

# Transformation of layered aluminosilicates and gallosilicates with kanemite structure into mesoporous materials

Qiubin Kan,<sup>\*a</sup> Vicente Fornés,<sup>b</sup> Fernando Rey<sup>b</sup> and Avelino Corma<sup>b</sup>

<sup>a</sup>Department of Chemistry, Jilin University, Changchun 130023, P. R. China.  
 E-mail: qkan@mail.jlu.edu.cn

<sup>b</sup>Instituto de Tecnología Química, UPV-CSIC, Universidad Politécnica de Valencia, Avenida los Naranjos s/n, 46022 Valencia, Spain

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Layered aluminosilicates and gallosilicates with kanemite structure and varied Si/M ratios have been prepared and can be transformed into mesoporous materials with MCM-41-like structure in an exchange solution of cetyltrimethylammonium chloride at pH 11.0–11.7 and 20–80 °C or at pH < 9.6 and 80 °C. The metal ions in both the layered metallosilicates and the corresponding mesoporous materials are in a tetrahedral environment. Together with the hydrolysis of the layered aluminosilicates (Al-kanemite) it is suggested that aluminium is incorporated into the framework of the layered materials. The formation of mesoporous materials derived from the layered aluminosilicates is believed to occur through lamellar phases at pH 11.0–11.7. One characteristic lamellar phase with a basal spacing of *ca.* 32 Å has been obtained at pH 10.6 at 80 °C, which can be partly transformed into mesoporous materials when the pH of exchange solution is reduced to a value of between 8.0 and 8.5. The lamellar phase has inorganic layers in a higher degree of silicate condensation, and is perhaps the reason that it does not form the hexagonal array at higher pH, such as pH 11.7 or 12.0. After removing the surfactant template and sodium ions by extraction with heptane–ethanol containing a small amount of hydrochloric acid, the mesoporous materials derived from the layered aluminosilicates in the exchange medium at pH 11.7 and 80 °C have Brønsted and Lewis acidity similar to Al-MCM-41. In contrast, no significant acid sites have been detected over the mesoporous samples obtained at pH < 9.6 and at 80 °C.

## Introduction

Interest in the silicon-based mesoporous materials, M41S, has expanded since it was shown that atoms other than silicon could be introduced into the wall.<sup>1–7</sup> Further investigations have clearly illustrated catalytic applications for the mesoporous family especially for the MCM-41 and MCM-48 structures.<sup>8–14</sup> Among the different ordered mesoporous structures, MCM-41 has been the most widely studied and this includes its synthesis mechanism. The first hypothesis for the formation of MCM-41 was the liquid crystal templating (LCT) mechanism.<sup>1,2</sup> By studying the physicochemical properties of MCM-41, Chen *et al.*<sup>3</sup> proposed that randomly ordered and rod-like organic micelles initially interacted with silicate species to generate a layer of silicate around the external surface of the micelles. These composite species spontaneously packed into the arrangement characteristic of MCM-41. This explanation for the formation of MCM-41 is in accord with the pathway postulated by Beck *et al.*<sup>2</sup> based on the fact that the liquid structures are very sensitive to the overall properties of the surfactant solution. Moreover, Monnier *et al.*<sup>15</sup> have developed a model comprised of cooperative organisation between inorganic and organic molecular species into tridimensionally structured arrays. They thought that the self-assembly processes to form specific structure types were governed by the criteria of charge density matching at the interface between organic and inorganic species.<sup>16</sup>

At the same time that researchers at Mobil R&D Corporation announced the discovery of the M41S family of mesoporous materials, Yanagisawa *et al.*<sup>17</sup> and Inagaki *et al.*<sup>18</sup> prepared mesoporous silicates and aluminosilicates, designated FSM-16, starting from a layered polysilicate

(kanemite) in the presence of alkyltrimethylammonium surfactant cations. The formation mechanism of FSM-16 proposed by its inventors was different from that of MCM-41. FSM-16 was thought to be formed by an intercalation of surfactant cations between the silicate layers of kanemite, and that inorganic layers were then folded to develop the mesostructure. Chen *et al.*<sup>19</sup> have suggested a similar reaction mechanism for the formation of mesoporous materials derived from kanemite by an exchange reaction with cetyltrimethylammonium surfactant cations at lower pH. On the other hand, at higher pH they postulated that the silicon species dissolved from kanemite were possibly responsible for the formation of the mesoporous materials and in this case MCM-41 was in fact obtained under conditions in which FSM-16 was thought to be formed.<sup>18</sup> An *in situ* time-resolved X-ray powder diffraction study showed that FSM-16 was generated from a medium containing intercalated silicate phases which were not observed during the formation of MCM-41,<sup>20</sup> indicating that FSM-16 and MCM-41 were formed by different reaction pathways. In addition, FSM-16 also showed unique hydrocarbon sorption capacity and physicochemical characteristics of the pore walls<sup>21,22</sup> further implying differences between the two similar types. Recently Inagaki *et al.*<sup>23</sup> reported the synthesis of mesoporous aluminosilicates from layered silicates containing aluminium. However, in this work there was lack of data concerning the layered precursor and on the specific conditions to produce the mesoporous materials. This paper reports on the synthesis of Al and Ga containing kanemite and the generation of mesoporous materials from these. A study on the layered metallosilicates and formation of mesoporous materials from the layered precursors has led to a further understanding of the mechanism of formation and the characteristics of mesoporous materials.

## Experimental

### Synthesis of layered aluminosilicates and gallosilicates with the kanemite structure

The layered aluminosilicates (Al-kanemite) and gallosilicates (Ga-kanemite) with different Si/M ratios were prepared by using water-glass as the silicon source and a vacuum-drying step was used to remove the excess water present in the precursor to generate the final kanemite structure.<sup>24</sup> In a typical procedure 100 g of a sodium silicate solution (PANREAC III, 26.8% Si<sub>2</sub>O<sub>5</sub>, 9.0% Na<sub>2</sub>O) was combined with 6.25 g of NaOH. After complete dissolution of NaOH, a measured amount of NaAlO<sub>2</sub> or GaOOH to give the desired Si/M ratio was added with vigorous stirring to form a homogeneous mixture. The reaction mixture was vacuum-dried for 3–4 days at room temperature and then heated at 120 °C for 1 h. The resultant sample was calcined at 700 °C. After cooling to room temperature, the solids were dispersed in 20 times their weight of water. Finally the layered metallosilicates were recovered by filtration, washed with water (water/solid = 10 wt%) and air-dried at room temperature.

### Treatment of Al-kanemite with an aqueous solution of ammonium salts or hydrochloric acid

5 g of the Al-kanemite with Si/Al = 20 (reaction mixture) was added to a 1 M aqueous solution of (NH<sub>4</sub>)<sub>2</sub>O<sub>2</sub>CMe or a mixed solution of NH<sub>4</sub>Cl and NH<sub>3</sub>(aq) with total ammonium content of 0.2 M in 200 ml water. The pH of the mixed aqueous solution was kept at > 12.0 by adjusting the concentration of NH<sub>3</sub>(aq). The resulting solution was continuously stirred at room temperature for 12 h. In order to produce H-type Al-kanemite, 5 g of Al-kanemite with Si/Al = 20 was treated with 100 ml of ca. 0.1 M hydrochloric acid at room temperature for 24 h.

### Transformation of Al- and Ga-kanemite into mesoporous materials

An ion exchange approach was used to obtain C<sub>16</sub>TMA-metallosilicates (metal = Al or Ga) derivatives.<sup>18,19</sup> Al- or Ga-kanemite was first added to an aqueous solution of C<sub>16</sub>TMACl (ca. 0.1 M) with a solid to liquid ratio varying from 15 to 200. To form different mesoporous products, the suspension containing the layered metallosilicates and organic surfactant was brought to a pH of between 8.0 and 12.0 using either dilute hydrochloric acid or NaOH solution and then stirred at a temperature between 20 and 80 °C for 20 min to 30 days. In most cases, the solid products were filtered off, washed and dried at 40 °C. In order to form thermally stable samples, the resultant organic-metallosilicate mesophases obtained in more basic media (pH > 11.0) were made less basic by addition of hydrochloric acid at 80 °C to a pH of < 9.5 and treated in the solution for 24 h. The filtered materials were dried at 60 °C and calcined in air at 550 °C for 6 h to remove the organics. Most of the surfactant could also be extracted with an azeotropic mixture of heptane and ethanol (52:48 wt/wt) containing 0.5 wt% HCl, in a refluxing system at 80 °C for 24 h.<sup>25,26</sup> Finally the samples were subjected to calcination in an air flow at 550 °C for ca. 4 h.

### Characterisation

X-Ray diffractograms were recorded on a Philips PW 1830 diffractometer using Cu-K $\alpha$  radiation. <sup>27</sup>Al, <sup>29</sup>Si and <sup>71</sup>Ga MAS NMR spectra were obtained on a Varian Unity VXR-400 WB spectrometer operating at 104.21 MHz (<sup>27</sup>Al), 79.46 MHz (<sup>29</sup>Si) and 121.98 MHz (<sup>71</sup>Ga). Transients were accumulated using a recycle delay of 0.5 s (<sup>27</sup>Al), 40 s (<sup>29</sup>Si) and 1 s (<sup>71</sup>Ga) and an acquisition time of 0.005 s (<sup>27</sup>Al), 0.063 s (<sup>29</sup>Si) and 0.050 s (<sup>71</sup>Ga). Al<sub>2</sub>(SO<sub>4</sub>) $\cdot$ 18H<sub>2</sub>O, SiMe<sub>4</sub> and Ga(H<sub>2</sub>O)<sub>6</sub><sup>3+</sup> were

used as external reference materials. IR spectra were recorded with a Nicolet 710 FTIR instrument. The measurement of IR spectra for the framework region was carried out using the KBr pellet method (1 wt% sample). To study the acidity of the mesoporous materials, self-supporting wafers (10 mg cm<sup>-2</sup>) were prepared, and evacuated in a vacuum cell at 400 °C for 16 h. Pyridine was then adsorbed at room temperature. After equilibration the samples were evacuated for 1 h at 150 °C and the spectra were measured at room temperature. For acidity measurements of the H-type Al-kanemite, the samples were treated in the vacuum cell at 200 °C before adsorption of pyridine. TG-DTA analysis was carried out on Netzsch STA 409 apparatus with a temperature increment of 10 °C min<sup>-1</sup>. The chemical composition of the materials was determined by atomic adsorption spectroscopy (Varian SPECTR AA-10 plus) and elemental analysis (FISONS 1108). Argon and nitrogen adsorption measurements were performed on an ASAP 2010 Micromeritics apparatus. Temperature programmed desorption (TPD) of NH<sub>3</sub> was carried out on Micromeritics TPD 2900 equipment attached to a mass spectrometer (Balzers ThermoStar, QM 200).

## Results and discussion

### Synthesis of layered aluminosilicates and gallosilicates

X-Ray powder diffraction was used to elucidate the structure of the synthesised kanemite and Al-kanemite with Si/Al ratios from 10 to 100 (reaction mixture) (XRD spectra not shown). The Al-kanemite materials with Si/Al  $\geq$  20 have very similar X-ray diffraction patterns to kanemite.<sup>17,18</sup> On the other hand, when the Si/Al ratio is 10, other phases besides the kanemite structure are detected. Ga-kanemite materials with Si/Ga = 100 or 200 (reaction mixture) have also been obtained by a synthesis procedure similar to that used for the preparation of the Al-kanemite and the X-ray diffraction patterns are very similar to those of the Al-kanemite materials.

We note that Al-kanemite can also be obtained from a methanol medium using amorphous Aerosil as the silicon source on the basis of the procedure described in ref. 24. However, the resultant materials have lower crystallinity than those synthesised in an aqueous medium using water glass as the source of silicon.

### Hydrolysis and treatment with ammonium salts or hydrochloric acid of Al-kanemite

When the Al-kanemite is formed from its precursor in water, it is hydrolyzed and releases Na<sup>+</sup> into the solution.<sup>24</sup> From the chemical analysis results in Table 1, the sodium content of Al-kanemite decreases with increase in Si/Al ratio. The influence of the aluminium amount on the sodium content of Al-kanemite suggests that Al may be incorporated into the kanemite framework since sodium aluminosilicates should be less prone to hydrolysis than sodium silicates.

Treatment of Al-kanemite with a neutral (NH<sub>4</sub>)<sub>2</sub>O<sub>2</sub>CMe

**Table 1** Chemical composition of initial reaction mixture and crystalline products for synthesis of Al-kanemite

Reaction mixture			Crystalline product <sup>a</sup>	
Si/Al	Na/Al	Na/Si	Na/Al	Na/Si <sup>b</sup>
100	100	1.0	36.00	0.36
80	80	1.0	35.56	0.44
50	50	1.0	27.33	0.55
20	20	1.0	14.62	0.73

<sup>a</sup>The preparation conditions influence the analysis results; hydrolysis is allowed to proceed for 10 min. <sup>b</sup>The Si/Al ratio of the reaction mixture is used for this calculation.

aqueous solution at room temperature leads to collapse of the layered structure. In order to limit the hydrolysis of the Al-kanemite, a higher pH solution containing  $\text{NH}_4\text{Cl}$  and  $\text{NH}_3(\text{aq})$  was thus used. Under such conditions the layered structure is retained. If the treatment procedure is repeated, a loss of crystallinity occurs. It should be noted that the Al-kanemite samples treated with  $\text{NH}_4\text{Cl}$  and  $\text{NH}_3(\text{aq})$  do not incorporate nitrogen, as revealed by element analysis.

Al-kanemite is converted into its acid form by extracting the  $\text{Na}^+$  form with 0.1 M HCl solution using a liquid to solid ratio of 20 wt%. The materials formed show X-ray diffraction patterns similar to crystalline silicic acids generated from kanemite. We assume, therefore, that the acid form derived from the Al-kanemite should possess a structure similar to that of  $\text{H}_2\text{Si}_2\text{O}_5\text{-III}^{24}$  in which isomorphous substitution of silicon by aluminium has occurred. In order to prove that acidic materials are prepared, pyridine was adsorbed on the acid exchanged Al-kanemite, and the results clearly show the presence of Lewis and Brønsted acid sites.

### Characterisation of Al-kanemite and Ga-kanemite

Fig. 1 shows  $^{27}\text{Al}$  MAS NMR spectra of Al-kanemite samples with different Si/Al ratios. A single signal at  $-54$  ppm assigned to Al in a tetrahedral environment is observed in the NMR spectra of samples with  $\text{Si}/\text{Al} \geq 20$ , indicating that aluminium is incorporated into the framework. The intensity of this signal increases when decreasing the Si/Al ratio of the Al-kanemite. The  $^{29}\text{Si}$  MAS NMR spectra of the Al-kanemites (not shown) are similar to that of kanemite<sup>19</sup> showing a major signal at  $-97.4$  ppm associated with Si in a  $\text{Q}_3$  environment.

Al-kanemite and kanemite exhibit similar IR absorption spectra in the framework vibration region. The absorption band characteristic of the  $\text{SiO}_4$  asymmetric stretching vibration is around  $1048 \text{ cm}^{-1}$  for both samples and much lower than that for zeolites. Considering the fact that the silicon species within the sheets of Al-kanemite and kanemite are in  $\text{Q}_3$  sites while in zeolites most of silicon is tetrahedrally coordinated by four silicons through bridging oxygen ( $\text{Q}_4$ ), it can be concluded that the absorption at  $1048 \text{ cm}^{-1}$  is characteristic of Si in the  $\text{Q}_3$  environment. This will be further discussed.

Fig. 2 shows the TG-DTA spectra of kanemite, Al-kanemite and Al-kanemite samples treated with  $\text{NH}_4\text{Cl-NH}_3(\text{aq})$ . As for kanemite, three main endothermic peaks at 97, 155 and  $273^\circ\text{C}$  are observed for Al-kanemite, which are characteristic of three distinct types of water in the layered structure.<sup>27</sup> The first endothermic signal corresponds to a weight loss of 13.8% and is

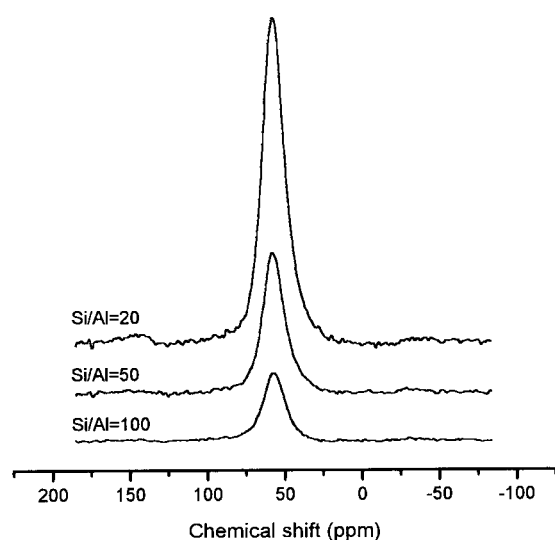


Fig. 1  $^{27}\text{Al}$  MAS NMR spectra of Al-kanemite with various Si/Al ratios.

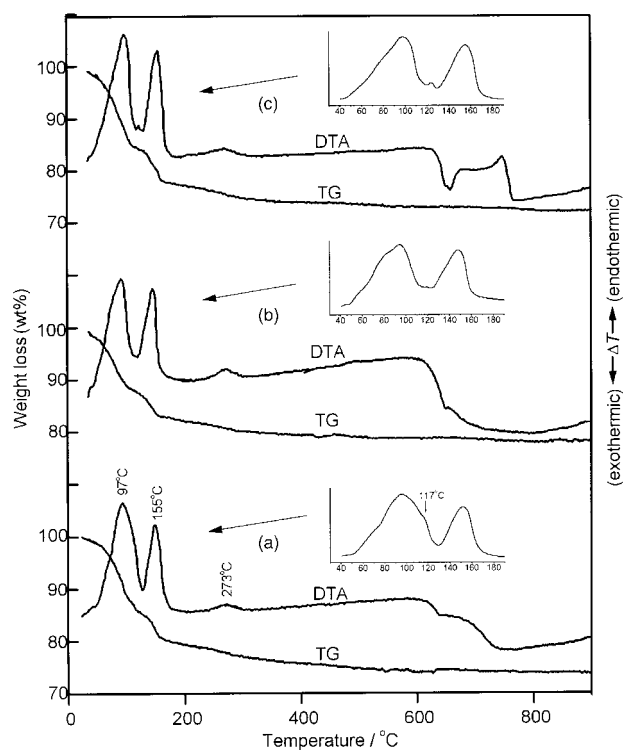


Fig. 2 TG-DTA of (a) Al-kanemite with  $\text{Si}/\text{Al}=20$  and (b) Al-kanemite treated with  $\text{NH}_4\text{Cl-NH}_3(\text{aq})$  and (c) kanemite.

associated with desorption of water coordinated to sodium ions between the sheets of Al-kanemite. The second peak at  $155^\circ\text{C}$  is accompanied by a loss of 7.0% and corresponds to the water located in hexagonal rings of the layered structure.<sup>24</sup> Finally the third endothermic effect corresponds to a weight loss of around 3.6% and it is attributed to the dehydration of Al-kanemite accompanied by formation of an amorphous phase. The exothermic signal at *ca.*  $656^\circ\text{C}$  is due to the recrystallisation of the amorphous phase. Unlike the kanemite, the Al-kanemite shows a fourth endothermic peak at *ca.*  $117^\circ\text{C}$ . After the treatment with  $\text{NH}_4\text{Cl-NH}_3(\text{aq})$  this peak disappears. Taking into account the work of Johan and Maglione<sup>27</sup> and the different types of water present in the kanemite,<sup>24</sup> the peak appearing at *ca.*  $117^\circ\text{C}$  is probably associated with the presence of aluminium or with the  $\text{Na}^+$  linked to framework Al.

The  $^{71}\text{Ga}$  MAS NMR spectrum of Ga-kanemite is illustrated in Fig. 3(a). Although only a small amount of gallium is incorporated into the Ga-kanemite, a signal at *ca.* 149 ppm which is assigned to the tetrahedral gallium in the framework<sup>28,29</sup> is clearly observed.

### Formation of mesoporous materials from Al-kanemite and Ga-kanemite

Mesoporous materials are obtained by ion exchange of Al-kanemite and Ga-kanemite in the presence of  $\text{C}_{16}\text{TMACl}$  solution under various conditions. The role of the different variables of the process, *i.e.* pH, temperature, time in the formation of mesoporous materials and lamellar phases derived from Al-kanemite has been studied.

Fig. 4 shows the effect of the pH of the exchange solution on the formation of mesoporous materials from the Al-kanemite with  $\text{Si}/\text{Al}=20$  at  $80^\circ\text{C}$ . Mesoporous materials can be formed at pH 11.7 and  $\text{pH} < 9.6$ , respectively. However, when the pH of the exchange solution is at 10.4 or 10.9, lamellar phases are formed. When the pH is  $< 9.6$ , the transformation into mesoporous materials from Al-kanemite is much slower than that at pH 11.7.<sup>19</sup> The hexagonal phases can also be obtained at lower temperatures, for instance, at 20, 40 and  $60^\circ\text{C}$  when pH

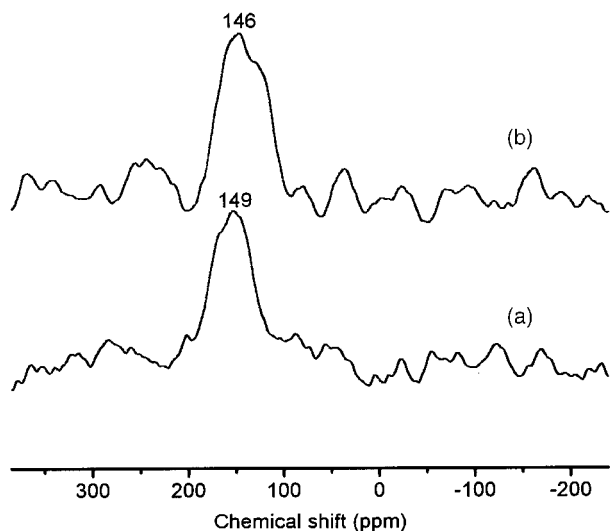


Fig. 3  $^{71}\text{Ga}$  MAS NMR spectra of (a) Ga-kanemite with Si/Ga=100 and (b) mesoporous materials obtained from Ga-kanemite at pH 11.4 and  $80^\circ\text{C}$ .

is above 11.0. This observation permits study by XRD of the formation of intermediate structures and therefore aids in rationalization of the mechanism for the formation of the mesoporous materials.

Fig. 5 illustrates the X-ray diffraction patterns of the solid products obtained at different reaction times after exchanging the Al-kanemite with  $\text{C}_{16}\text{TMACl}$  solution (0.1 M) at pH=11.0–11.7 and at 20, 40 and  $60^\circ\text{C}$ , respectively. It is clear that at low reaction temperatures a lamellar phase with smaller basal spacing (*e.g.* 27–28 Å) develops prior to the formation of the hexagonal mesoporous phases (we designate the solid products as L-3d which are generated at pH 10.4 and at  $20^\circ\text{C}$  over three days and predominantly exhibit X-ray diffraction patterns of the lamellar phase). With increasing time the mesoporous material appears and grows finally at the expense of the lamellar phase. As the temperature is raised to  $60^\circ\text{C}$ , the rate of formation of the mesoporous phase or of disappearance of the lamellar phase increases and the lamellar phase can only be observed during the first hour of the reaction, while at  $80^\circ\text{C}$  no lamellar phases are found during the transformation of Al-

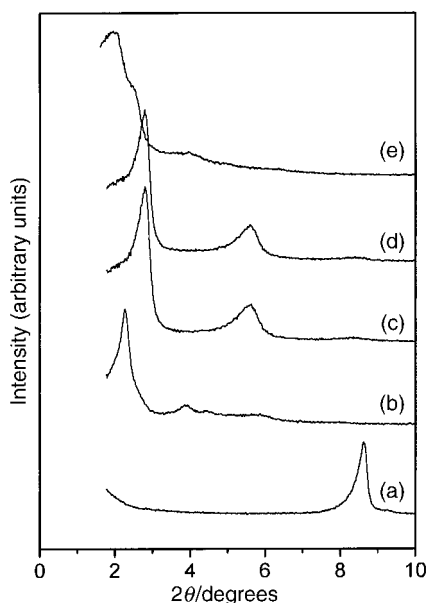


Fig. 4 Transformation of (a) Al-kanemite with Si/Al=20 into mesophases in  $\text{C}_{16}\text{TMACl}$  aqueous solution at  $80^\circ\text{C}$  and different pH values: (b) pH 11.7, (c) pH 10.9, (d) pH 10.4 and (e) pH <9.6.

kanemite into mesoporous materials. The pH of the solution has been monitored with time at the different temperatures. It is seen that the pH of solution rises with reaction time and reaches *ca.* 11.7. The hexagonal mesoporous phases formed at pH 11.7 are thermally unstable, and upon calcination the structures collapse. In order to form a thermally stable structure, treatment of the hexagonal phases with dilute hydrochloric acid is necessary.

The  $^{29}\text{Si}$  MAS NMR spectra in Fig. 6 reveal that the mesoporous phase produced from Al-kanemite at pH 11.7 and  $80^\circ\text{C}$  has a low  $Q_4/Q_3$  ratio and therefore is thermally unstable. Treatment of this sample in a hydrochloric acid solution results in an increase in the  $Q_4/Q_3$  ratio and makes the formed mesoporous materials stable upon calcination.

The Al-kanemite samples treated with  $\text{NH}_4\text{Cl-NH}_3(\text{aq})$  behaves very similarly to the original Al-kanemite in the  $\text{C}_{16}\text{TMACl}$  solution and can be transformed into mesoporous materials at pH 11.9. A mesoporous material containing gallium can also be obtained from Ga-kanemite with Si/Ga=100 at pH 11.4 and  $80^\circ\text{C}$ , by using the same procedures described for the preparation of mesoporous materials from Al-kanemite.

The  $^{27}\text{Al}$  and  $^{71}\text{Ga}$  MAS NMR spectra of the mesoporous materials formed from Al-kanemite and Ga-kanemite are shown in Fig. 7 and 3(b), respectively. The mesoporous materials derived from the Al-kanemite show a single resonance at *ca.* 54 ppm due to tetrahedral aluminium in the framework. After calcination the signal is slightly broadened but no significant peak associated with extraframework aluminium at *ca.* 0 ppm is found. Considering that extraframework gallium could not be detected by NMR and comparing the  $^{71}\text{Ga}$  MAS NMR spectrum in Fig. 3(b) with that of G-MCM-41,<sup>29</sup> it is evident that the signal at *ca.* 146 ppm corresponds to tetrahedral gallium in the framework of the mesoporous materials derived from the Ga-kanemite.

#### Lamellar phase formed from Al-kanemite and its transition to mesoporous materials

The lamellar phase with a basal spacing of *ca.* 32 Å (designated L-32) is the only solid product observed by X-ray diffraction when the pH of the solution is 10.6 and the reaction temperature is  $80^\circ\text{C}$ . Fig. 8 shows the X-ray diffraction patterns of the L-32 phase at different reaction times. The L-32 phase is sufficiently stable that it is largely retained under the reaction conditions for more than one month except for a slight increase in the basal spacing. When the pH of the solution is lowered to 8.0–8.5, the L-32 phase is partially transformed into the mesoporous phase. By contrast, if the pH of the solution is brought to 11.7 or 12.0 by addition of sodium hydroxide solution, the L-32 phase is preserved except for a slight reduction of basal spacing and some dissolution; no mesoporous materials are formed (see Fig. 9).

Elemental analysis shows that L-32 has a similar organic content as the L-3d phase. From solid state NMR spectra we know that  $Q_3$  silicon species predominate in Al-kanemite. It is logical to consider that condensation between  $Q_3$  silicon species will take place when the Al-kanemite is subjected to an exchange solution of  $\text{C}_{16}\text{TMACl}$  under appropriate reaction conditions, especially at lower pH and higher temperatures. Fig. 10 shows the  $^{29}\text{Si}$  MAS NMR spectra of the two phases, L-32 and L-3d, from which it is evident that  $Q_4$  silicon species are formed, likely arising from condensation between  $Q_3$  siliceous species. The  $Q_4/Q_3$  ratio is about 1 : 1 in the L-32 phase, indicating that a high degree of silanol condensation has occurred. In contrast, for the L-3d phase, most of silicon is still in  $Q_3$  environments and only a small fraction of  $Q_4$  silicon species are observed. The signal at  $-97.4$  ppm ( $Q_{3K}$ ) is associated with silicon species from the Al-kanemite precursor which has not reacted. Two

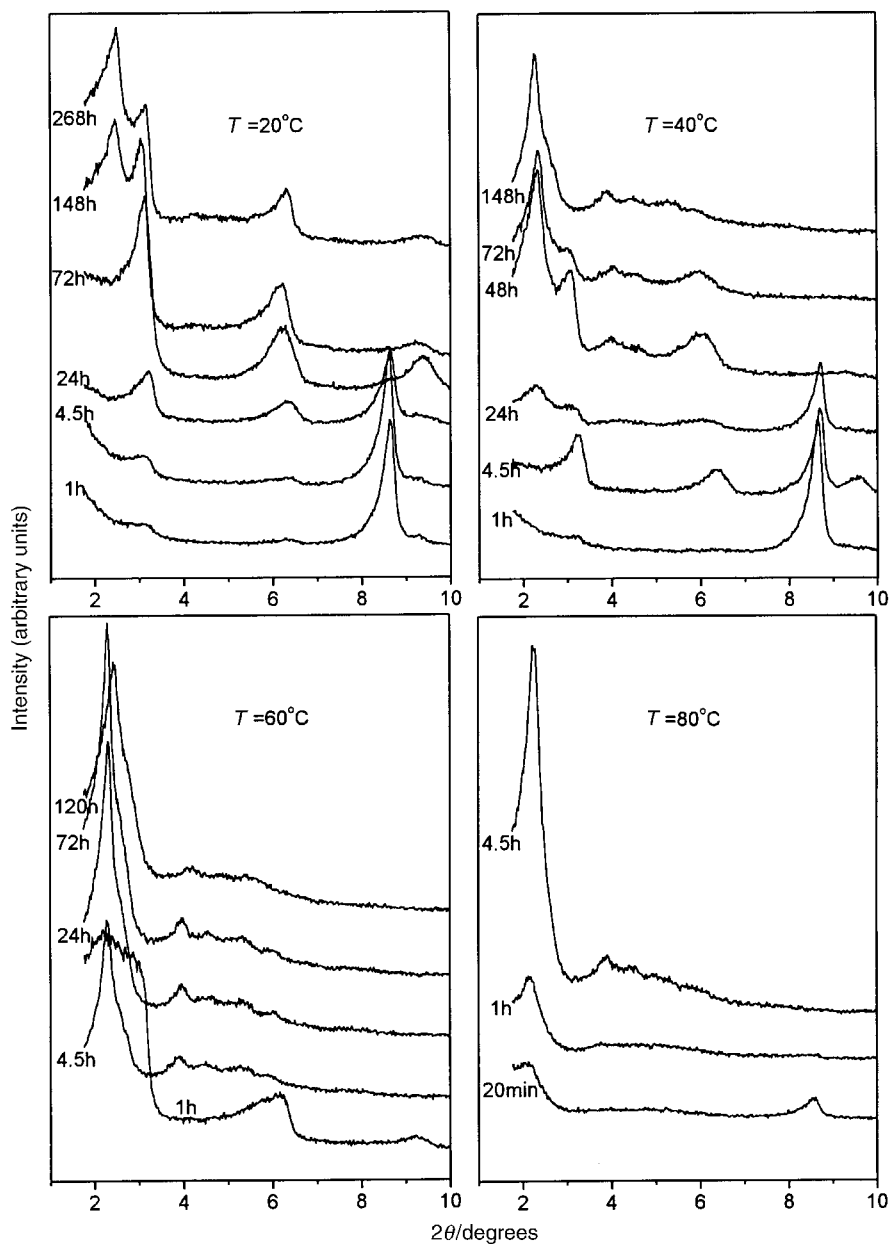


Fig. 5 Transformation of Al-kanemite with Si/Al=20 into mesoporous materials in  $C_{16}TMACl$  aqueous solution at different temperatures and times.

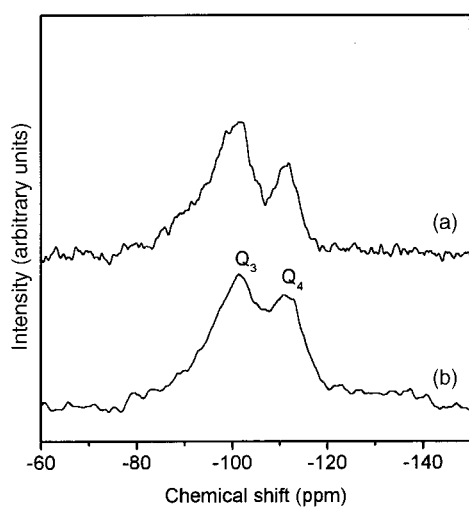


Fig. 6  $^{29}Si$  MAS NMR spectra of the mesoporous phases obtained from Al-kanemite at pH 11.7 and  $80^\circ C$ : (a) before and (b) after treatment in hydrochloric acid solution.

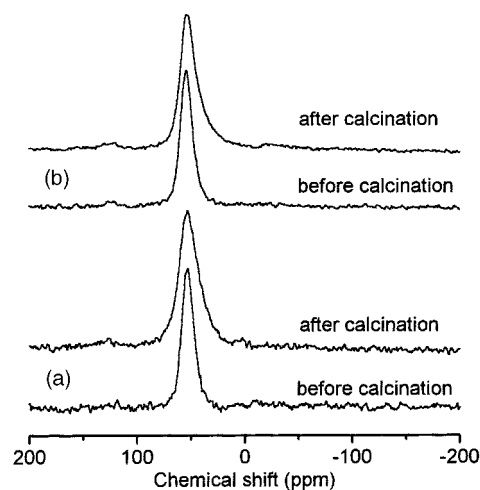
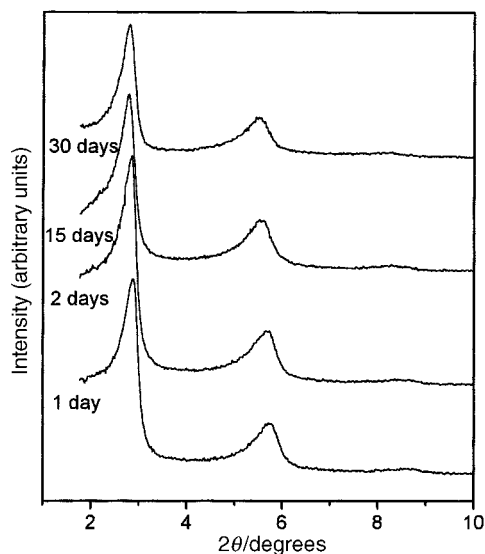
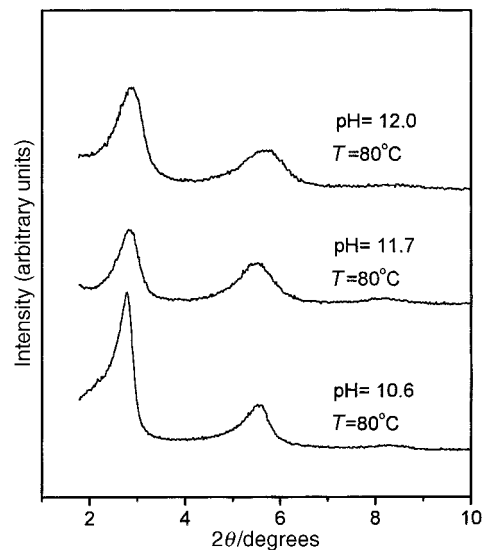


Fig. 7  $^{27}Al$  MAS NMR spectra of mesoporous materials (upon hydrochloric acid treatment) obtained from Al-kanemite at (a) pH 11.7 and (b) pH  $< 9.6$  at  $80^\circ C$ .



**Fig. 8** X-Ray diffraction patterns of lamellar phases formed from Al-kanemite with Si/Al=20 at pH 10.6 and 80 °C for various times.



**Fig. 9** XRD evidence that the lamellar phase L-32 is not transformed into other mesophases at 80 °C and pH 10.6 or 12.0.

condensation mechanisms should be possible for the  $Q_3$  silicon species in Al-kanemite during intercalation of the surfactant cations in the layered Al-kanemite structure: *i.e.*, within the same inorganic sheet (intralayer) or between different layers (interlayer).

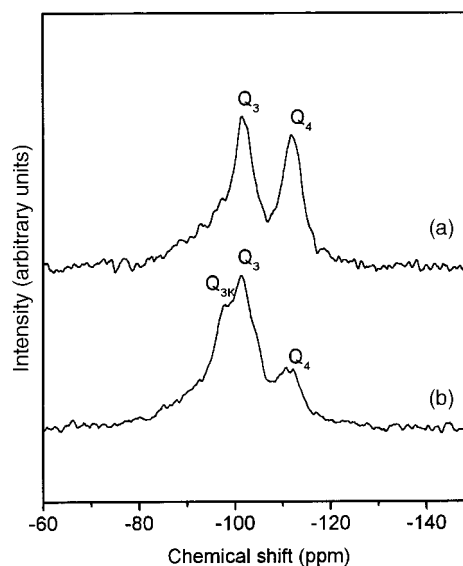
In the first case, the inorganic sheets of the layered derivatives must be deformed and increase in thickness owing to silanol condensation. Lower pH and higher reaction temperature favour the condensation and therefore the L-32 phase formed at pH 10.6 and 80 °C has a much higher  $Q_4/Q_3$  ratio than the L-3d phase obtained at pH 11.4 and 20 °C. A significant degree of silanol condensation in the L-32 phase may result in multilayer inorganic sheets which should be thicker than those in the L-3d phase. When the pH of the solution is adjusted from 10.6 to 11.7 or 12.0, the thicker sheets of the L-32 phase would be hard to fold and perhaps is the reason that intercalated surfactants are unable to transform the L-32 phase into mesoporous materials. However, at lower pH of the solution the L-32 phase can be partly transformed into mesoporous materials. On the other hand, the L-3d phase in which most of silicon species are of the  $Q_3$  type should be flexible and be able to transform under the influence of surfactant from a bilayered structure into mesoporous hexagonal phase at higher pH (Fig. 5). When the lamellar phases are folded to form mesophases, subsequent interlayer condensation probably takes place.

Fig. 11 shows the IR spectra in the framework vibration region of Al-kanemite, L-3d, L-32 and mesoporous phases. As mentioned previously, the Al-kanemite has a characteristic IR absorption band at *ca.* 1048  $\text{cm}^{-1}$ , which can be attributed to an  $\text{SiO}_4$  asymmetric stretching vibration in a  $Q_3$  environment. The L-3d phase and the lamellar L-32 show absorption bands of  $\text{SiO}_4$  asymmetric stretching vibrations at *ca.* 1048 and 1061  $\text{cm}^{-1}$ , respectively. The higher IR absorption value of the L-32 relative to the L-3d phase is a consequence of the development of more  $Q_4$  silicon species. For the mesoporous phase obtained from Al-kanemite at pH 11.7 and 80 °C the absorption band of the  $\text{SiO}_4$  asymmetric stretching vibration appears at *ca.* 1053  $\text{cm}^{-1}$ . After treatment in hydrochloric acid solution, the mesoporous phase becomes thermally stable and the IR absorption band shifts to 1061  $\text{cm}^{-1}$  owing to the further formation of  $Q_4$  silicon species by condensation between silanol groups. IR absorption assigned to C–H bonds of the organic surfactant is also observed at 1450–1500  $\text{cm}^{-1}$ .

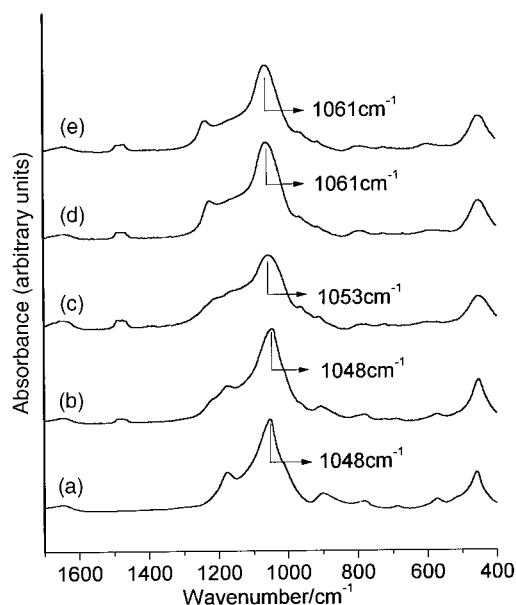
### Nitrogen and argon adsorption and acidic properties of mesoporous materials obtained from Al-kanemite

Physical adsorption of nitrogen and argon were used to determine the surface area ( $N_2$ ) and pore size ( $Ar$ ) of the samples calcined at 550 °C. The mesoporous materials formed from Al-kanemite have essentially similar pore size but smaller surface area than normal AIMCM-41.

IR spectroscopy using pyridine as a probe was carried out over the mesoporous materials derived from Al-kanemite after removal of the organic molecules. If the organic surfactant molecules in the mesoporous structures are removed by direct calcination at 550 °C in air for 6 h, no peaks attributed to Brønsted or Lewis acid sites can be detected for the two samples obtained at pH 11.7 or <9.6 (at 80 °C). An alternative route involves the extraction of the surfactants and sodium ions using an azeotropic mixture of heptane–ethanol with added hydrochloric acid.<sup>25,26</sup> This treatment was then followed by calcination at 550 °C in air for 6 h. From the chemical analysis of the resultant samples it is clear that the organic and sodium ions are removed. By contrast with the direct route, the IR spectra of pyridine adsorption in Fig. 12 show that both



**Fig. 10**  $^{29}\text{Si}$  MAS NMR spectra of the lamellar phases (a) L-32 and (b) L-3d.



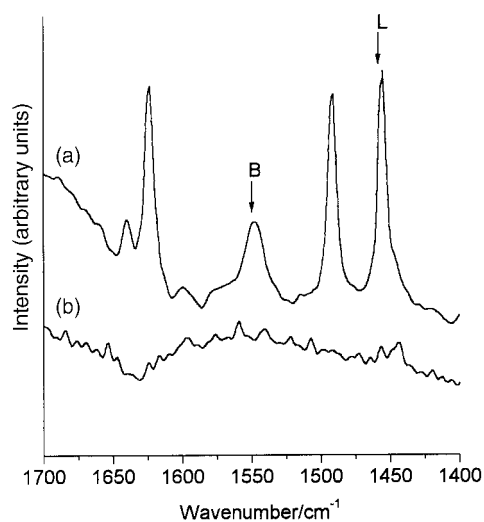
**Fig. 11** IR spectra of the Al-kanemite with Si/Al=20, the L-3d and L-32 phases, and mesoporous phases obtained from Al-kanemite at pH 11.7 and 80 °C: (a) the Al-kanemite, (b) the L-3d phase, (c) the mesoporous phase (without hydrochloric acid treatment) obtained from Al-kanemite at pH 11.7 and 80 °C, (d) sample (c) treated with hydrochloric acid solution and (e) the L-32 phase.

Brønsted and Lewis acidity have been developed for the mesoporous materials obtained from Al-kanemite at pH 11.7 and 80 °C. However, no significant acid sites were observed for the mesoporous samples formed from Al-kanemite at pH <9.6.

Temperature programmed desorption of NH<sub>3</sub> confirms the presence of acid sites over the mesoporous materials obtained at pH 11.7 after removal of surfactants and sodium ions. However, the mesoporous materials formed at pH <9.6 resemble the pure siliceous MCM-41 in their NH<sub>3</sub>-TPD profiles.

## Conclusions

Al- and Ga-containing kanemites with different Si/M (M=Al or Ga) ratios have been prepared which can be transformed into mesoporous materials in the presence of cetyltrimethylammonium chloride. Several physical techniques, such as XRD, MAS NMR, IR, TG-DTA, NH<sub>4</sub>-TPD, physical adsorption of N<sub>2</sub> and Ar, have been used to characterise Al-kanemite and Ga-kanemite and their mesoporous derivatives. The Na-form of the Al-kanemite shows a lower rate of hydrolysis than purely siliceous kanemite and the reduction of hydrolysis rate can be enhanced by increasing the aluminium content in the layered structure. <sup>27</sup>Al MAS NMR data show that aluminium in Al-kanemite and in the corresponding mesoporous derivatives is tetrahedral, which together with the above hydrolysis data for Al-kanemite implies that aluminium may be incorporated into the framework of Al-kanemite. Gallium is also found to be incorporated in tetrahedral positions in Ga-kanemite and its mesoporous derivatives according to <sup>71</sup>Ga MAS NMR, suggesting the incorporation of gallium in the framework. Mesoporous materials can be obtained by exchanging the Al-kanemite with C<sub>16</sub>TMA<sup>+</sup> under a variety of conditions. Effects of exchange conditions, such as pH, temperature and time on formation of mesoporous materials or lamellar phases have been investigated. Mesoporous materials are formed when the pH of the exchange solution is <9.6 (at 80 °C) or ca. 11.0–11.7 (at 20–80 °C). A lamellar phase, L-32, with a basal spacing of ca. 32 Å has been obtained at pH 10.6 and 80 °C. The L-32 phase can be partially transformed into mesoporous materials by adjusting the pH



**Fig. 12** IR spectra of pyridine adsorption over mesoporous materials (with hydrochloric acid treatment) obtained from Al-kanemite with Si/Al=20 after removal of surfactant and sodium ions; (a) sample obtained at pH 11.7 and 80 °C and (b) sample derived at pH <9.6 and 80 °C.

of the exchange solution from 10.6 to 8.0–8.5. The L-32 phase, however, is suggested to consist of multilayer sheets with a higher degree of silicate condensation resulting in more difficulty in folding to form the mesoporous structure at higher pH. After removing the surfactant and sodium ions by extraction with a heptane–ethanol–hydrochloric acid mixture, the mesoporous materials derived from the Al-kanemite at pH 11.7 and at 80 °C show Brønsted and Lewis acidity similar to conventional Al-MCM-41. On the other hand, the mesoporous materials obtained at pH <9.6 and at 80 °C do not show significant acidity.

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