

Hydrothermal conversion of Na-magadiite to a new silicate layered structure in a TMAOH–water–1,4-dioxane system

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The hydrothermal conversion of Na-magadiite in tetramethylammonium hydroxide (TMAOH) and 1,4-dioxane to form a new layered silicate structure, assigned as KLS1, is described. Total conversion of Na-magadiite to KLS1 was achieved in a short reaction time of 4 hours. The nature of the new silicate structure was characterized by using ²⁹Si MAS NMR and found to contain predominantly Q³ type (SiO)₃-Si-OH building units.

1. Introduction

Zeolites and related silicate molecular sieves have found wide application as catalysts, sorbents and ion-exchange materials.¹ The industrial applications of zeolites are now finding limitations due to their small pore structures. Improvements of known applications and the prospect of new ones are driving fresh investigations into the synthesis of zeolitic materials with new properties.² In the search for new silicate frameworks, many different types of templates or structure directing agents (SDA) have been applied to the synthesis of zeolites and related materials.

Crystallization in the reaction mixture 1,4-dioxane–NaOH–amorphous SiO₂–TMAOH–H₂O under hydrothermal conditions at 150 °C was recently found to produce a new layered structure with an unusual helical morphology. The material was designated as HLS.³ The framework of HLS consists of two-dimensional silicate layers containing hemihedral cages and is regarded to be an interrupted sodalite framework.⁴ TMA⁺ cations were found to be incorporated into the cages and Na⁺ and water were also located between the anionic layered silicate sheets. This two-dimensional cage structure contained micropores in the silicate framework in addition to the interlayer space that was available for intercalation reactions. The organic solvent 1,4-dioxane was essential to obtain the HLS phase. During the formation of HLS, amorphous silica was transformed into a silicate layer structure in the presence of NaOH. TMA⁺ cations were subsequently incorporated into this structure. Given that the silicate layer structure was formed in the first reaction stage, it seemed interesting to use a layered silicate structure as a source of silica and as a source of sodium to see if other novel materials might be formed. In this way the use of NaOH in the reaction mixture might be avoided and reaction times might be reduced.

Layered silicates such as magadiite (Na₂Si₁₄O₂₉·11H₂O), kanemite (NaHSi₂O₅·H₂O), makatite (Na₂Si₄O₉·5H₂O) and ilerite (Na₂Si₈O₁₇·xH₂O) have previously been employed as precursors for the synthesis of porous framework materials.^{5–7} Pál-Borbély *et al.*^{8,9} prepared MFI and MEL type zeolites by recrystallization of magadiite varieties in the presence of tetrapropylammonium (TPA⁺) cations.^{10,11} While the TMA⁺ cation is also an interesting SDA allowing the preparation of a variety of zeolite structures,^{12–14} to date no reports concerning the recrystallization of magadiite varieties in the presence of TMA⁺ cations have been reported.

In this contribution we describe the hydrothermal conversion of Na-magadiite in the presence of TMA⁺ and 1,4-dioxane into a new phase that is structurally similar to HLS, which we denote as KLS1. The influence of various synthesis parameters such as temperature and the amounts of TMAOH, 1,4-dioxane and water were studied. The resulting materials were characterized by powder X-ray diffraction (XRD), chemical analysis, and solid-state ²⁹Si MAS NMR.

2. Experimental

2.1 Synthesis

KLS1 was typically prepared by the addition of TMAOH (2.3 g of a 15% aqueous solution, 3.7 × 10^{−3} mol), H₂O (0.5 g, 2.77 × 10^{−3} mol) and 1,4-dioxane (5 g, 5.7 × 10^{−3} mol) to Na-magadiite (1 g, 9.4 × 10^{−4} mol SKS6 provided by Clariant Tokoyama, Japan). The mixture was sealed into a 30 cm³ stainless steel Teflon[®] lined autoclave, and reacted under static hydrothermal reaction conditions at different temperatures for between 1 and 60 days. The crystalline products that resulted were recovered by centrifugation, washed with acetone and air-dried at 40 °C overnight. For comparison purposes the HLS phase was prepared using amorphous silica as the silica source as previously reported.³ The KLS1 products formed are hereafter assigned as follows; with KLS1(100) denoting a product from the conversion of Na-magadiite at 100 °C for 5 days. To study the effect of different reaction variables such as; TMAOH, water and dioxane contents on the conversion of Na-magadiite, each parameter was varied individually at 150 °C for a reaction time of 5 days. Different alkyltrimethylammonium KLS1 (C_nTMA–KLS1) products were prepared by ion-exchange of 0.5 g of the KLS1(150) sample with 10 cm³ of C_nTMA⁺Cl[−] solution (0.5 mol dm^{−3}) at room temperature. The product was filtered off and washed with 150 cm³ of deionized water then dried in air at 40 °C.

2.2. Characterization of the materials

The powder XRD patterns were collected on an MXP 18 diffractometer (Mac-Science Co., Ltd.) with monochromatic Cu-Kα radiation. Thermogravimetric analyses were performed using a Mac-Science TG-DTA 2000 analyzer. All samples were heated to 1000 °C at a heating rate of 5 °C min^{−1} in flowing air. Si and Na elemental analyses were obtained with a Thermo

Jarrel Ash IRIS/AP ICP spectrometer. Chemical analyses of C, H and N were obtained using a CE instruments model EA 1110. Solid state ^{29}Si MAS NMR spectra were measured with a Bruker AMX 500 solid NMR spectrometer operating at 99.36 MHz. A recycle delay of 800 s was used in order to obtain quantitative results and 25 to 30 transients were recorded for each sample. Scanning electron micrographs were taken with a Hitachi S-800 electron microscope.

3. Results and discussion

When Na-magadiite was treated with 1,4-dioxane and water at 150 °C, without TMAOH, it remained unreacted for 5 days. The powder XRD pattern of Na-magadiite (Fig. 1a) exhibits several 00l reflections corresponding to an interlayer spacing of 1.53 nm. The peak positions agree with values reported for both natural and synthetic magadiites.^{15,16} The reaction of magadiite with 1,4-dioxane, water and TMAOH at 150 °C for 5 days, resulted in the formation of a white crystalline product that we assign as KLS1(150). The powder XRD pattern of this material was significantly different to that of Na-magadiite (Fig. 1c), but bore some similarity to that of the HLS phase prepared from amorphous SiO_2 under otherwise identical reaction conditions (Fig. 1e). Na-magadiite was also converted into KLS1 over longer reaction times of up to 30 days, suggesting that the KLS1 phase is perhaps more than a metastable phase. An additional unidentified silica phase was obtained after 60 days reaction.

3.1. Influence of temperature

Fig. 1 shows the powder XRD patterns of Na-magadiite treated at different temperatures for 5 days. Na-magadiite was transformed completely into KLS1 at temperatures between 100 and 150 °C with an increase in the crystallinity as the reaction temperature was increased. At 170 °C however, an impurity was detected along with the KLS1 phase. At reaction temperatures greater than 180 °C, KLS1 was not obtained and Na-magadiite was converted into an unidentified silica phase (Fig. 1f) probably as a result of decomposition of the TMAOH reagent. Further investigation of reaction variable effects was hereafter confined to reactions at 150 °C over 5 days.

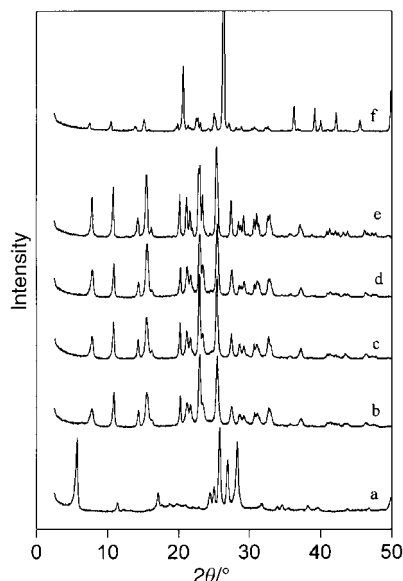


Fig. 1 Powder XRD patterns of Na-magadiite (a) and KLS1 phases after reaction of Na-magadiite with TMAOH, water and 1,4-dioxane for 5 days at different temperatures: (b) 100 °C, (c) 130 °C, (d) 150 °C, (f) 180 °C. Pattern (e) corresponds to an HLS phase prepared under conditions similar to sample (d).

3.2. Influence of the TMAOH content

For low TMAOH (0.5 g) concentrations, Na-magadiite was transformed into an unidentified silica phase along with KLS1 and a third phase detected as a minor impurity. As the amount of TMAOH was increased up to 1.3 g, the diffraction peaks of KLS1 became more intense and the silica phase was not observed. Na-magadiite was completely transformed into KLS1 for TMAOH amounts greater than 1.3 g. The XRD patterns show only reflections characteristic of highly crystalline KLS1 phase.

3.3. Influence of water content

From Fig. 2, it can be concluded that no added water was required to convert Na-magadiite into KLS1 but that increasing the amount of water to 5 g facilitates the formation and crystallization of KLS1. Further increasing the water content of the reaction led to the conversion of Na-magadiite to another new phase in addition to KLS1. The intensity of the XRD reflections of the new phase increased while those of the KLS1 phase decreased and completely vanished at 10 g of added water. This second new phase was labelled FLS1. Interestingly, for water contents greater than 12 g, Na-magadiite was converted neither to the FLS1 nor the KLS1 phases and no further transformations were observed.

3.4. Influence of organic solvents

In the SiO_2 -TMAOH- H_2O -NaOH-1,4-dioxane system, it was found that dioxane was critical in obtaining the HLS phase. We found that Na-magadiite was converted to KLS1 phase, after treatment with TMAOH and water, whatever the concentration of 1,4-dioxane. This suggested that the conversion of Na-magadiite to KLS1 phase was independent of 1,4-dioxane in the reaction. We noted however, that the crystallinity of KLS1 was 1,4-dioxane dependent with the crystallinity decreasing as the amount of 1,4-dioxane was increased. When other organic solvents are added to the reaction mixture instead of 1,4-dioxane, such as alcohols (ethanol, propanol), the crystallized product contained the KLS1 phase in varying amounts. Na-magadiite was converted to the KLS1 phase when the ethanol quantities added were lower than 10 g. Further increasing the amount of alcohol added resulted in no transformation of Na-magadiite.

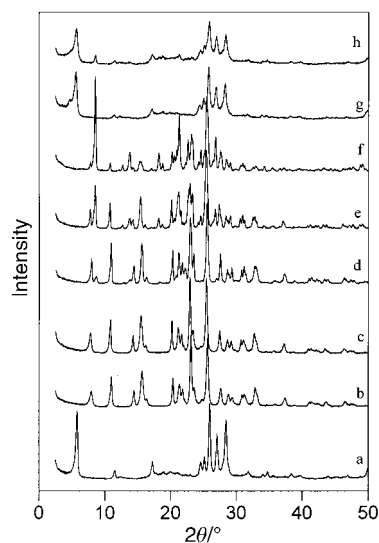


Fig. 2 Powder XRD patterns of Na-magadiite (a) and KLS1 phases after reaction of Na-magadiite with TMAOH and 1,4-dioxane at 150 °C for 5 days with different amounts of water: (b) 0 g, (c) 0.5 g, (d) 5 g, (e) 7.5 g, (f) 10 g, (g) 15 g and (h) 20 g.

Table 1 Chemical composition of Na-magadiite and KLS1 phases obtained at different reaction temperatures

| Samples ^a | Si/Na | C (%) | H (%) | N (%) | H ₂ O (%) | Q ³ /Q ⁴ ratio |
|----------------------|-------|-------------------|-------------------|-------------------|----------------------|--------------------------------------|
| Na-magadiite | 7.20 | n.d. ^b | n.d. ^b | n.d. ^b | 13.5 | 0.32 |
| KLS1(100) | 7.50 | 13.48 | 5.25 | 2.86 | 22.3 | 4.94 |
| KLS1(130) | 7.92 | 12.26 | 5.07 | 3.10 | 27.3 | 4.24 |
| KLS1(150) | 7.88 | 10.62 | 4.27 | 3.34 | 11.97 | 4.07 |
| KLS1(170) | 8.51 | 9.82 | 3.84 | 3.29 | 9.09 | 3.68 |
| KLS1(180) | 9.91 | 3.36 | 1.38 | 3.06 | 4.04 | n.d. ^b |
| HLS | 5.00 | 10.02 | 4.32 | 3.01 | 4.04 | 4.02 |
| FLS1 | 62.00 | 8.52 | 2.76 | 2.30 | 3.88 | 0.28 |

^aValues in parentheses indicate the conversion temperature of Na-magadiite (°C) over 5 days. ^bn.d. = not determined.

3.5. Characterization

The chemical compositions of the products are shown in Table 1. We observed that the Si/Na ratio in the KLS1 phases increased with conversion temperature and reaction time over 5 days. This ratio was higher than that of the starting Na-magadiite (Si/Na ratio about 7.2), indicating that some of the Na⁺ cations from the magadiite are excluded during the conversion process. The Si/Na ratio in the KLS1 phases was also higher than that of the HLS phase (Table 1). Interestingly, the FLS1 phase (prepared with high water content) contained fewer Na⁺ cations than KLS1 with an Si/Na ratio of 62.

Thermogravimetric analysis of the as-synthesized KLS1 materials prepared at different temperatures (Fig. 3) showed four general weight losses that were distinct from those observed for Na-magadiite. The first endotherm below 100 °C, corresponded to evaporation of surface adsorbed water. The second weight loss between 100 and 200 °C followed the loss of more strongly bound water molecules incorporated between the KLS1 layers and bound to Na⁺ cations. Indeed, the TGA curve of H⁺ exchanged KLS1 did not exhibit this weight loss. The third weight loss was exothermic and observed above 290 °C. It is assigned to the oxidative elimination of TMA⁺ cations occluded in the silicate sheets. An additional low intensity exotherm at 820 °C was observed and could be related to the oxidation of carbonaceous residues remaining from incomplete combustion of TMA⁺ cations.¹⁷ The TMA⁺ weight loss and the intensity of the related exotherm at 380 °C increased as the KLS1 formation temperature was raised from 150 to 170 °C. C, H and N analyses however, indicated that the carbon content in KLS1 decreased as the synthesis temperature was increased (Table 1). The C, H and N contents were not

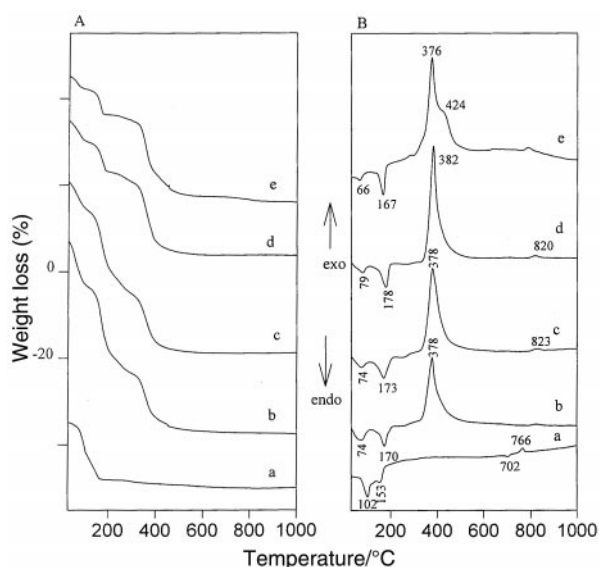


Fig. 3 TGA traces (A) and corresponding DTA features (B) of Na-magadiite (a) and KLS1 phases prepared over 5 days reaction at different temperatures: (b) 100 °C, (c) 130 °C, (d) 150 °C and (e) 170 °C.

affected by the reaction time when less than 30 days at 150 °C, and were in agreement with the TG weight loss observed around 290 °C. From the TGA and chemical analysis data, the following empirical formula was calculated for KLS1(150): H_{0.45}Na_{0.13}SiO_{2.4}[(CH₃)₄N]_{0.22}·0.47H₂O. The composition of the similar HLS phase was earlier found to be H_{0.4}Na_{0.2}SiO_{2.4}[(CH₃)₄N]_{0.2}·0.55H₂O.⁴

The synthetic data in Table 1 suggest that KLS1 develops a more hydrophobic character as the reaction temperature is increased. The change from hydrophilic to hydrophobic character can be related either to a decrease in the number of surface silanol groups when the reaction temperature is raised,¹⁸ or to a decrease in the number of Na⁺ cations retained within the KLS1 phase.

Fig. 4 compares the solid-state ²⁹Si MAS NMR spectra of as-prepared KLS1 materials with those of Na-magadiite and HLS. The spectrum of Na-magadiite shows that Na-magadiite possesses two general Si environments. These Si atoms were Q³ [Si*(OSi)₃(OR)] (R = H, Na) species at -99 ppm and multiple Q⁴ [Si*(OSi)₄] species in the range -110 to -114 ppm,^{19,20} with a Q³/Q⁴ ratio of 0.32. KLS1 prepared at different temperatures possesses two different Si environments with the spectra showing resonances at -104.4 and -114.3 ppm. The -104.4 ppm signal is ascribed to Q³ silanols, [Si*(OSi)₃(OH)] while the -114.3 ppm resonance arises from Q⁴ framework [Si*(OSi)₄] atoms. In the case of the HLS phase, the Q⁴ signal was split into two signals at -113.8 and -114.7 ppm, assigned to Q⁴ Si species in two different

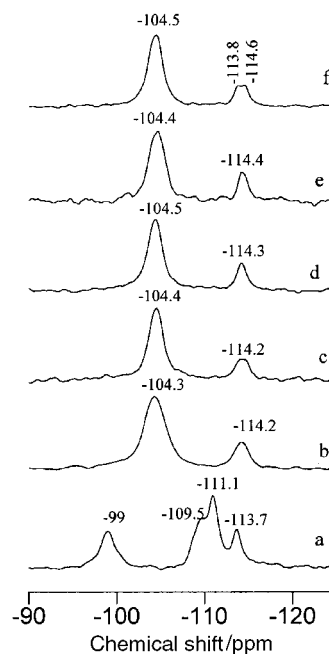


Fig. 4 ²⁹Si MAS NMR spectra of Na-magadiite (a) and KLS1 phases prepared over 5 days at different temperatures: (b) 100 °C, (c) 130 °C, (d) 150 °C and (e) 170 °C. Spectrum (f) corresponds to HLS phase prepared under conditions similar to (d).

crystalline environments (Fig. 4). Such was not the case for the KLS1 samples. The KLS1 Q³/Q⁴ ratio was about 4.07 for material prepared at 150 °C for 5 days and was close to that reported for HLS.⁴ The increase in the number of Q³ species in the KLS1 phase indicated that the layered structure of the Na-magadiite reagent was somewhat modified during the reaction with TMA⁺ and that significant numbers of new Si–O–H linkages were formed. The Q³/Q⁴ ratio decreased as the conversion temperature was raised, indicating a decrease in the number of silanol groups. This observation is in good agreement with the perceived hydrophobic character of the samples.

The SEM micrographs presented in Fig. 5 show the particle morphologies of the as-synthesized KLS1 phases prepared at different reaction temperatures. Na⁺-magadiite possesses aggregates composed of loosely packed plates. This platy morphology was also observed in KLS1 except that the crystallites are more dispersed and reduced in size. The similarity between the platy morphology of KLS1 phases and the starting Na-magadiite indicates that the hydrothermal conversion of Na-magadiite to KLS1 occurred in a topotactic fashion.

Lagaly and Beneke^{21–23} have shown that interlayer cations in layered silicates and other materials can be exchanged by organic cations with long alkyl chains such as C₁₆TMA⁺. Since the as-synthesized KLS1 phase possesses a layered structure it was of interest to see if the interlayer Na⁺ cations could be exchanged. Exchange of the interlayer Na⁺ cations with long alkylammonium cation chains might be expected to expand the

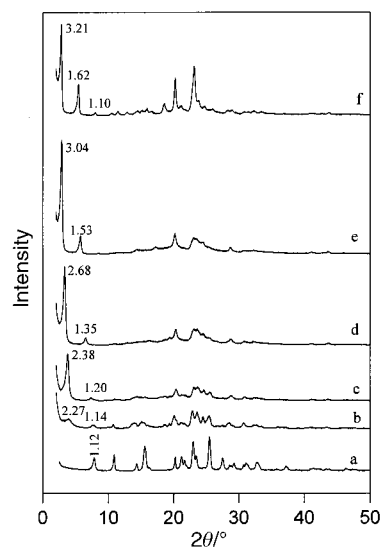


Fig. 6 Powder XRD patterns of the KLS1(150) phase (a) and of the KLS1(150) phase exchanged with different C_nTMA⁺ cations (*n* = number of carbon atoms in the alkyl chain) at room temperature: (b) C₈TMA⁺, (c) C₁₀TMA⁺, (d) C₁₂TMA⁺, (e) C₁₄TMA⁺ and (f) C₁₆TMA⁺.

interlayer region. The basal spacing of KLS1(150) showed a systematic increase after exchange with alkyltrimethylammonium cations with an increasing number of carbon atoms in the alkyl chain (Fig. 6). The powder XRD patterns

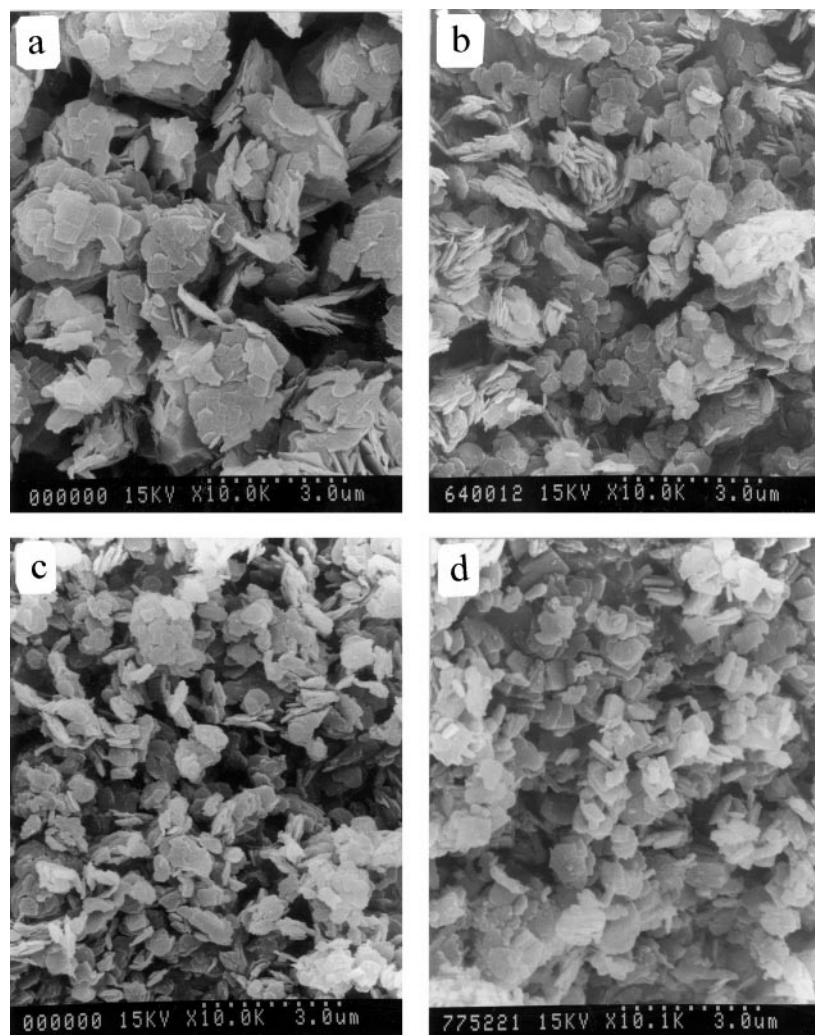


Fig. 5 Scanning electron micrographs of Na-magadiite (a) and KLS1 phases prepared over 5 days at different temperatures: (b) 130 °C, (c) 150 °C and (d) 170 °C.

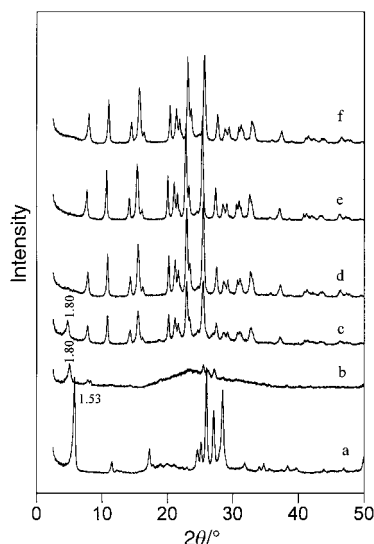


Fig. 7 Powder XRD patterns of Na-magadiite (a) and of Na-magadiite treated with TMAOH, 1,4-dioxane and water at 150 °C over short reaction times: (b) 1 h, (c) 2 h, (d) 3 h, (e) 4.5 h and (f) 6 h.

showed strong reflections at integer multiple spacings indicating that the layered structure exhibited long-range order in the individual tactoids.

3.6 Reaction sequences

In order to elaborate a preliminary reaction sequence for this hydrothermal transformation of Na-magadiite to KLS1, we performed the synthesis experiments at reaction times shorter than 24 h at 150 °C. Powder XRD patterns of the intermediate products that were formed are presented in Fig. 7. After 1 h of reaction, TMA⁺ cations were found to be intercalated between the magadiite layers (TMA-magadiite) with a basal spacing, slightly larger than Na-magadiite, of 1.8 nm being observed. No further change occurred until after 2 h reaction when reflections characteristic of the KLS1 phase were found, indicating a partial transformation of TMA-magadiite to the KLS1 phase. XRD reflections due to TMA-magadiite disappeared after 3 h of reaction, indicating a complete transformation to KLS1. ²⁹Si MAS NMR spectra for Na-magadiite and the intermediate reaction products are given in Fig. 8. After 1 h reaction the materials exhibited Q³ and Q⁴ silicon signals at -104.2 ppm and -114.1 ppm, respectively. Traces of other broad signals were detected after 2 h reaction, indicating the presence of an impurity phase, similar to that obtained after 1 h reaction. Structural irregularity of the layer configuration is reflected in broad ²⁹Si MAS NMR signals.²⁴ The spectra of the intermediate products indicated that they are highly disordered. The Q³/Q⁴ ratio increased from 0.3 to 3.92 for the Na-magadiite to KLS1 transition after 4.5 h reaction, due to the increased presence of silanol groups. This value is close to that observed for KLS1 material prepared over 5 days reaction (Q³/Q⁴ ratio of 4.07). These data therefore, suggest that KLS1 was obtained from Na-magadiite at 150 °C even after the short reaction time of 4 h. In the case of amorphous silica treated with NaOH, TMAOH and 1,4-dioxane, formation of pure HLS phase required treatment at 150 °C for a period of at least 5 days. The transformation of TMA-magadiite to the KLS1 phase was accelerated by using 1,4-dioxane as solvent and it was difficult to identify a transition phase between TMA-magadiite and KLS1. However, when 1,4-dioxane was not used, a transition phase was detected and it will be reported elsewhere, a mechanism will also be proposed.²⁵

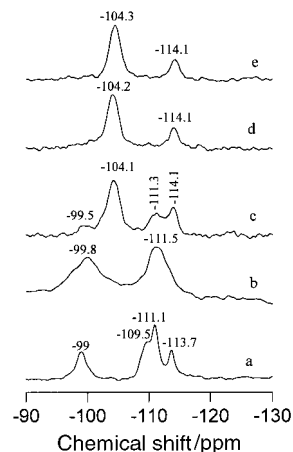


Fig. 8 ²⁹Si MAS NMR spectra of Na-magadiite (a) and of Na-magadiite treated with TMAOH, 1,4-dioxane and water at 150 °C over short reaction times: (b) 1 h, (c) 2 h, (d) 4.5 h and (e) 6 h.

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