JOURNAL OF
Materials
CHEMISTRY

Influence of solid-state transformation time on the nucleation and growth of silicalite 1 prepared from layered silicate

Martine Salou, Yoshimichi Kiyozumi, Fujio Mizukami,* Padmakumar Nair, Kazuyuki Maeda and Shuichi Niwa

National Institute of Materials and Chemical Research, 1-1, Higashi, Tsukuba, Ibaraki 305, Japan

The nucleation and crystal growth of silicalite 1 precursors synthesized by solid-state transformation were studied using X-ray diffraction, thermal analysis, IR spectroscopy, ^{29}Si and ^{13}C NMR and electron microscopy. Silicalite 1 was obtained after 16 h at 130 °C in a closed glass ampoule. Comparison with hydrothermal synthesis showed that the characterization of the precursors presents some similarities, however, nucleation and crystal growth were much shorter for solid-state transformation. ^{29}Si NMR showed that nucleation started during the first stage (cation exchange) for solid-state transformation, but only during the second stage for solid-state transformation. It was also observed that the major changes occurred during the beginning of crystal growth for solid-state transformation but during nucleation for hydrothermal synthesis. The results were explained by the fact that the starting materials were completely different: single layered silicate for solid-state transformation and colloidal silica for hydrothermal synthesis.

Recently, the synthesis of silicalite 1 and fabrication of systems based on it is becoming more and more important because of its good gas and liquid separation behaviour.[1,2] Its hydrophobic and organophilic nature[3] makes it a good candidate for liquid separation. Silicalite 1 can be synthesized by a hydrothermal method in an autoclave at 110 °C for 10 h.[4] However, to shape silicalite 1 into a disk with this method, it is necessary to use binders which decreases the crystallinity of the material. Making disks before the crystallization process enables avoidance of the use of binders. Tao *et al.*[5] have synthesized silicalite 1 by solid-state transformation from a mixture of sodium hydroxide and amorphous dehydrated silica in an ethylenediamine atmosphere. However, the synthesis still required high temperature (180 °C) and a long time (96 h). A new solid-state transformation method which enables construction of silicalite disks without using binders has been reported by Shimizu *et al.*[6] They have prepared silicalite disks from single layered silicate (kanemite) and short-chain alkylammonium cations after 46 h of thermal treatment at 130 °C. As a matter of fact, kanemite ($NaHSi_2O_5{\cdot}3H_2O$) can readily exchange cations because of the presence of interlayer water molecules.[7] They have also observed by SEM that silicalite crystals were more uniform and smaller compared to those prepared through hydrothermal synthesis. Smaller crystals are particularly important for technological applications.

In this paper, silicalite 1 synthesized by solid-state transformation is studied and characterized as a function of time using several techniques in order to obtain a better understanding of the solid state nucleation and growth. We also compare the synthesis of silicalite 1 through a solid route with the synthesis of silicalite 1[4] and zeolite ZSM-5[8–10] through a hydrothermal route.

Experimental

Synthesis

The starting materials were kanemite and an aqueous solution of tetrapropylammonium hydroxide (TPAOH).

Kanemite was prepared by following the procedure described by Shimizu *et al.*[6] Sodium hydroxide was added to a hydrated sodium silicate glass solution and ratio of SiO_2 to NaOH was adjusted to 1.00. The solution was then dried at 150 °C overnight and calcined at 700 °C for 6 h. The product was immersed in water overnight (between 40 and 50 g of powder in 1 l of water) and collected by filtration. Kanemite was obtained by drying the substance at 50 °C overnight.

Silicalite 1 precursors were prepared by dispersing 1 g of kanemite in an aqueous solution of tetrapropylammonium hydroxide (20–25% by weight). The pH was adjusted to 11 with 6 mol dm^{-3} HCl and the mixture was heated at 70 °C for 3 h with stirring. After cooling to room temperature, the pH of the suspension was adjusted to 8.5 (a gel was obtained) in order to exchange the remaining sodium cations with protons and form Si–OH groups. The resulting product was filtered and washed with 300 ml of deionized water and dried at 50 °C overnight to yield kanemite-TPA powder. K-TPA powder was shaped into a disk using an uniaxial compression molder at a pressure of 443 MPa. The disk was 20 mm in diameter and *ca.* 1 mm thick. Silicalite 1 was synthesized in a closed glass ampoule of *ca.* 5 cm^3 in volume in an oven at 130 °C. Kanemite-TPA powder placed in an open vessel was not transformed to zeolite by heating at 130 °C for 24 h.[6] The probable reason is that most of the water adsorbed in the starting powder vaporized at an early stage of the thermal treatment if the system is open. We have also observed that the crystallinity of silicalite decreased with increasing drying temperature of kanemite-TPA powder (after cation exchange). Amorphous products were obtained for a drying temperature $\geqslant$100 °C, indicating that adsorbed water plays an important role during the transformation.

Analysis

X-Ray powder diffraction patterns of the samples were recorded using a MXP 18 diffractometer (Mac Science Co.Ltd.) with monochromatic CuKα radiation. %XRD crystallinity is taken as the sum of the peak heights of the given material divided by the sum of the peak heights of a standard silicalite 1 material that has been designated to be 100% crystalline.

TG–DTA measurements were carried out with a Mac-Science TG-DTA 2000 analyzer. The water and organic contents were 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}.

IR spectra were recorded on a Shimadzu FTIR-8600PC spectrometer mixing the sample and KBr powder. The %IR crystallinity is taken as the ratio of the absorptions of the 550 and 450 cm^{-1} bands of the given material divided by the ratio of the absorptions of the 550 and 450 cm^{-1} of a standard silicalite 1 material that has been designated to be 100% crystalline.

^{29}Si and ^{13}C MAS NMR spectroscopic characteristics of the samples were measured using a Bruker AMX500 spectrometer operating at 99.36 MHz, fitting the samples in a 4 mm ZrO_2 rotor, spinning at 4 kHz.

The morphology of the samples was investigated by scanning electron microscopy using a Hitachi S-800 SEM operated at 15 keV and by transmission electron microscopy using a JEOL JEM-2000 FXII electron microscope.

Results

X-Ray diffraction

Solid-state transformation at 130 °C for 46 h of intercalated kanemite after 10, 20 and 30 min of cation exchange at 70 °C gave amorphous products. For cation exchange after 1; 2 and 3 h, crystalline products were obtained, however, the highest crystallinity was obtained after 3 h. XRD patterns of kanemite and TPA-silicalite precursors *vs.* reaction time are represented in Fig. 1. The spectra of intercalated kanemite and silicalite 1 precursor after 5 min of solid-state transformation are quasi-amorphous and a broad peak starts to form between $2\theta = 15–30°$, however, all the peaks of kanemite are still present, indicating that crystallinity decreases and loss of layered structure proceeds.[11] After 20 min of solid-state transformation, the product is mainly amorphous, indicating that the kanemite structure is almost completely lost. After 1 h 50 min of solid-state transformation, crystallization starts and the linewidth of the peaks decreases with reaction time, indicating that the regularity of the framework increases. For X-ray crystallinity, the sum of the intensities of the peaks at $2\theta = 7.97$, 8.88, 23.24, 23.96 and 24.42° was calculated. The variation of crystallinity for different crystallization times is given in Table 1. The crystallinity increases drastically between 1 h 50 min and 4 h of solid-state transformation. No noticeable increase is observed between 4 and 36 h. However, after 46 h, the crystallinity increases again.

The unit cell parameters were calculated from the data of the XRD patterns. The results showed that after 16 h of solid-state transformation, the values are in good agreement with those reported in the literature[3,5] ($a = 20.00$, $b = 19.88$ and $c = 13.40$ Å).

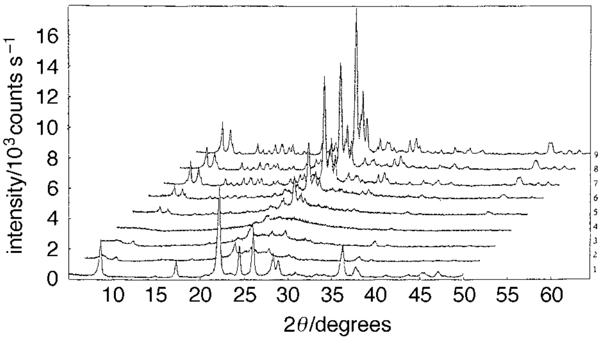


Fig. 1 X-Ray diffraction patterns of kanemite (1), intercalated kanemite after 3 h of cation exchange (2), silicalite 1 precursors after 5 min (3), 20 min (4), 1 h 50 min (5), 2 h (6), 4 h (7), 16 h (8) and 46 h (9) of thermal treatment

Table 1 XRD crystallinity *vs.* crystallization time

time	XRD crystallinity/counts s^{-1}
1 h 50 min	7231
2 h	9812
4 h	16 108
16 h	15 725
26 h	15 418
36 h	16 041
46 h	20 906

In order to determine the manner in which the TPA$^+$ are intercalated between the sheets of kanemite, one has to have in mind the structure of kanemite. Kanemite is a sodium silicate whose layers are composed of single layered sheets of SiO_4 tetrahedra.[12] The precise structure has been recently determined by Hayashi.[13] In kanemite, water molecules are present at the external surface, between the layers around the sodium cations and within the hexagonal rings constituting the layers. The sodium species have a fixed orientation and the water molecules are not directly coordinated to them. From XRD data, kanemite and intercalated kanemite *d*-spacings were *ca.* to 10.2 and 12.7 Å, respectively. These results show that the intercalation of the template widens the space between the layers of kanemite. Taking account the size of a water molecule and TPA$^+$ (8.0–9.0 Å),[14] it can be concluded that the silicate sheets are intercalated by a monolayer of TPA$^+$.

It can be concluded from XRD experiments that after 1 h 50 min of solid-state transformation the first crystals of silicalite 1 were detected; after a thermal treatment of 16 h in closed glass ampoule, crystals are of sufficient size in order to reveal a proper XRD pattern and silicate sheets are intercalated by a monolayer of TPA$^+$.

Thermal analysis

The results of thermal analysis *vs.* cation exchange time are presented in Table 2. It is known that weight loss for temperatures below 300 °C corresponds to the amount of water present and that between 300 and 600 °C to the amount in TPA$^+$.[9] Weight losses *vs.* cation exchange time show that between 30 min and 1 h, both water and TPA$^+$ amounts increase drastically. After 1 h of stirring, the amount of intercalated template has reached its maximum value. However, according to the XRD results, 3 h are necessary to obtain an XRD pattern. DTA curves of intercalated kanemite and silicalite 1 precursors are shown in Fig. 2. The exothermic peak corresponding to the decomposition of TPA$^+$ is sharp before solid-state transformation and becomes increasingly broad with progressive loss of the kanemite structure. After 1 h 50 min of solid-state transformation, the peak becomes sharper again. After 4 h, the shape of the peak is the same as after 46 h. The shape of the TPA$^+$ decomposition peak reveals the degree of crystallinity of the material: the sharper the peak, the higher the crystallinity the material. The change in the shape of the TPA$^+$ decomposition peak with increasing synthesis time is explained by the increase of the degree of freedom of the template as the silicalite framework is being built. The decomposition temperature of TPA$^+$ increases until 16 h of treatment and is constant until 36 h and decreases after 46 h. Thus, after 16 h, TPA$^+$ is stabilized in the crystalline silicalite 1 framework.

Table 2 Thermogravimetric weight loss *vs.* stirring time at 70 °C (cation exchange)

	Δm (%)	
stirring time	$T < 300$ °C	$300 < T/°C < 600$
5 min	14.2	2.6
10 min	14.9	2.7
20 min	15.5	2.1
30 min	15.6	2.8
1 h	20.5	4.4
2 h	19.5	3.9
3 h	21.3	3.8

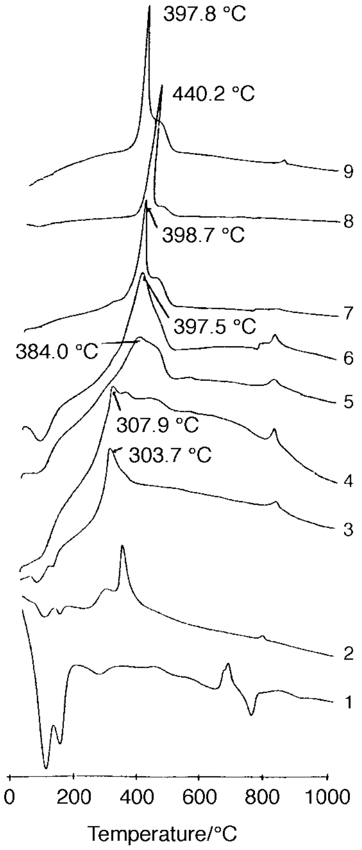


Fig. 2 DTA curves of kanemite (1), intercalated kanemite (2) and silicalite 1 precursors *vs.* solid state transformation time: 5 min (3), 20 min (4), 1 h 50 min (5), 2 h (6), 4 h (7), 16 h (8) and 46 h (9)

Fig. 3 shows that there is a change in the slope of TG curves after 1 h 50 min of solid-state transformation, corresponding to a decrease in water loss. Table 3 shows that the water amount decreases from 1 h 50 min of thermal treatment to 4 h and then is constant. A parallel can be established with the XRD results and the beginning of interlayer water decrease coincides with the beginning of crystallization. The framework is almost completely built after 4 h of solid-state transformation and any small amount of water that is released between 4 and 16 h cannot be detected by thermal analysis.

The weight loss for the decomposition of TPA cations occluded in silicalite 1 (after 16 h of solid-state transformation) corresponds to three to four TPA^+ entities per unit cell. This confirms the template role played by the TPA cations (one per intersection, there are four linear-zigzag channel intersections per unit cell).[8]

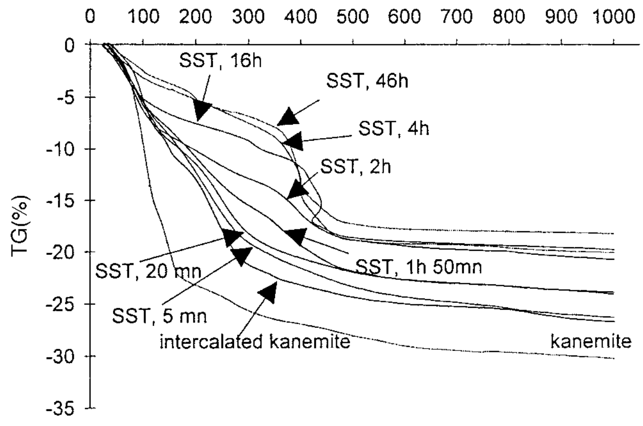


Fig. 3 TG curves of kanemite, intercalated kanemite and silicalite 1 precursors *vs.* solid state transformation time: 5 min, 20 min, 1 h 50 min, 2 h, 4 h, 16 h and 46 h

Table 3 Thermogravimetric water weight loss *vs.* solid state transformation (SST) time at 130 °C

SST time	Δm (%)
5 min	18.2
20 min	18.5
1 h 50 min	15.5
2 h	12.4
4 h	7.2
16 h	8.8
46 h	6.9

It can be concluded from thermal analysis that dehydration starts after 1 h 50 min of solid-state transformation and continues during the crystallization period, the template is stabilized in the silicalite 1 framework after 16 h of solid-state transformation and after 16 h, three to four TPA^+ entities are present per unit cell.

IR studies

The IR spectrum of silicalite 1 in the framework absorption region (1500–400 cm^{-1}) is the same as that observed for zeolite ZSM-5.[9] The absorptions near 1100, 700 and 450 cm^{-1} were assigned to internal vibrations of SiO_4 tetrahedra.[15] The 650–550 cm^{-1} band has been attributed to the presence of double-rings of tetrahedra in the framework. For crystallinity measurement, the absorbance at 550 cm^{-1} was followed[16] since it is known that this band is a good probe for detecting the presence of a silicalite framework. Ratios of the absorptions of the 550 and 450 cm^{-1} bands, $A(550)/A(450)$, were calculated and results are given in Table 4. As can be seen, IR crystallinity increases with time. For well crystallized silicalite 1, the $A(550)/A(450)$ ratio is *ca.* 0.56.[15] For our samples, this value is reached after 4 h of solid-state transformation. The variations in IR crystallinity are negligible between 4 and 36 h, but a slight increase is observed after 46 h. As for zeolite ZSM-5,[9] comparison of the IR spectrum of TPABr and TPA-silicalite 1 precursor showed that almost all absorption bands observed for the samples were different from those of TPABr, indicating that TPA^+ interacts strongly with silicalite framework.

It can be concluded from IR study that IR crystallinity characteristic of silicalite 1 is obtained after 4 h of solid-state transformation and that TPA^+ interacts strongly with the silicalite framework.

NMR measurements

^{29}Si MAS NMR. Fig. 4 shows the ^{29}Si MAS NMR spectra of kanemite and TPA-silicalite 1 powders as a function of reaction time. The ^{29}Si MAS NMR spectrum of kanemite shows one peak at $\delta -97.4$ which is assigned to the Q_3 environment in SiO_4 tetrahedra $[OSi(OSi{\equiv})_3]$[17] indicating a single layered structure. The weak peak at $\delta -110.9$ which is related to Q_4 Si atoms $[Si(OSi{\equiv})_4]$ is due to impurities. The

Table 4 IR crystallinity $A(550)/A(450)$ *vs.* crystallization time

time	$A(550)/A(450)$
1 h 50 min	0.30
2 h	0.35
4 h	0.55
16 h	0.57
26 h	0.61
36 h	0.55
46 h	0.66

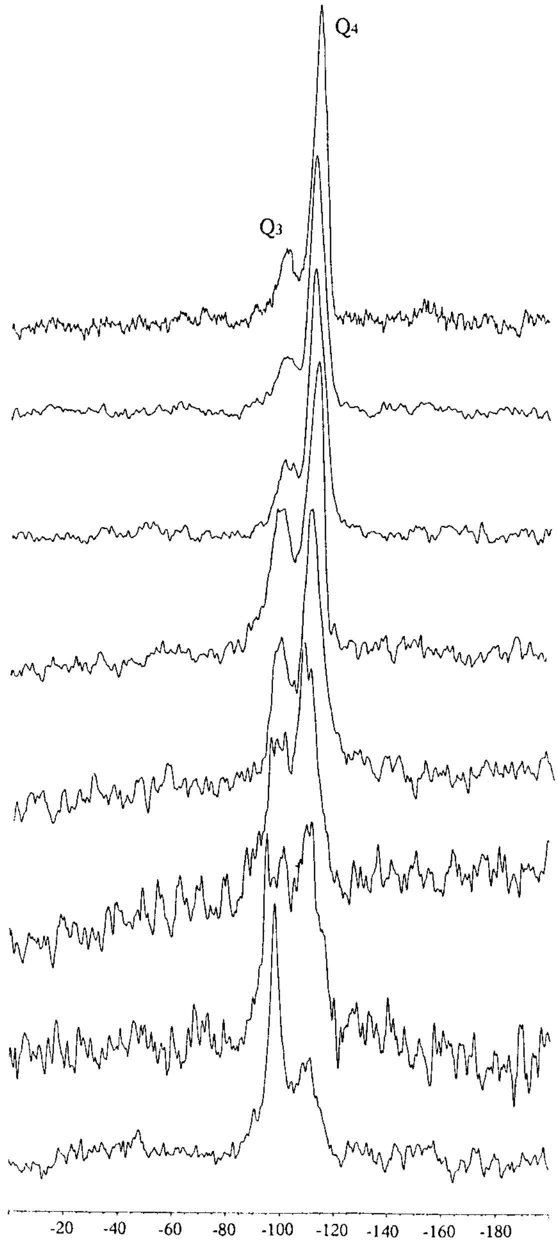


Fig. 4 ^{29}Si NMR spectra of kanemite (1), intercalated kanemite (2) and silicalite precursors *vs.* solid state transformation time: 5 min (3), 1 h 50 min (4), 2 h (5), 4 h (6), 16 h (7) and 46 h (8)

intensity of the Q_4 peak of intercalated kanemite is higher than that of kanemite and increases during solid-state transformation. After 16 h of solid-state transformation, the Q_4 content is four times as high as the Q_3 content (Table 5). These results show that silicate layers of kanemite start condensing during the cation exchange reaction and the phenomenon continues during solid-state transformation, leading to the formation of a three-dimensional network. It is noticed that the Q_4 peak becomes sharper with solid-state transformation time, indicating that the network is becoming more and more ordered.

Table 5 ^{29}Si NMR Q_4/Q_3 ratios *vs.* reaction time (K = kanemite)

sample	Q_4/Q_3
kanemite	0.41
K + TPA	1.12
K + TPA (5 min)	1.53
K + TPA (1 h 50 min)	1.88
K + TPA (2 h)	2.04
K + TPA (4 h)	3.57
K + TPA (16 h)	4.17
K + TPA (46 h)	4.19

^{13}C MAS NMR. Fig. 5 shows the ^{13}C NMR spectra of TPABr and silicalite 1 precursors as a function of reaction time. TPABr and silicalite 1 precursor spectra show different intensities, linewidth and chemical shift. The resonance of the methylene carbon C^1 bonded to the nitrogen is shifted downfield (δ 60.03 for TPABr and δ 62.86 for occluded TPA^+ after 4 h solid-state transformation). The resonance of the methyl carbon C^3 is shifted upfield and is split into two peaks (δ 13.55 for TPABr and δ 10.22 and 11.22 for occluded TPA^+ after 4 h of solid-state transformation). The resonance of the second methylene carbon C^2 in the propyl chain is essentially unchanged (δ 15.96 for TPABr and δ 16.36 for occluded TPA^+). Those results suggest that the conformation of occluded TPA^+ is different from that of free TPABr and indicates that TPA^+ interacts strongly and specifically with the framework. The peaks of intercalated kanemite are broad and their intensity is low. The peaks become sharper and their intensity increases with solid-state transformation time as the template gains more freedom in the framework which is being built. The C^3 peak is split into a doublet after 2 h of solid-state transformation, during the beginning of construction of the silicalite 1 structure. This splitting is attributed to the influence of the two different channels in silicalite 1 and shows that, as for zeolite ZSM-5, TPA cations are located at the channel intersections with the propyl chains extended into both linear and sinusoidal channels. This splitting is also a good probe for detecting the presence of the silicalite 1 framework and confirms the results obtained with the previous techniques.

From the NMR analysis it is concluded that the building of the three-dimensional framework starts during cation exchange (increase of Q_4/Q_3 ratio) and that after 16 h of solid-state transformation, the Q_4/Q_3 ratio is constant. In addition splitting of the methyl carbon C^3 peak occurs after 2 h of solid-state transformation.

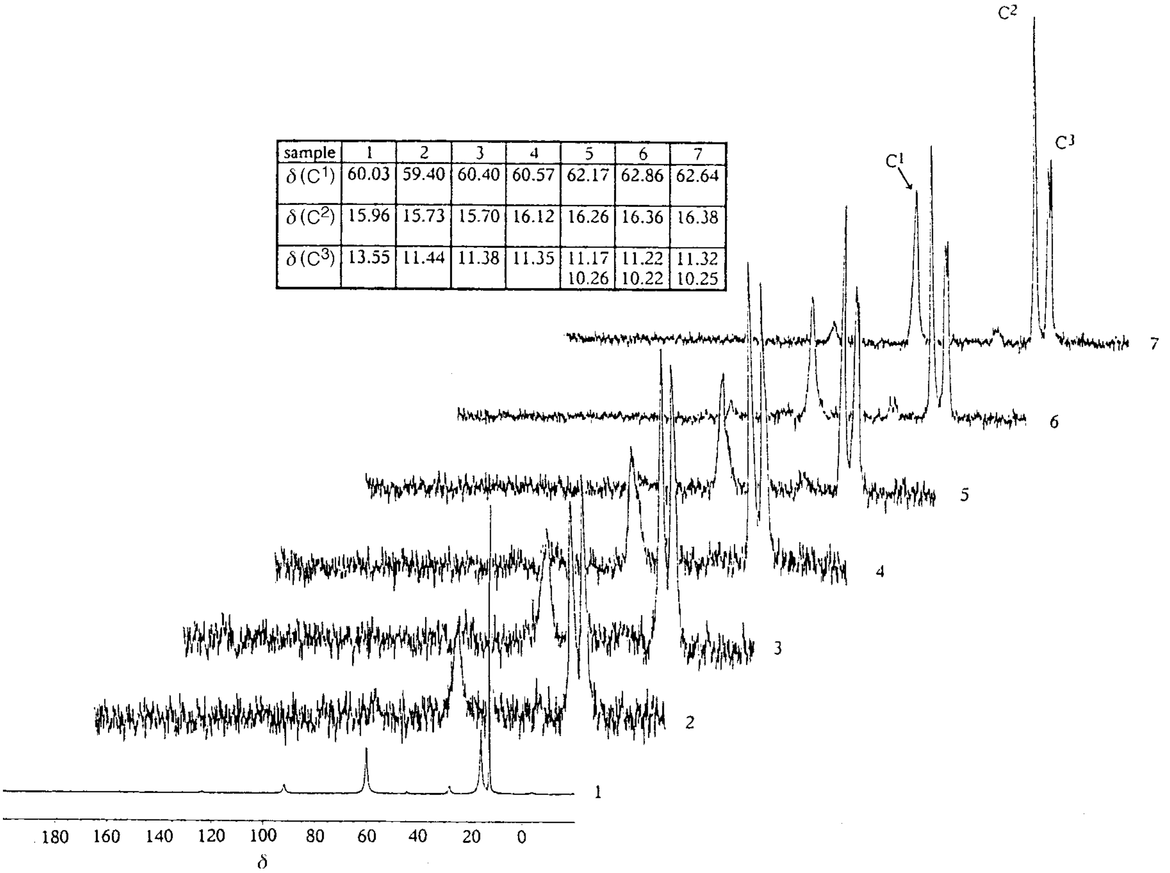
Electron microscopy

The morphology and crystal size of the samples have been studied by scanning electron microscopy (Fig. 6). After 2 h of solid-state transformation, small crystals of diameter *ca.* 30 nm are observed on the amorphous particles of *ca.* 250–400 nm, indicating that crystals grow at the expense of the amorphous phase. After 4 h, crystals are uniform and their size is *ca.* 200–230 nm. After 16 h, crystals are uniform and their size is *ca.* 200–250 nm. After 46 h of solid-state transformation, the crystals have a size of *ca.* 250–350 nm. Fibers of 6500 × 600 nm average size are also present. After calcination of TPA-silicalite 1 at 700 °C for 6 h, fibers were still present. These observations show that the fibers are due to the silicalite 1 framework and not to the template. TEM images show that these fibers are crystalline (Fig. 7). The absence of quartz in the XRD pattern led us assume that the fibers may be silicalite 1. Further experiments will have to be carried out in order to determine the exact nature of the fibers and the precise conditions in which they are formed.

From SEM observations it can be concluded that after 2 h of solid-state transformation, crystal growth at the expense of the amorphous phase was observed, after 16 h, silicalite 1 crystals were quite uniform and their size was *ca.* 200–250 nm and after 46 h, crystalline fibers were observed.

Discussion

From XRD, TG, ^{13}C NMR and SEM, it can be stated that the beginning of crystallization starts after 2 h of solid-state



sample	1	2	3	4	5	6	7
$\delta(C^1)$	60.03	59.40	60.40	60.57	62.17	62.86	62.64
$\delta(C^2)$	15.96	15.73	15.70	16.12	16.26	16.36	16.38
$\delta(C^3)$	13.55	11.44	11.38	11.35	11.17 10.26	11.22 10.22	11.32 10.25

Fig. 5 ^{13}C NMR spectra of TPABr (1), intercalated kanemite (2) and silicalite 1 precursors *vs.* solid state transformation time: 5 min (3), 1 h 50 min (4), 2 h (5), 4 h (6) and 46 h (7). Resonances are assigned to the carbon atoms of the propyl chains as $(C^3H_3C^2H_2C^1H_2)_4N^+$.

transformation. Fig. 8 shows the variations of XRD and IR crystallinities as a function of crystallization time. After 5 min, IR crystallinity is increases, while according to XRD, the sample is apparently amorphous up to 1 h 50 min. The amorphous XRD patterns can be explained by the very small size of the crystals and their low quantity.[16] From XRD, DTA, ^{29}Si NMR and SEM, it can be stated that after 16 h of solid-state transformation, a material characteristic of silicalite 1 is obtained. The increase in crystallinity after 46 h, as observed by XRD and IR analyses, and the decrease in TPA$^+$ decomposition temperature are explained by the presence of crystalline fibers. It was considered that 100% crystallinity was obtained after 16 h of treatment, the increase of crystallinity observed subsequently being due to the formation of fibers. Thus, the material obtained after 16 h of thermal treatment is regarded as the standard silicalite 1 material for the calculation of XRD and IR crystallinities.

Silicalite 1 synthesized by solid-state transformation and hydrothermal method[4] and zeolite ZSM-5 prepared by hydrothermal synthesis[8–10] were compared (starting products, experimental conditions and characterization of the materials). For the characterization of the materials, we will focus on the study of the products from the stage after which a gel is obtained for the hydrothermal route and from the stage after which a powder is obtained for the solid route until a product characteristic of the microporous material is obtained.

The starting materials and the experimental conditions are different for each kind of synthesis. For solid-state transformation, one starts from a crystalline layered silicate and for hydrothermal synthesis from amorphous silica powder. After the first stage, intercalated kanemite powder is obtained by the solid-state route and a colloidal silica gel (or aluminosilica gel for the synthesis of zeolite ZSM-5) by the hydrothermal route. Silicalite 1 is synthesized by solid-state transformation after 16 h at 130 °C and by the hydrothermal method after 10 days at 110 °C[4] (13 days at 120 °C,[8] 8 days at 150 °C[9] or 14 days at 95 °C[10] for zeolite ZSM-5).

As for the characterization of the products, some similarities were observed. The increase of the 550 cm^{-1} absorption band (IR), the dehydration phenomenon (TG), the increase in TPA$^+$ decomposition temperature (DTA), the decrease in Q_3/Q_4 ratio (^{29}Si NMR) (or the increase in Q_4/Q_3 ratio) and the splitting of the methyl group resonance of the template (^{13}C NMR) were also observed for the hydrothermal synthesis. However, although a sigmoidal nucleation–growth crystallization kinetics is obtained for both kinds of synthesis[10] (Fig. 8), nucleation and crystal growth are much faster for solid-state transformation. Nucleation occurs over 2 h to *ca.* 2 days for hydrothermal synthesis whereas crystal growth takes *ca.* 14 h to *ca.* 12 days for hydrothermal synthesis.[10] It is also observed that the greatest variations in Q_3/Q_4 ratio occur during the beginning of crystallization time for solid-state transformation (Fig. 9) and during nucleation for hydrothermal synthesis.[10] The same observations are seen for the variations of the chemical shift of Q_4 Si atom[10] (Fig. 10). The upfield shift of the Q_4 Si atom is due to the decrease in Si—O—Si bond angles. A linear correlation between chemical shift and mean Si—O—Si bond angles and between chemical shift and mean Si—O bond lengths of zeolites has been found by several workers.[17] Those results are consistent with increasing crystallinity. It is observed that the greatest variations in water loss also occur during the beginning of crystallization time (Fig. 11). TG and ^{29}Si NMR suggest that the major changes in intercalated kanemite structure occur during the beginning of crystallization. Unlike hydrothermal synthesis, no noticeable changes are observed during the nucleation period.[10] Those results are explained by the different structure of the starting materials; for solid-state transformation, the starting material

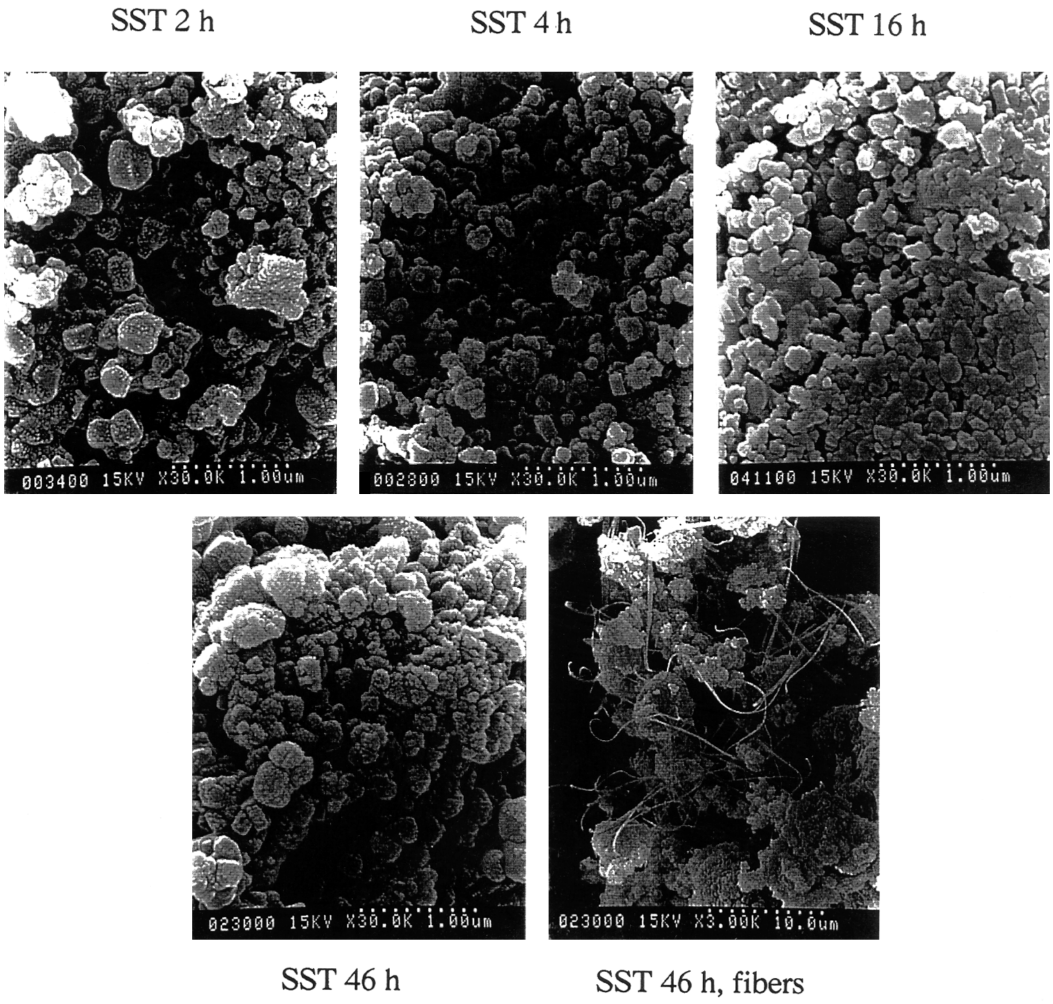
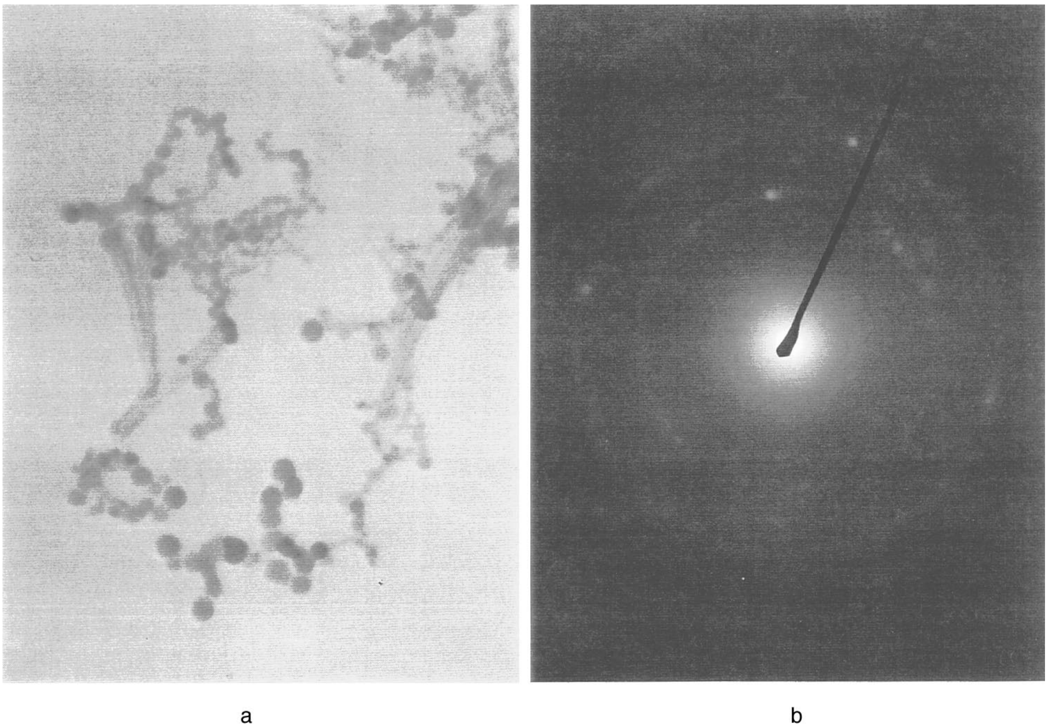


Fig. 6 SEM images of silicalite 1 precursors as a function of synthesis time



a

b

Fig. 7 TEM image (a) and electron diffraction pattern (b) of silicalite 1 fibers obtained after 46 h of solid state transformation at 130 °C

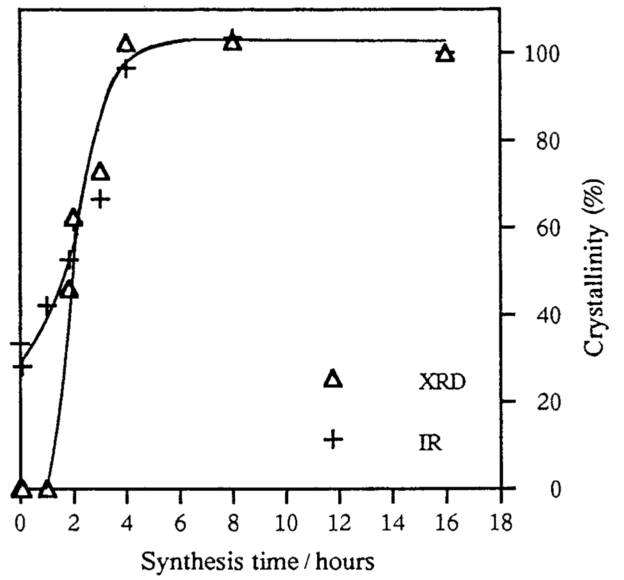


Fig. 8 Change in silicalite 1 crystallinity with synthesis time

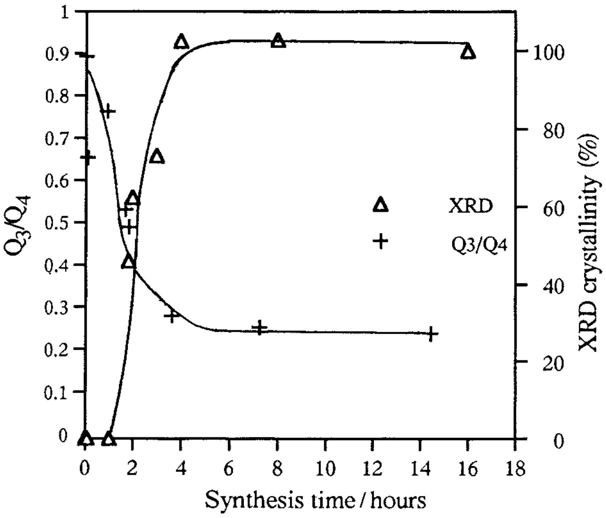


Fig. 9 Change in silicalite 1 crystallinity and Q_3/Q_4 ratio with synthesis time

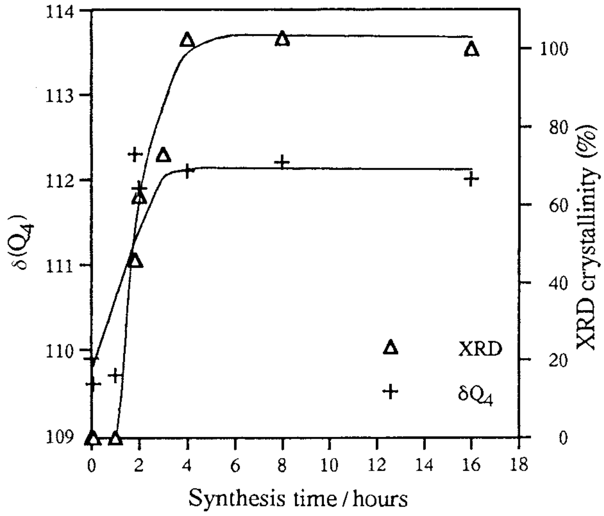


Fig. 10 Change in silicalite 1 crystallinity and Q_4 Si atom chemical shift with synthesis time

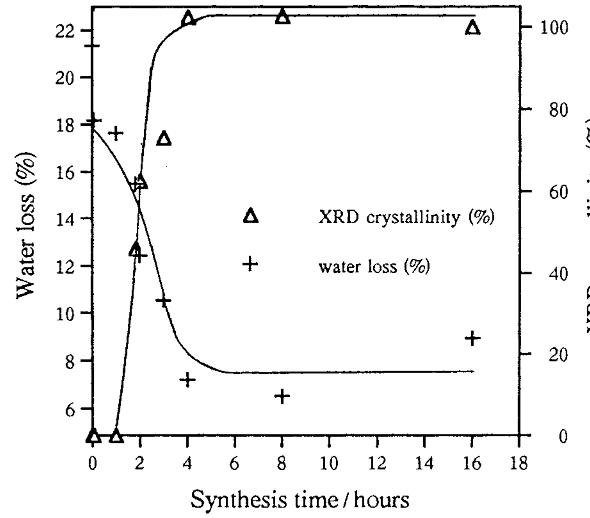


Fig. 11 Change in silicalite 1 crystallinity and water content with synthesis time

has a two-dimensional structure. From such a two-dimensional structure, the three-dimensional structure of the silicalite 1 framework can be easily and rapidly built up. The decrease of Q_3/Q_4 ratio which is observed during cation exchange shows that the building up of the three-dimensional framework starts prior to solid-state transformation. However, for the hydrothermal route, one starts from a colloidal silica or aluminosilica gel before hydrothermal treatment in an autoclave, the formation of the hydrophobic hydration sphere and its subsequent replacment by silicate species occurring later during treatment in the autoclave.

In order to better understand the solid-state transformation, the following experiments have been carried out. Because it was noticed that after cation exchange, 40% of kanemite was dissolved in the solution due to breaking of Si—O—Si bonds, the dissolved and undissolved species were separated after stirring at 70 °C for 3 h. The undissolved species were redispersed in water, the pH was adjusted to 8.5 and after filtration, washing and drying, the powder was treated in a closed glass ampoule at 130 °C for 46 h. Silicalite 1 crystals were obtained (XRD), indicating that the undispersed species could transform into microporous material without the aid of dispersed species. Inagaki *et al.*[18] have proposed a 'folded sheets' mechanism for the formation of FSM-16 from kanemite and long-chain alkyltrimethylammonium. The silicate sheets are folded and cross-linked to each other to form the three-dimensional network. The interlayer cross-linking occurs by condensation of silanols on the silicate sheets. The difference with the synthesis of silicalite 1 is that no further thermal treatment was necessary after cation exchange at 70 °C for 3 h, *i.e.* the folding of the silicate sheets occurs in the liquid phase. ^{29}Si NMR showed that for the synthesis of silicalite 1, the interlayer cross-linking occurs during both cation exchange and solid-state transformation. The question arises as to whether the 'folded sheets mechanism' be applied to a solid-state transformation? The fact that the undispersed species could transform into microporous material without the help of the dispersed species allow us to propose that it is possible. Nevertheless, further experiments will have to be carried out in order to better understand the solid-state transformation.

Conclusions

The study of the influence of solid-state transformation time on nucleation and crystal growth of silicalite 1 prepared from layered silicate showed that the microporous material can be obtained after 16 h at 130 °C. From comparison with hydrothermal synthesis, it was noted that nucleation and crystal growth were much faster for solid-state transformation. It was also observed that the major changes occurred during the beginning of crystal growth for the solid-state transformation and during nucleation for hydrothermal synthesis. The results were explained by the fact that the starting materials were completely different. For the solid-state transformation, the initial layered structure enables nucleation to start during cation exchange and drastically shortens the synthesis time. Further experiments will have to be carried out in order to propose a mechanism for solid-state transformation.

This investigation was supported by a grant of the Science and Technology Agency of the Japanese government.

References

1 V. R. Choudhary and S. Mayadevi, *Zeolites*, 1996, **17**, 501.
2 T. Sano, H. Yanagishita, Y. Kiyozumi, F. Mizukami and K. Haraya, *J. Membr. Sci.*, 1994, **95**, 221.
3 E. M. Flanigen, J. M. Bennett, R. W. Grose, J. P. Cohen, R. L. Patton, R. M. Kirchner and J. V. Smith, *Nature* (*London*), 1978, **271**, 512.
4 S. L. Burkett and M. E. Davis, *J. Phys. Chem.*, 1994, **98**, 4647.
5 D. Tao, F. Fangxia, X. Yongzhuang and C. Jinghui, *React. Kinet. Catal. Lett.*, 1997, **61**, 97.
6 S. Shimizu, Y. Kiyozumi, K. Maeda, F. Mizukami, G. Pál-Borbély, R. M. Mihályi and H. Beyer, *Adv. Mater.*, 1996, **8–9**, 759.
7 G. Lagaly, *Adv. Colloid Interface Sci.*, 1979, **11**, 105.
8 E. G. Derouane, S. Detremmerie, Z. Gabelica and N. Blom, *Appl. Catal.*, 1981, **1**, 201.
9 K. F. M. G. J. Scholle, W. S. Veeman, P. Frenken and G. P. M. van der Velden, *Appl. Catal.*, 1985, **17**, 233.
10 C. D. Chang and A. T. Bell, *Catal. Lett.*, 1991, **8**, 305.
11 T. Yanagisawa, T. Shimizu, K. Kuroda and C. Kato, *Bull. Chem. Soc. Jpn.*, 1990, **63**, 988.
12 Z. Johan and G. F. Maglione, *Bull. Soc. Minéral. Cristallogr.*, 1972, **95**, 371.
13 S. Hayashi, *J. Mater. Chem.*, 1997, **7**, 1043.
14 B. M. Lok, T. R. Cannan and C. A. Messina, *Zeolites*, 1983, **3**, 282.
15 G. Coudurier, C. Naccache and J. C. Vedrine, *J. Chem. Soc.*, *Chem. Commun.*, 1982, 1413.
16 P. A. Jacobs, E. G. Derouane and J. Weitkamp, *J. Chem. Soc.*, *Chem. Commun.*, 1981, 591.
17 G. Engelhardt and D. Michel, in *High-Resolution Solid-State NMR of Silicates and Zeolites*, John Wiley & Sons, Chichester, 1987, p. 129.
18 S. Inagaki, Y. Fukushima and K. Kuroda, *Stud. Surf. Sci. Catal.*, 1994, **84**, 125.

Paper 8/03085E; *Received* 24*th April*, 1998