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Recrystallization of a new layered silicate from Na-kanemite–tetramethylammonium hydroxide–water–1,4-dioxane mixture

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Na-kanemite has been completely converted to a new layered silicate in a reaction mixture of tetramethylammonium hydroxide (TMAOH) solution, water and 1,4-dioxane as solvent *via* hydrothermal treatment at temperatures above 130 °C. The effects of the content of TMAOH and water as well as the type of organic solvents on the conversion of Na-kanemite were investigated. TMA and Na cations were found to be essential for the formation of the new phase (designated as KLS3). Without the use of organic solvent, Na-kanemite was also converted to a KLS3 phase at higher temperatures (*e.g.*150 °C) and for 5 days. ^{29}Si MAS NMR and FT-IR data indicated that a structural change into the kanemite sheets occurred leading to the formation of a three-dimensional silicate network where Q^4 silicon species were detected.

1. Introduction

Interest in kanemite stems from its high charge density (compared to clays), reactivity between its silicate sheets, and potential use as a catalyst support and novel absorbent.[1–3] Kanemite ($NaHSi_2O_5 \cdot H_2O$) is a naturally occurring mineral first found in lake beds at Lake Magadi, Kenya,[4] and in Trona on the northeastern edge of Lake Chad.[5] It is conveniently prepared in the laboratory *via* hydrothermal synthesis.[6–9] Recently, the kanemite structure has been defined in detail by Gies *et al.*[10,11] The single silicate sheets are wrinkled regularly and the adjacent Si–OH groups alternately face each other. Ion-exchangeable Na^+ ions are present in the interlayer region.[10,12] and can be exchanged with large alkylammonium cations to form organic derivatives.[13]

Another field of potential applications has recently been developed by the transformation of layered alkali silicates into porous materials. Kanemite is used as starting precursor to prepare mesoporous materials due to the flexibility of its single silicate layers. Several mechanisms for the transformation have been proposed. It was assumed that the silicate layers are folded around the ion-exchanged surfactants and cross-linked by condensation of silanol groups on adjacent silicate sheets to form the three dimensional framework called a folded sheet mesoporous (FSM) material.[14] Chen *et al.*[15] proposed a dissolution mechanism in the course of which a loss of structural integrity of the kanemite layers occurs and, 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. Thiesen *et al.*[16] have reported the synthesis of micro- and mesoporous materials from other single layer silicates. The silicate layers were partially destroyed by the long alkylammonium ions, followed by aggregation of the alkylammonium ions and fragments of the silicate layers to cylindrical forms. After calcination, the micro- and mesopore frameworks were formed.

Few studies have reported the formation of microporous zeolites from kanemite by exchanging sodium cations with short-chain alkylammonium cations. The transformation of kanemite intercalated with tetrapropylammonium (TPA) and tetrabutylammonium (TBA) cations to silicalite-1 and silicalite-2 in the solid state has been reported.[17,18] The optimum crystallization conditions concerning the conversion of kanemite to silicalite-1 have been examined in details by Salou *et al.*[19] Using piperidine, high silica ferrierites (Si/Al = 12–35) were prepared from aluminium-containing kanemite varieties *via* solid recrystallization.[20]

In our effort to broaden the diversity of silicon sources for the synthesis of new silicate layered structures, we have investigated the conversion of Na-magadiite and its protonated derivative to new layered silicate and microporous silica materials, using the shorter chain tetramethylammonium cation (TMA). The Na-magadiite was converted to a layered silicate (assigned as the KLS1 phase) *via* hydrothermal treatment in the presence of 1,4-dioxane, TMAOH and H_2O at different temperatures.[21] The conversion of Na-magadiite was also achieved in a TMAOH–water mixture without the addition of 1,4-dioxane solvent.[22] According to powder X-ray diffraction data, the KLS1 material exhibited the same powder pattern as the helix layered silicate (HLS) phase, indicating a similarity in the silicate structure. The framework consists of two-dimensional silicate layers containing hemihedral cages and is considered to be an interrupted sodalite framework. TMA^+ cations were incorporated into the cages, and Na^+ and water were located between the anionic layered silicate sheets.[23] The protonated derivative of Na-magadiite was also converted to a new microporous silica material (denoted as FLS1, without the use of 1,4-dioxane solvent) at 150 °C for 5 days, with high thermal stability (up to 800 °C) and a surface area of 457 $m^2 g^{-1}$.[24]

This present study reports the recrystallization of Na-kanemite to yet another new layered silicate structure (designated as KLS3) with a similar silicate structure obtained from Na-magadiite, but with different chemical composition and particle morphologies. The present conversion was achieved *via* hydrothermal treatment in a TMAOH–H_2O system with or without different organic solvents. The aim of this paper was to determine the optimal experimental conditions for complete conversion of kanemite and to characterize the products by different techniques.

2. Experimental

2.1. Preparation of kanemite and KLS3

The starting Na-kanemite was prepared from an SKS6 (δ-$Na_2Si_2O_5$) precursor (provided by Clarian Tokoyama

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Company, Japan) as follows: 22 g of SKS6 was suspended overnight in 500 cm^3 of deionized water at room temperature. The solid was collected by filtration, washed with deionized water, and dried in air at 40 °C overnight.

The protonated form of Na-kanemite (H-kanemite) was obtained by suspending Na-kanemite in an aqueous solution of 0.1 M HCl (1 g solid per 100 mL acid) under stirring for 2 hours at room temperature. The resulting solid was separated by filtration, washed with a large excess of deionized water, and air-dried at 40 °C overnight.

One gram of Na-kanemite (or H-kanemite) was added to 2.3 g of TMAOH (15%), 0.5 g of water and 5 g of one of various solvents. The reaction mixture was heated under autogenous pressure in a Teflon-lined autoclave at different temperatures and periods of time. The resulting product was separated by centrifugation, washed with acetone and air-dried overnight at 40 °C.

The synthesis parameters (temperature, reaction time, amount of TMAOH, water and organic solvent, *etc.*) were varied individually in order to study their influence on the synthesis of new layered silicate at 150 °C for 5 days.

2.2. Characterization

Powder X-ray diffraction patterns (XRD) were collected using a MXP 18 diffractometer (Mac Science Co. Ltd.) with monochromatic Cu-Kα radiation (λ = 0.15405 nm). Chemical analyses of Si and Na were performed using a Thermo Jarrel-Ash IRIS/AP ICP spectrophotometer. C, H, and N contents were obtained using a CE instruments model EA 1110, CHN analyzer. The thermogravimetry (TG) and differential thermal analysis (DTA) were carried out in air on a Mac-Science TG-DTA 2000 analyzer using a heating rate of 5 °C min^{-1}. Solid ^{29}Si magic-angle spinning (MAS) nuclear magnetic resonance (NMR) spectra were measured on a Bruker AMX-500 spectrometer at 99.366 MHz with a 90° pulse length of 4.7 μs and 800 seconds recycle delay time. Typically, 25 to 70 scans were accumulated and the chemical shifts are reported with respect to external hexamethyldisiloxane. Fourier transform infrared (FTIR) spectra were recorded on a BioRad FTS-45RD spectrometer, using the KBr pellet technique. Crystal morphology was determined by scanning electron microscopy (SEM, Hitachi 800).

3. Results

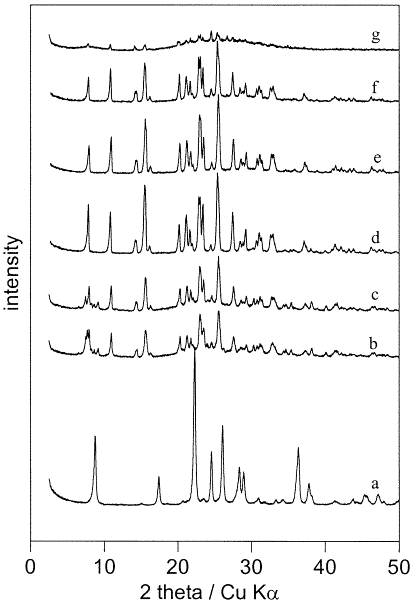

Fig. 1 Powder XRD patterns of (a) Na-kanemite and as synthesized products after hydrothermal treatment in a TMAOH–water–1,4-dioxane mixture for 5 days, at different temperatures (b) 100 °C, (c) 130 °C, (d) 150 °C, (e) 170 °C, (f) 180 °C and (g) 190 °C.

Fig. 1 indicates that after 5 days reaction time in the temperature range 150 to 180 °C, Na-kanemite was completely converted to a new phase from a TMAOH–H$_2$O–1,4-dioxane system. The most crystalline KLS3 material was obtained from a reaction temperature of 150 °C. At lower temperatures *e.g.* 100 °C, Na-kanemite was also converted to a KLS3 phase of low crystallinity in addition to amorphous material (indicated by the hump in the powder XRD pattern) and an unknown phase. Qualitatively the amount of these two phases decreased with the increase of reaction temperature to 130 °C.

The conversion of Na-kanemite to KLS3 was achieved at 150 °C for a reaction period of 1 day with an amorphous silica phase. We noted that as the reaction time became longer, the amorphous phase disappeared and the crystallinity of the KLS3 phase was drastically improved. For example, after 60 days reaction time, the KLS3 phase was found to be stable and no secondary product was detected. At 170 °C, it was possible to obtain a KLS3 phase (with better crystallinity compared to that formed at 150 °C) after a reaction period of 1 day. However, mainly an amorphous phase was formed with traces of KLS3 material at 190 °C. When Na-kanemite was reacted with only a TMAOH–water mixture (without the addition of 1,4-dioxane), the KLS3 phase was obtained only after longer reaction times than three days at 150 °C and with traces of sodalite. After 1 day of reaction, Na-kanemite was converted to a sodalite structure.

Table 1 gives the relative intensities for the major peaks in the powder X-ray diffraction of HLS (prepared from amorphous silica) and KLS3. Slight differences in *d*-spacing and variation in peak intensities were noted.

Further investigations of the effect of reaction parameters were therefore performed at 150 °C over 5 days.

3.1. Effect of the nature of solvents

Fig. 2 presents the powder XRD patterns of the products after reaction of Na-kanemite with TMAOH, water and different alcohols. Na-kanemite was converted to the KLS3 phase when ethanol and propanol were used as solvents. However, in the case of methanol, amorphous silica and unknown phases were

Table 1 Powder XRD data for KLS3 and HLS phases

Distance of KLS3/Å	Rel. int. (I/I_o)	Distance of HLS/Å	Rel. int. (I/I_o)
11.325	53	11.383	40
8.167	48	8.215	56
6.258	16	6.215	21
5.712	70	5.756	61
4.401	42	4.414	44
4.215	46	4.215	44
4.107	32	4.118	30
4.055	15	4.062	11
3.897	68	3.900	80
3.860	70	3.877	79
3.801	61	3.811	40
3.509	100	3.517	100
3.247	48	3.254	39
3.135	18	3.140	19
3.058	41	3.060	24
2.878	28	2.882	25
2.852	21	2.852	14
2.746	27	2.747	25
2.718	25	2.728	26
2.421	19	2.423	16

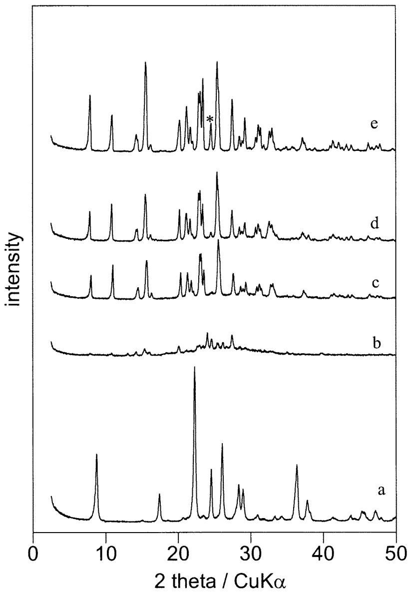

Fig. 2 Powder XRD patterns of (a) Na-kanemite and KLS3 phases after reaction with TMAOH–water mixture and different solvents at 150 °C for 5 days: (b) methanol (c) ethanol and (d) propanol, (e) no solvent was added; * corresponds to sodalite traces.

formed. The KLS3 phase was also obtained when Na-kanemite was reacted only with TMAOH and water.

3.2. Effect of TMAOH content

Different amounts of TMAOH were added to the reaction mixture prior to the hydrothermal treatment. Na-kanemite was not stable in a water and 1,4-dioxane mixture; it was transformed to quartz and amorphous silica phases. This fact indicated that TMAOH plays an important role in the transformation of Na-kanemite to the KLS3 phase. For lower amounts of TMAOH of 0.3 g, Na-kanemite was converted to the KLS3 phase in addition to a silica phase. For TMAOH amounts higher than 1.3 g, the conversion of Na-kanemite to KLS3 was completely achieved with highest crystallinity of the product for a TMAOH content of 5 g.

3.3 Effect of water

Fig. 3 indicates that Na-kanemite was converted to a KLS3 phase in a TMAOH–1,4-dioxane mixture, without addition of extra amounts of water. This conversion was also achieved when water was added up to 12 g. A KLS3 phase was not obtained for further increase in water content up to 20 g, and Na-kanemite was converted to a tridymite phase.

3.4. Effect of solvent content.

The conversion of Na-kanemite to a KLS3 phase was independent of the amount of 1,4-dioxane used. It was achieved even without the addition of 1,4-dioxane. However, the crystallinity of the KLS3 phase decreased as the amount of 1,4-dioxane increased.

When ethanol was used as a solvent, Na-kanemite was converted to the KLS3 phase for ethanol amounts of up to 10 g. At higher amounts *e.g.* 19 g, mainly an amorphous phase was obtained with traces of a KLS3 phase.

3.5. Effect of kanemite forms

As we described above, Na-kanemite was converted to a KLS3 phase in the TMAOH–water–1,4-dioxane mixture. However, when H-kanemite was used as silica precursor, the KLS3 phase was not formed and a new phase with a basal spacing of 1.6 nm was obtained. This phase is assumed to be due to the intercalation of TMA cations between the silicate sheets. Similar intercalation of TMA cations occurred when H-magadiite was reacted with a TMAOH, water and 1,4-dioxane mixture.[25] However, in the case of Na-kanemite containing aluminium, sodalite was obtained. This indicates that even though Na cations were present in the kanemite, the presence of Al cations caused the transformation of KLS3 to a sodalite phase.

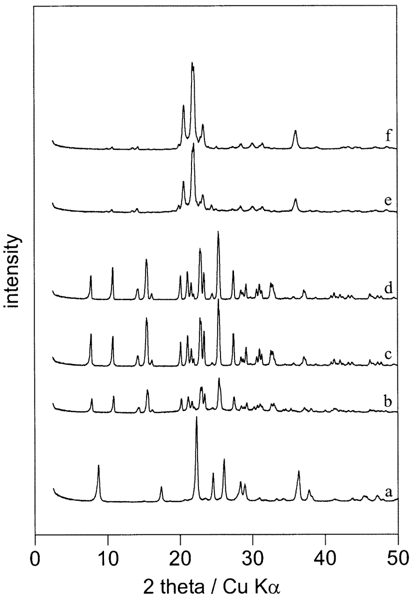

Fig. 3 Powder XRD patterns of (a) Na-kanemite and as prepared phases after reaction with TMAOH–1,4-dioxane and different amounts of water at 150 °C for 5 days: (b) 0 g, (c) 0.5 g, (d) 10 g, (2) 15 g and (f) 20 g.

3.6 Characterization

Table 2 indicates that the molar Si/Na ratios in the different products were higher compared to the starting Na-kanemite and close to 2.21, indicating that a part of Na cations were not involved in the formation of KLS3 phase and were excluded during the conversion the process.[21] The molar Si/Na ratio increased with increase of reaction temperature up to 150 °C and reaction times over 10 days, then it decreased. We note also that the carbon content decreased as the temperature and period of hydrothermal treatment increased. A high carbon content was obtained in the temperature range of 100–130 °C. The molar C/N ratio was always higher than 4, indicating that organic species other than TMA cations were adsorbed onto the samples.

Thermal analysis of Na-kanemite (Fig. 4) suggested two mass losses assigned to the desorption of two distinct types of water in the layered structure below 160 °C,[5,26] indicated by endothermal effects at 85 °C and 135 °C, respectively. A continuous mass loss of 4.4% above 160 °C could be associated with the dehydroxylation of the kanemite layers and formation of an amorphous phase. The exothermal peak at 662 °C was related to the recrystallization of the amorphous phase (Fig. 4).

The KLS3 prepared at 150 °C for 5 days showed five mass losses that were different from those of Na-kanemite and related to release of different types of water and oxidative combustion of the TMA cations. The two first mass losses were related to physisorbed and structural water molecules with two endothermal peaks occurring in the DTA at 88 and 162 °C, respectively. The mass losses at temperatures above 300 °C were assigned to the oxidative combustion of TMA cations and other organic species, and indicated by three exothermal effects

Table 2 Chemical analysis of different KLS3 phases prepared at different conditions

Sample	C (%)	H (%)	N (%)	Si/Na	H_2O (%)[a]	TMA (%)[a]
Na-kanemite	nd	nd	nd	2.21	19.62	nd
KLS3 (100)[b]	14.8	5.12	3.47	3.78	16.16	9.47
KLS3 (130)	14.09	4.95	3.23	4.27	18.56	12.27
KLS3 (150)	9.14	3.77	2.3	4.23	6.39	16.96
KLS3 (170)	6.50	3.29	1.51	4.01	6.10	15.03
KLS3 (180)	5.80	2.98	1.28	3.80	5.50	11.32
KLS3 (190)	2.72	2.30	0.38	3.51	3.55	6.33
KLS3 (1d)	13.91	4.70	3.07	3.11	24.19	8.52
KLS3 (3d)	10.74	3.95	2.50	3.95	5.35	13.70
KLS3 (5d)	9.14	3.77	2.3	4.23	6.39	16.96
KLS3 (10d)	8.41	3.40	1.91	4.34	4.83	15.97
KLS3 (30d)	5.61	3.42	1.41	3.28	5.13	8.76
KLS3 (60d)	5.65	2.88	1.07	2.60	2.33	7.59

[a]deduced from TG weight losses. [b](100) indicates that the reaction was performed at 100 °C for 5 days. (1d) corresponds to a reaction period of 1 day at 150 °C.

at 387, 530 °C and 754 °C, demonstrating that TMA cations were located in different environments. In the case of KLS1 and HLS materials, only one mass loss was detected for TMA cations.[21,27] Qualitatively, the intensity of the exothermic peak at 387 °C decreased and that at 525 °C increased with increase of reaction time. It was difficult to ascribe the weight losses for materials prepared for longer than 30 days reaction time. These materials had a continuous mass loss from room temperature up to 400 °C (see Fig. 4). The values of weight losses related to water and organic molecules are reported in Table 2. The total weight loss related to the organic molecules from TG data was higher compared to the total elemental analyses for carbon and nitrogen, except for KLS3 prepared at 100 and 130 °C. The grey color of the sample after thermal analysis indicated that the amorphous silica species prevented the organic species from being completely oxidised during calcination.

The ^{29}Si MAS NMR spectra of Na-kanemite and the different products are illustrated in Fig. 5. Na-kanemite shows a strong signal at -97 ppm, due to Q^3 silicate species ($(SiO)_3\mathit{Si}ONa$ and $(SiO)_3\mathit{Si}OH$) as expected from the crystal structure.[28] After reaction of KLS3 with TMAOH, water and 1,4-dioxane at 150 °C for 5 days, the ^{29}Si MAS NMR spectrum of the KLS3 phase exhibited three signals at -104.6 ppm, and -113.9 and -114.3 ppm, assigned to Q^3 and Q^4 Si species, respectively. The Q^4 type had two different environments, so two signals were recorded. The presence of Q^4 species indicated the formation of a three-dimensional network in the KLS3 structure. The Q^3/Q^4 ratio in the KLS3 phase is about of 4.02. A similar spectrum was reported for the HLS material.[29] When H-kanemite reacted with TMAOH, water and 1,4-dioxane at 150 °C for 5 days, the ^{29}Si MAS NMR spectrum of the product showed the presence of SiO_4 species in both Q^3 and Q^4 environments at -103.4 and -113.2 ppm respectively. The formation of Q^3 species originated from the cross-linkage of kanemite layers during the exchange of Na by protons,[29] or from condensation of Q^3 species during the intercalation of TMA cations.[30,31]

When ethanol was used as a solvent instead of 1,4-dioxane, the ^{29}Si MAS NMR spectrum of the resulting material was similar to that obtained for KLS3 (not shown). As the amount of ethanol increased, new broad signals at -98 ppm and -108.9 ppm were detected and those of KLS3 decreased in intensity. The broadness of the signals was related to an amorphous phase as indicated by powder X-ray diffraction.

Fig. 6 shows the FT-IR spectra of Na-kanemite and the converted products from different synthesis conditions. The FT-IR spectrum of Na-kanemite agrees well with those reported elsewhere.[15,32] The bands between 1300 and 950 cm^{-1} were

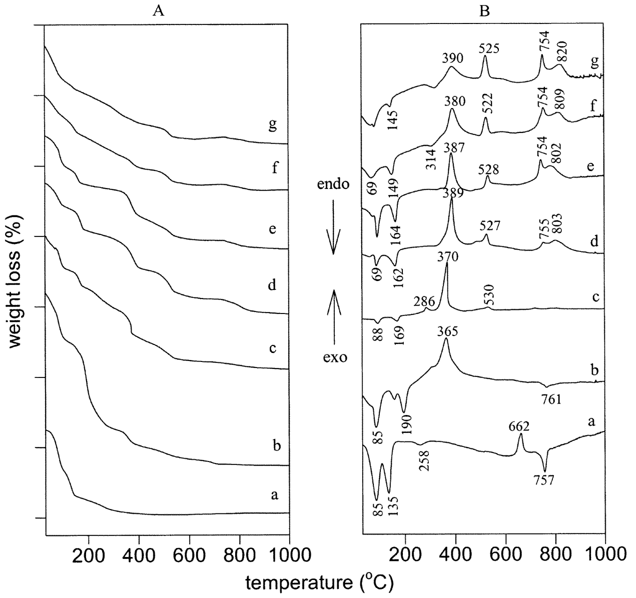

Fig. 4 TG curves (A) and corresponding DTA traces (B) of (a) Na-kanemite and KLS3 phases prepared at 150 °C for different reaction periods: (b) 1 day, (c) 3 days, (d) 5 days, (e) 10 days, (f) 30 days and (g) 60 days.

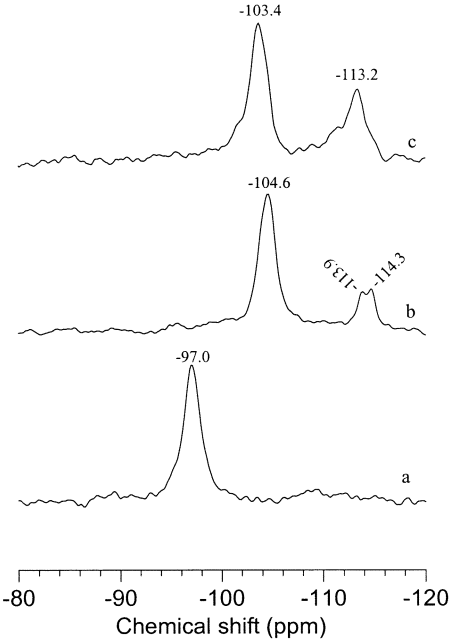

Fig. 5 ^{29}Si MAS NMR of (a) Na-kanemite, (b) KLS3 phase and (c) TMA- intercalated kanemite prepared from H-kanemite.

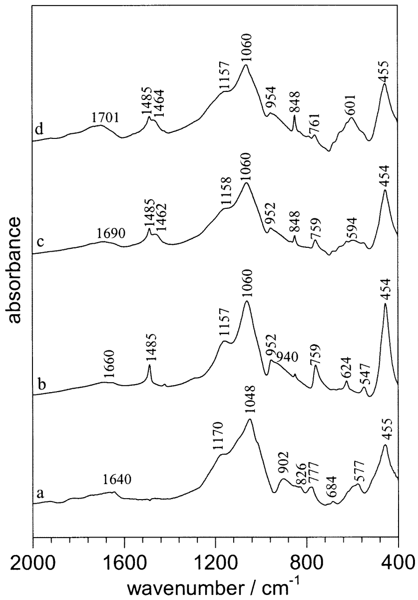

Fig. 6 FT-IR spectra of (a) Na-kanemite, and KLS3 phases prepared at 150 °C for 5 days (b) and 60 days (c). (d) corresponds to as-synthesized KLS3 prepared at 190 °C for 5 days.

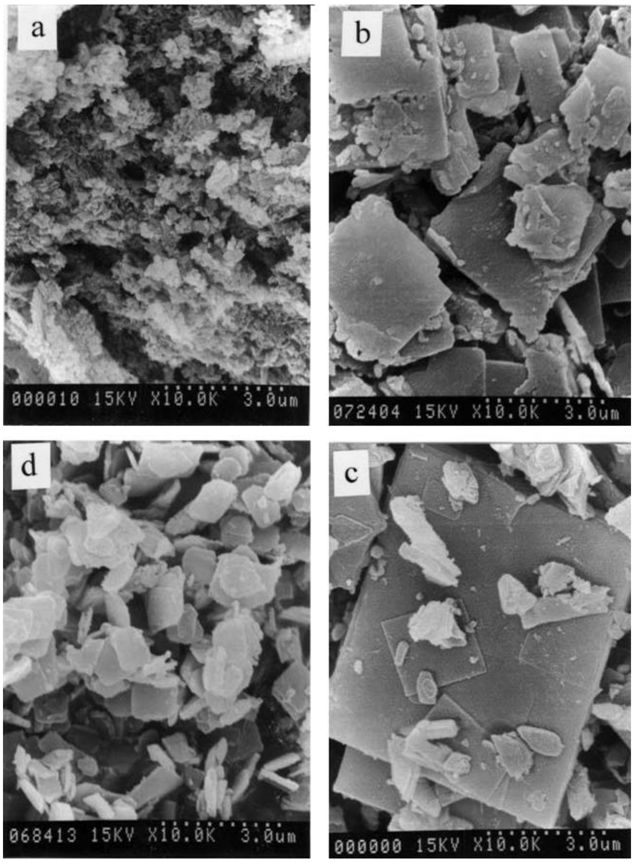

Fig. 7 SEM micrographs of (a) Na-kanemite and after treatment with TMAOH–water and 1,4-dioxane at 150 °C for (b) 3 days and (c) 5 days. (e) corresponds to KLS3 phase using ethanol as solvent at similar conditions to (c).

assigned to the asymmetric stretching vibrations of Si–O–Si linkages and the stretching vibrations of terminal Si–O– bonds. Considering that the silicon species within sheets of Na-kanemite were in Q^3 sites, it could be concluded that the absorption band at 1048 cm^{-1} was characteristic of Si in the Q^3 environment.[30] The bands between 900 and 500 cm^{-1} are associated with the symmetric stretching vibrations of Si–O–Si bridges. The band at 455 cm^{-1} was due to the silicon–oxygen bending vibrations and the stretching vibrations arising from Na–O. The FT-IR spectrum of KLS3 phase (prepared at 150 °C for 5 days) exhibited similar overall characteristics to that of KLS1 prepared from Na-magadiite, with a band centered at 1157 cm^{-1}. This band suggested the existence of Si–O–Si linkages with a bond angle lower than or close to 180°.[33] The shift of the band at 1048 cm^{-1} to a higher value of 1061 cm^{-1} in KLS3 material was a consequence of development of Q^4 silicon species.[30] The absorption bands assigned to TMA cations were also observed at 1485 and 952 cm^{-1}. The characteristic bands of Na-kanemite between 1000 and 400 cm^{-1} were altered indicating that the structure of the silicate sheets had changed. The broad band at 942 cm^{-1} was assigned to the Si–O stretch of the SiOH groups.[34–35] The symmetric stretch mode of the Si–O–Si chain corresponds to the band at 760 cm^{-1}. The absorption at 650–550 cm^{-1} was assigned to the presence of a double ring of tetrahedra in a zeolitic framework.[36] The intensity ratio of the peaks at 550 cm^{-1} to 450 cm^{-1} is often used as a quantitative measurement of zeolite crystallinity.[37]

After reaction at 150 °C and for 60 days, the absorption bands of KLS3 phase became less intense and broad, especially in the 700–520 cm^{-1} region, and new peaks appeared at 848 cm^{-1} and 594 cm^{-1}. The intensity of these bands increased with increase in the reaction temperature at 190 °C, and they may be related to the formation of amorphous silica.[38] (see Fig. 6). The bands at 848 cm^{-1} and 1470 cm^{-1} can also be assigned to residual entrapped organic species in the amorphous phase.[39]

From the scanning electron micrograph (Fig. 7a), the Na-kanemite predominantly consisted of aggregates of small crystallites with irregular size that did not exhibit a clearly definable morphology. However, these particles of Na-kanemite were transformed to a plate-like morphology of irregular shape and size (Fig. 7b) after reaction with a TMAOH– water–1,4-dioxane mixture for 3 days. Fig. 7b might suggest the presence of a secondary phase with different particle sizes. At longer reaction periods of 5 days, the morphology of KLS3 material consisted of good quality and clean square plates with sizes from 2 μm to 6 μm (Fig. 7c). When ethanol was used as a solvent instead of 1,4-dioxane at 150 °C for 5 days, the square-like shape of the plates was also observed with a decrease in the size range to between 0.5 and 1 μm (Fig. 7d).

4. Discussion

The crystallization in the reaction of amorphous SiO_2 in the TMAOH–H_2O–NaOH–1,4-dioxane mixture under hydrothermal treatment at 150 °C produced a new layered silicate (designated as HLS). The organic solvent 1,4-dioxane was essential to obtain the HLS phase, and during the formation of HLS, amorphous silica was transformed into a silicate layer structure in the presence of NaOH, and TMA cations were subsequently incorporated into this structure.[27] Given that the silicate layer structure was formed at an early stage, it seemed interesting to use another a layered silicate as source of silica and sodium. When Na-kanemite was used, a KLS3 phase was obtained in the TMAOH–water system with or without the addition of 1,4-dioxane, at 150 °C. According to the powder XRD, the KLS3 material exhibited almost the same powder pattern as the HLS phase, indicating a similarity in the silicate structure, with half of the sodalite cages forming the silicate sheets. The TMA cations were essential to the formation of this phase and were confined in the silicate "cups", as confirmed by FT-IR spectroscopy. H-kanemite was not converted to a KLS3 phase at 150 °C, probably due to the absence of Na cations in the reaction mixture. Similar results were obtained when H-magadiite was reacted with TMAOH, water and 1,4-dioxane at the same temperature and reaction time.[25] Thus, the TMA and Na-cations are both essential to obtain the KLS3 phase. According to the literature,[40] TMA and Na cations were used as structure-directing agents to form the sodalite structure. However, when TPAOH was used, Na-kanemite was converted to a silicalite-1 phase.

From the chemical analysis, Q^3/Q^4 ratios and TGA, the empirical formula of the as synthesized KLS3 in the 150 to 180 °C range was calculated to be: $H_xNa_ySiO_{2.4}$ $[(CH_3)_4N]_n{\cdot}mH_2O$. ($x = 0.35$–$0.41$, $y = 0.24$–0.27, $n = 0.13$–0.21 and $m = 0.26$–0.31). The composition of the HLS phase was proposed as $H_{0.4}Na_{0.2}SiO_{2.4}$ $[(CH_3)_4N]_{0.2}{\cdot}0.55H_2O$;[23] these data indicated that the KLS3 phase was rich in Na content compared to HLS material.

The ^{29}Si MAS NMR spectrum indicated a shift of Q^3 species in the KLS3 phase compared to that of Na-kanemite, indicating a structural change of the silicate framework and the formation of a three-dimensional-silicate network. The Q^3/Q^4 ratio of 4.02 was close to that estimated from the proposed structure of HLS. The presence of two types of Q^4 silicon species indicated that the local chemical environments of the Q^3-type Si atoms neighboring each Q^4site differed slightly and that the SiO_4 tetrahedra were somewhat distorted.[23] In the case of KLS1 material prepared from Na-magadiite, only one signal related to Q^4 Si species was observed.[21] The FT-IR spectroscopy confirmed also the change in the structure of Na-kanemite sheets during its conversion to KLS3 phase. New bands at 624 and 547 cm^{-1} were assigned to the presence of a double ring of tetrahedra in the zeolitic framework. The shift of the band characteristic of SiO_4 asymmetric stretching vibration from 1048 cm^{-1} to 1061 cm^{-1} was a consequence of the development of Q^4 species. The KLS3 phase had a high Q^3/Q^4 ratio of 4.02 and therefore is thermally unstable. The structure collapsed upon calcination at mild temperatures about 300 °C. Meanwhile, FLS1 material prepared from H-magadiite in the TMAOH–water mixture at 150 °C for 5 days (with a low Q^3/Q^4 value of 0.38), was found to be thermally stable at temperatures above 800 °C.[24] Similar observations were reported in the case of transformation of the layered aluminosilicate into mesoporous materials.[30]

The conversion of Na-kanemite to a KLS3 phase could proceed *via* complete destruction of the kanemite sheets and its recrystallization in the presence of TMA cations to a new layered structure. The way in which the silicate species reorganize around the TMA cations is not yet clarified. Nevertheless, the powder XRD patterns of Na-kanemite reacted with TMAOH–water–1,4-dioxane at 150 °C for short reaction times in terms of hours (Fig. 8) indicated that Na-kanemite was converted to mainly an amorphous phase and quartz after 1 h of reaction. The intensity of quartz increased and complete absence of the amorphous phase occurred after 4 h. The characteristic reflections of the KLS3 phase appeared after 6 h of reaction along with quartz reflections. Longer reaction times led to the development of KLS3 reflections and a decrease of quartz phase intensity. It was difficult to identify TMA-intercalated kanemite at a reaction temperature of 150 °C as observed in the case of Na-magadiite.[21] The difference between the two starting silicate layers could be related to the lower stability of Na-kanemite in the basic medium during the exchange reaction[41] compared to Na-magadiite.

The helix morphology of HLS material was obtained only from an amorphous silica–TMAOH–water–1,4-dioxane system. The KLS3 phase had platelets with square-like shapes. The difference could be due to the different morphologies of sources of silica used during the synthesis. We have also noted that by starting from rigid silicate sheets such as Na-magadiite, the obtained KLS1 phase has platelet morphology with different shapes and smaller size.[21]

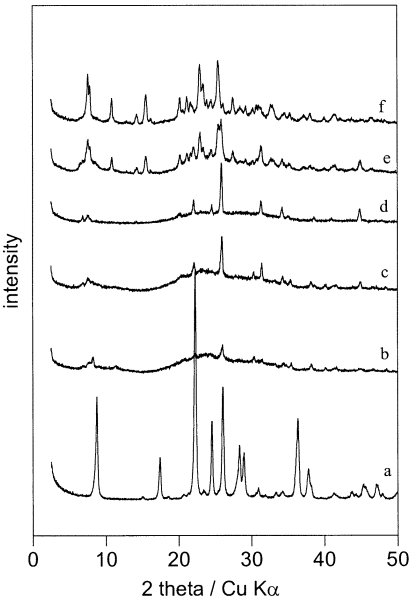

Fig. 8 Powder XRD patterns of (a) Na-kanemite treated with TMAOH, 1,4-dioxane and water at 150 °C over short reaction times: (b) 1 h, (c) 2 h, (d) 4 h, (e) 6 h and (f) 8 h.

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