand, the crystallinity of silicalite 1 increases down to pH = 8.5 (Fig. 9). At pH = 6.5, the product obtained after solid-state transformation was amorphous.

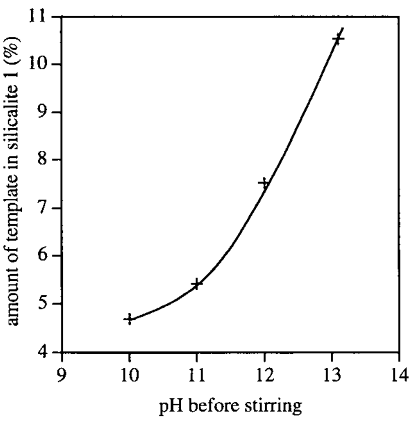

Fig. 3 Change in the amount of template in silicalite 1 (%) *vs.* pH before stirring the template–kanemite solution at 70 °C.

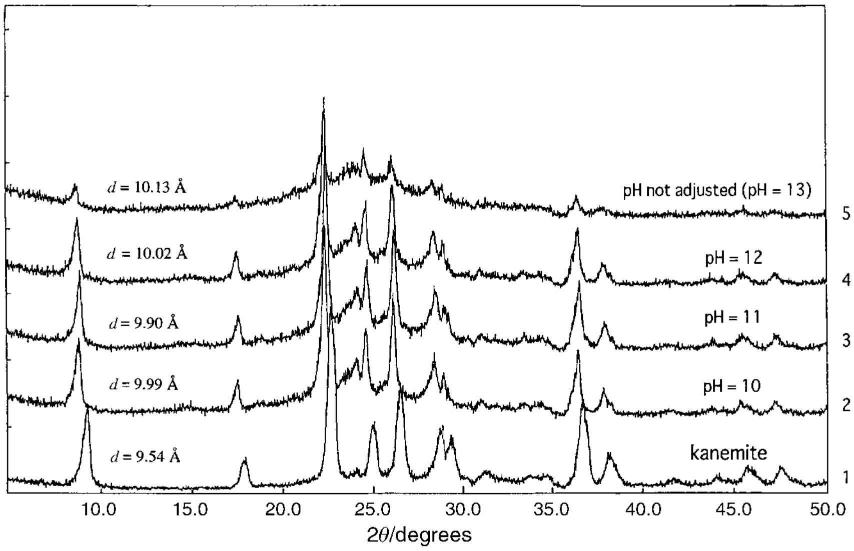

Fig. 4 X-Ray powder diffraction patterns of kanemite (1), intercalated kanemite when the pH was adjusted to 10 (2), 11 (3) and 12 (4), and not adjusted (5), before stirring the template–kanemite solution at 70 °C.

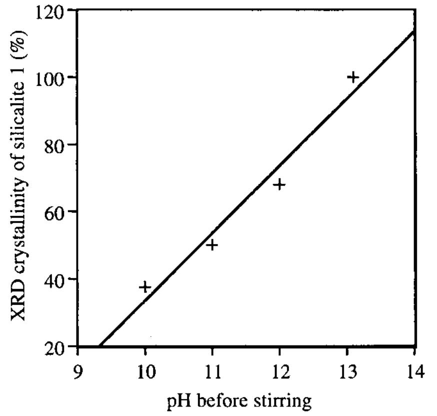

Fig. 5 Change in XRD crystallinity (%) of silicalite 1 *vs.* pH before stirring the template–kanemite solution at 70 °C.

Discussion

As far as the kind of template is concerned, the better results obtained with TPAOH template (Figs. 1 and 2) have been explained by the fact that the concentration of Na^+ cations is higher when the TPABr template is used. As a matter of fact, in this case, the pH is adjusted to 12 by adding sodium hydroxide. Thus, there is a competition between Na^+ and TPA^+ cations, leading to a lower amount of intercalated template. Consequently, in the following, the TPAOH template will be preferred to the TPABr template and, according to the results of the concentration effect, the TPA/Si ratio will be taken as equal to 0.94.

The powder weight loss after cation exchange indicates that a fraction of the kanemite becomes soluble in the template solution. The powder which is obtained after filtration and drying when the pH of the suspension is not adjusted after stirring is the fraction of kanemite which did not dissolve during the stirring. And it was observed (Fig. 8) that this fraction has the same structure as that of kanemite (same crystallinity). Furthermore, its Q_4/Q_3 ^{29}Si ratio (Fig. 7) was also found to be equal to that of kanemite. Thus, during the stirring at 70 °C, the silicate layers give rise to the formation of silica colloids (soluble fraction) and shorter silicate layers (insoluble fraction). When the pH of the suspension is lowered after stirring, the soluble fraction precipitates. As the pH decreases, the Q_4/Q_3 ^{29}Si ratio of the kanemite–TPA powder increases, indicating that the precipitation of the soluble part is due to the condensation of silica colloids, leading to the formation of silica polymers. During this condensation, the template is more easily incorporated (Fig. 6). The amount of incorporated template obtained when the pH was adjusted to 7.5 was smaller than when the pH was adjusted to 8.5 because TPA^+ cations started to be replaced by protons, leading to the beginning of the formation of the hydrogen-exchanged form of kanemite $H_2Si_2O_5$. The increase in the amount of silica polymers

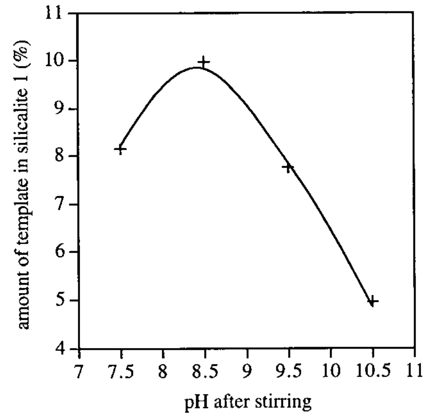

Fig. 6 Change in the amount of template in silicalite 1 (%) *vs.* pH after stirring the template–kanemite solution at 70 °C.

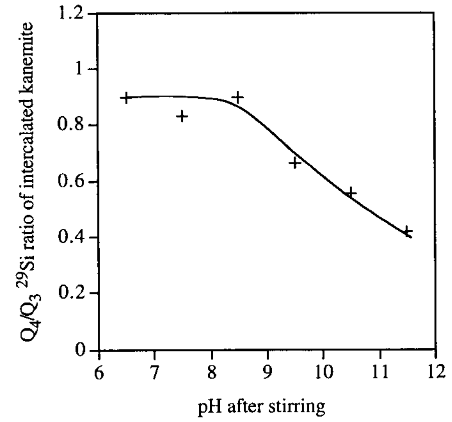

Fig. 7 Change in the Q_4/Q_3 ^{29}Si ratio *vs.* pH after stirring the template–kanemite solution at 70 °C.

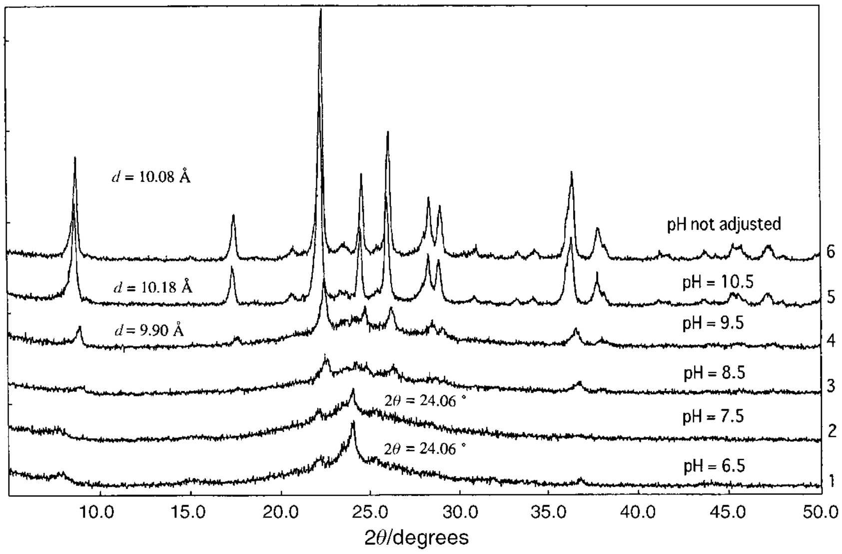

Fig. 8 X-Ray powder diffraction patterns of intercalated kanemite when the pH was adjusted to 6.5 (1), 7.5 (2), 8.5 (3), 9.5 (4) and 10. 5 (5), and not adjusted (6), after stirring the template–kanemite solution at 70 °C.

(amorphous silica) with decreasing pH explains the decrease in the crystallinity of the structure of the kanemite–TPA powder. The suspension becomes clearer when the pH before stirring is increased because the amount of the soluble fraction is increased. Thus, the higher the pH before stirring, the higher the amount of the soluble fraction during the stirring and the higher the amount of silica polymers when lowering the pH after stirring, *i.e.* the condensation phenomenon becomes more important. This is why the layered structure of kanemite disintegrates and the amount of incorporated template increases when the pH before stirring is increased.

As in the case of long-chain alkylammonium cations, disintegration of the layered structure of kanemite due to the intercondensation of the layers occurs during cation exchange with TPA cation, however, a second step is necessary to lead the building of the three dimensional framework to completion. Concerning the synthesis of mesoporous materials from kanemite, Chen *et al.*[18] showed the active role played by the long-chain alkylammonium cation in the dissolution process of kanemite independently on the basicity of the medium. As a matter of fact, the dissolution of kanemite in water in the absence of template is negligible for pH$\leqslant$10. Thus, at pH$=$9–9.5, at which they carried out their cation exchange, kanemite dissolves, but not as a result of the alkalinity of the medium, rather because the silicate layers are reorganized thanks to the ability of the surfactant molecules to change from a bilayered structure to a cylindrical micelle-like aggregate. Thiesen *et al.*,[19] who carried out their experiments in similar conditions to ours (the pH was adjusted to 12.5 and the dispersion was held at 70 °C for 3 h; after cooling to room temperature, the pH was adjusted to 8.5), have explained the dissolution process as a partial destruction of the silicate structure by alkylammonium ions which then carry the fragments of the silicate layers and finally aggregate to cylindrical forms. In our case, the partial dissolution of kanemite during the stirring of the suspension at 70 °C for 3 h occurs mainly because of the high basicity of the medium. Then, when the pH is lowered to 8.5, the dissolved silica species condense and form a three dimensional framework[22] in which a fraction of the template is trapped. As far as the silicate layers are concerned, they condense under the influence of the intercalated template leading to the formation of a partial three dimensional

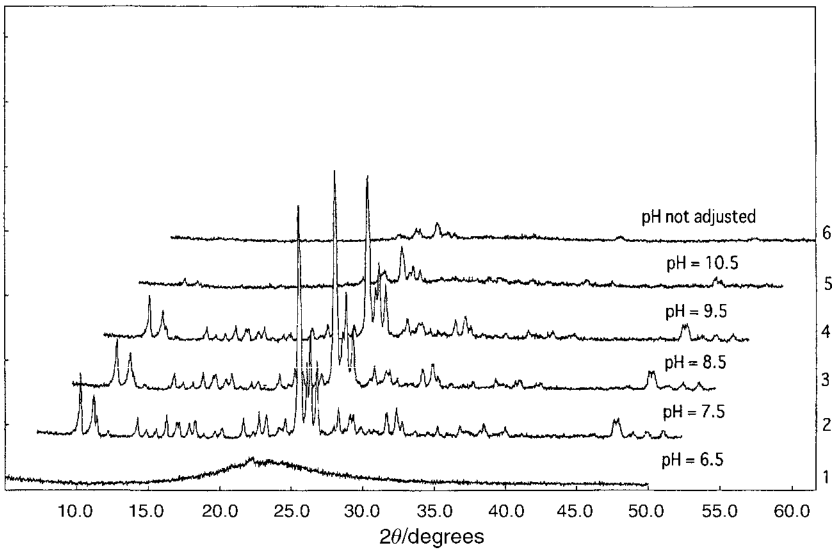

Fig. 9 X-Ray powder diffraction patterns of silicalite 1 when the pH was adjusted to 6.5 (1), 7.5 (2), 8.5 (3), 9.5 (4) and 10. 5 (5), and not adjusted (6), after stirring the template–kanemite solution at 70 °C.

framework. Then, in the course of an as yet unknown process, solid-state transformation leads to the formation of the framework of silicalite 1.

Conclusions

The synthesis of silicalite 1 from kanemite through solid-state transformation is favored by:

(1) the use of TPAOH template in preference to TPABr template

(2) highly basic conditions during the stirring of the kanemite–TPA mixture at 70 °C for 3 h and adjustment to the appropriate pH after stirring.

$pH = 8.5$ was found to be the lowest pH for which no $TPA^+ \rightarrow H^+$ cation exchange occurs. The more important the dissolution of kanemite is during the stirring at 70 °C for 3 h, the higher the amount of amorphous silica polymers is when the pH is lowered after stirring, the higher the amount of incorporated template is and the higher the crystallinity of silicalite 1 is after solid-state transformation.

Comparison with the synthesis of mesoporous materials from kanemite showed that the dissolution mechanisms that occur during the cation exchange reaction with short-chain and long-chain alkylammonium cations are different. Further experiments will have to be carried out in order to explain in detail the dissolution mechanism through which kanemite transforms into silicalite 1.

Acknowledgements

This investigation was supported by a grant from the European Union.

References

1 V. R. Choudhary and S. Mayadevi, *Zeolites*, 1996, **17**, 501.
2 E. M. Flanigen, J. M. Bennett, R. W. Grose, J. P. Cohen, R. L. Patton, R. M. Kirchner and J. V. Smith, *Nature*, 1978, **271**, 512.
3 S. Shimizu, Y. Kiyozumi, K. Maeda, F. Mizukami, G. Pál-Borbély, R. M. Mihályi and H. Beyer, *Adv. Mater.*, 1996, **8–9**, 759.
4 S. Shimizu, Y. Kiyozumi and F. Mizukami, Japanese patent JP 95-125040/JP 95-125041, 1995.
5 S. Shimizu, Y. Kiyozumi and F. Mizukami, *Chem. Lett.*, 1996, 403.
6 M. Salou, Y. Kiyozumi, F. Mizukami, P. Nair, K. Maeda and S. Niwa, *J. Mater. Chem.*, 1998, **8**, 2125.
7 I. Kiricsi, S. Shimizu, Y. Kiyozumi, M. Toba, S. Niwa and F. Mizukami, *Appl. Catal.*, 1997, **3825**, 335.
8 I. Kiricsi, S. Shimizu, Y. Kiyozumi, M. Toba, S. Niwa and F. Mizukami, *Micropor. Mesopor. Mater.*, 1998, **21**, 453.
9 Z. Johan and G. F. Maglione, *Bull. Soc. Fr. Mineral. Cristallogr.*, 1972, **95**, 371.
10 K. Beneke and G. Lagaly, *Am. Mineral.*, 1977, **62**, 763.
11 D. C. Apperley, M. J. Hudson, M. T. J. Keene and J. A. Knowles, *J. Mater. Chem.*, 1995, **5**, 577.
12 G. G. Almond, R. K. Harris, K. R. Franklin and P. Graham, *J. Mater. Chem.*, 1996, **6**, 843.
13 G. G. Almond, R. K. Harris and K. R. Franklin, *J. Mater. Chem.*, 1997, **7**, 681.
14 S. Hayashi, *J. Mater. Chem.*, 1997, **7**, 1043.
15 M. Hanaya and R. K. Harris, *J. Mater. Chem.*, 1998, **8**, 1073.
16 L. A. J. Garvie, B. Devouard, T. L. Groy, F. Camara and P. R. Buseck, *Am. Mineral.*, 1999, **84**, 1170.
17 S. Inagaki, Y. Fukushima and K. Kuroda, *Stud. Surf. Sci. Catal.*, 1994, **84**, 125.
18 C. Y. Chen, S. Q. Xiao and M. E. Davis, *Microporous Mater.*, 1995, **4**, 1.
19 P. Thiesen, K. Beneke and G. Lagaly, *J. Mater. Chem.*, 2000, **10**, 1177.
20 R. Szostak, *Molecular Sieves*, Blackie Academic & Professional, London, 1998, p. 290.
21 M. L. Occelli and H. E. Robson, *Expanded Clays and Other Microporous Solids*, Van Nostrand Reinhold, New York, 1992, p. 192.
22 C. J. Brinker and G. W. Scherer, *Sol-Gel Science, The Physics and Chemistry of Sol-Gel Processing*, Academic Press, Inc., Boston, 1990, p. 102.