JOURNAL OF Materials CHEMISTRY

Synthesis of $LiAl_2(OH)_6^+$ intercalated montmorillonite by a hydrothermal soft chemical reaction

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Received 21st June 1999, Accepted 9th December 1999

A $LiAl_2(OH)_6^+$ intercalated montmorillonite was prepared from a montmorillonite by using a hydrothermal soft chemical process. As a first step, lithium aluminium hydroxide complex ions ($Li_xAl_n(OH)_m^{z+}$) were inserted into the interlayer space of the montmorillonite by an ion-exchange reaction. In the second step, the ion-exchanged montmorillonite was hydrothermally treated to polymerize the complex ions in the interlayer space, forming a sandwich-like layered compound. The mechanism of formation of the sandwich layered structure was investigated by XRD, TG–DTA, chemical analyses and FTIR spectroscopy. Na^+ and Ca^{2+} ions in the interlayer space of the montmorillonite were first exchanged with $Li_xAl_n(OH)_m^{z+}$ complex ions, and during this process the basal spacing of the montmorillonite increased from 1.6 to 2.0 nm after the ion-exchange. Two types of reactions of the ion-exchanged montmorillonite were observed under the hydrothermal conditions. In the temperature range 100–150 °C, the basal spacing changed from 2.0 to 1.7 nm, corresponding to polymerization of $Li_xAl_n(OH)_m^{z+}$ complex ions to $LiAl_2(OH)_6^+$ layers between the silicate layers. At temperatures over 200 °C, Li^+ ions of $LiAl_2(OH)_6^+$ layers probably migrated into the octahedral sheets of silicate layers, accompanied by a decrease of the basal spacing from 1.7 to 1.4 nm. The $Li_xAl_n(OH)_m^{z+}$ complex ion was also used for pillaring montmorillonite, and a pillared montmorillonite with a basal spacing of 1.5 nm was obtained by heat treatment of this $Li_xAl_n(OH)_m^{z+}$ ion-exchanged montmorillonite in air at 500 °C.

Introduction

Montmorillonite is a crystalline hydrated aluminosilicate with a two-dimensional layered structure (phyllosilicate). Each layer is composed of one octahedral sheet sandwiched between two tetrahedral sheets with an interlayer space to make up the unit cell. In the structure, the higher valent metal cation, typically Al(III), is partially substituted by lower valent cations, such as Mg(II), in the octahedral sheet, or Si(IV) is partially substituted by Al(III) in the tetrahedral sheet, or both, thereby developing a net negative charge. Negative charge thus created is balanced by hydrated cations occupying the interlayer spaces. The charge balancing cations in the interlayer spaces are ion-exchangeable.

The ion-exchange properties of montmorillonite and layered silicate minerals can be used to modify their layered structures. A large number of studies have been carried out on the intercalations of insoluble metal hydroxides into the interlayer spaces of the layered silicate minerals for preparations of chlorite-like compounds.[1–10] Divalent metal hydroxides, such as Ni(II), Mg(II), Ca(II), Mn(II), Fe(II), Co(II), Zn(II) and Cd(II) hydroxides and trivalent metal hydroxides, such as Al(III) and Fe(III) hydroxides, can be intercalated into the interlayer spaces of the layered silicates. Three types of procedure have been used previously to prepare the chlorite-like compounds:[3,8] (1) solutions containing hydroxy-metal cations formed by addition of a base, usually NaOH, to a metal salt solution to give a desired OH/M ratio can be added to a dispersed layered silicate; (2) the base and the salt solution may be added simultaneously in a dropwise manner to a vigorously agitated, dispersed layered silicate; (3) the salt solution can be added first to the dispersed layered silicate, and the system subsequently titrated with base.

Most of these preparations were carried out at room temperature. Ohtsuka *et al.*[10] have proposed that the metal hydroxides with the structure of a layered double hydroxide, such as metal hydroxides with CdI_2 type of structure and aluminium hydroxide, could be intercalated into the layered silicate. It is well known that divalent and trivalent metal ions with small ionic radii, as well as Li(I) and Al(III), can form hydrotalcite-like compounds with the layered double hydroxide structure.[11,12] Mixed-metal hydroxides, such as $Mg^{II}Al^{III}$ or $Li^{I}Al^{III}$ hydroxide, intercalated layered silicates have been reported in natural specimens.[3,5] However, to the best of our knowledge, the preparation of a sandwich compound of $LiAl_2(OH)_6^+$ and layered silicate has not been reported.

Recently, we found that lithium aluminium hydroxide complex ions ($Li_xAl_n(OH)_m^{z+}$) can be formed by dropping a LiOH solution into an $Al(NO_3)_3$ solution with Li/Al mol ratio = 2, at 60 °C.[13] Lithiophorite with a sandwich layered structure, which is constituted by stacking of MnO_6 octahedral sheets and $LiAl_2(OH)_6^+$ octahedral sheets, can be prepared from a layered manganese oxide with $Li_xAl_n(OH)_m^{z+}$ as the intercalation ion by using a hydrothermal soft chemical process.[13,14] During the first step, $Li_xAl_n(OH)_m^{z+}$ ions are intercalated into the interlayer spaces of the layered manganese oxide by an ion-exchange reaction. In the second step, the ion-exchanged manganese oxide was hydrothermally treated to polymerize the complex ions in the interlayer spaces, forming the sandwich layered structure. We postulate that this is a generalizable method for the preparation of sandwich compounds.

In the present study, we describe the synthesis of $LiAl_2(OH)_6^+$–montmorillonite sandwich compound by using a hydrothermal soft chemical process and evaluate the properties of $Li_xAl_n(OH)_m^{z+}$ intercalated montmorillonite.

Experimental

Preparation of samples

An unpurified Wyoming montmorillonite SWy-1, obtained from Source Clay Minerals was used as starting material in the preparation of sandwich-type layers. The montmorillonite contained a small amount of quartz impurity. The cation-exchange capacity of the montmorillonite was determined to be 76.4 meq/100 g by using a method described in literature.[6] A solution of lithium aluminium hydroxide complex ion ($Li_xAl_n(OH)_m{}^{z+}$) was prepared by slowly dropping a solution of 0.5 M LiOH into a solution of 0.2 M $Al(NO_3)_3$ with a Li/Al mol ratio of 2.0 at 60 °C with stirring. The solution was aged at 60 °C for 2 h, and filtered to remove any precipitate formed. The solution had a pH value of 3.8.

The montmorillonite (5 g) was treated with the solution (1.8 L) of lithium aluminium hydroxide complex ions at room temperature for 1 day to exchange ion-exchangeable metal ions in the interlayer space with $Li_xAl_n(OH)_m{}^{z+}$ complex ions. The ion-exchange treatment was repeated twice to complete the ion-exchange reaction. The ion-exchanged sample was washed with distilled water and hydrothermally treated in distilled water at the desired temperature for 1 day under autogeneous pressure. The montmorillonite was also hydrothermally treated in distilled water in a similar manner for comparison with the ion-exchanged sample. All the samples were washed with distilled water, and dried at room temperature in air.

Chemical analysis

50 mg of sample was dissolved in HF solution (5 mL), followed by the addition of saturated H_3BO_3 solution (25 mL). The lithium, sodium, potassium and calcium contents in the solution were determined by atomic absorption spectrometry, and the aluminium and silicon contents by inductively coupled plasma (ICP) spectrometry.

Physical analysis

An X-ray diffraction (XRD) analysis was carried out using a Rigaku Rotaflex Type X-ray diffractometer (RAD-RC). IR spectra were obtained by the KBr method on a Perkin Elmer IR spectrometer (1600 Series FTIR). DTA–TG curves were obtained on a Seiko thermal analyzer (SSC5200) at a heating rate of 10 °C min^{-1}.

Results and discussion

Ion-exchange reaction of montmorillonite

The montmorillonite was treated with the $Li_xAl_n(OH)_m{}^{z+}$ solution to exchange initial cations in the interlayer spaces with $Li_xAl_n(OH)_m{}^{z+}$ complex ions. X-Ray diffraction patterns of the ion-exchanged sample revealed that the layered structure remained and the basal spacing increased from 1.61 to 1.97 nm after the ion-exchange treatments (Fig. 1). The basal spacing of the ion-exchanged montmorillonite was found to be larger than that of Keggin ion ($Al_{13}O_4(OH)_{24}{}^{7+}$) exchanged montmorillonite (1.9 nm).[15] The $Al_{13}O_4(OH)_{24}{}^{7+}$ ion can be prepared in a similar manner to $Li_xAl_n(OH)_m{}^{z+}$ ion by using NaOH instead of LiOH. The increase of the basal spacing by the ion-exchange treatment indicates that the $Li_xAl_n(OH)_m{}^{z+}$ complex ions can be intercalated into the interlayer spaces of the montmorillonite by the ion-exchange treatment.

Structure change under hydrothermal conditions

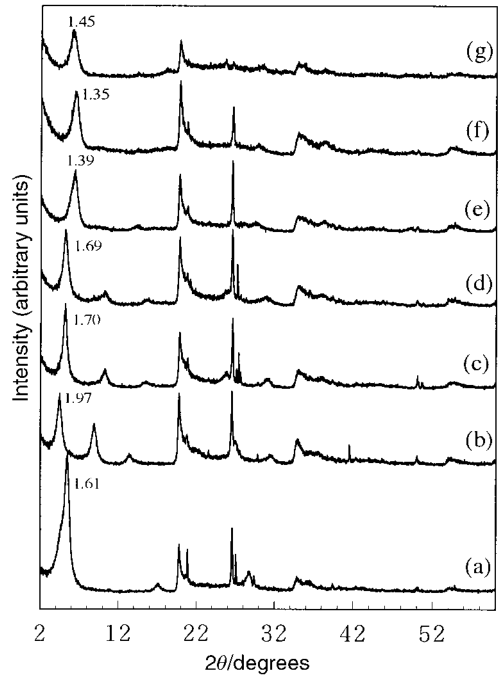

Fig. 1 X-Ray diffraction patterns of (a) montmorillonite used as starting material, (b) ion-exchanged sample with $Li_xAl_n(OH)_m{}^{z+}$ complex ions and hydrothermally treated samples at (c) 100, (d) 150, (e) 200, (f) 250 and (g) 300 °C for 1 day.

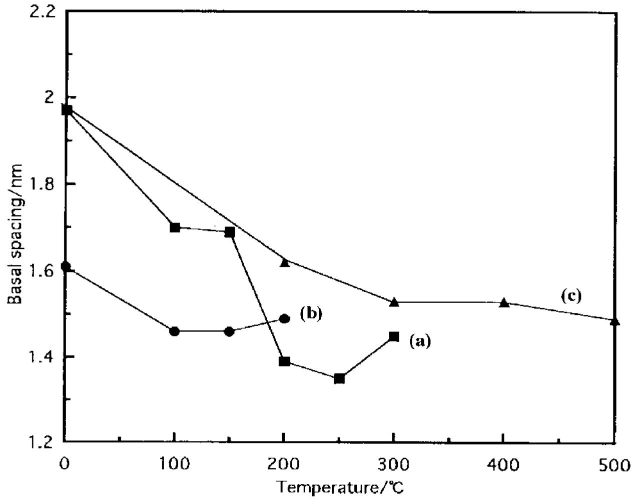

Fig. 2 Dependence of basal spacing of the montmorillonites on the reaction temperature: (a) hydrothermally treated $Li_xAl_n(OH)_m{}^{z+}$–montmorillonite; (b) hydrothermally treated montmorillonite without ion-exchange treatment; (c) heat-treated $Li_xAl_n(OH)_m{}^{z+}$ montmorillonite in air.

The ion-exchanged montmorillonite and the montmorillonite used as starting material were hydrothermally treated in distilled water. X-Ray diffraction studies indicated that the layered structure of the ion-exchanged montmorillonite did not change even after hydrothermal treatment at 300 °C (Fig. 1). However, the basal spacing of the ion-exchanged montmorillonite decreased after hydrothermal treatment. The dependence of the basal spacing on the hydrothermal treatment temperature is shown in Fig. 2. The basal spacing of the ion-exchanged montmorillonite decreased from 1.97 to 1.70 nm at 100 °C, stayed almost constant in the temperature range 100–150 °C, and decreased from 1.69 to 1.39 nm at 200 °C. These results suggest that there are two types of reaction under the hydrothermal conditions. One is below a temperature of 150 °C, and the other is above a temperature of 200 °C. In another study, we found that the polymerization reaction of $Li_xAl_n(OH)_m{}^{z+}$ ions to $LiAl_2(OH)_6{}^{+}$ octahedral layers in the interlayer space of layered manganese oxide was completed at 150 °C under hydrothermal conditions.[14] We postulate that the reaction occurring below 150 °C is the polymerization reaction of $Li_xAl_n(OH)_m{}^{z+}$ ions to $LiAl_2(OH)_6{}^+$ octahedral layers in the interlayer space of the montmorillonite. The reaction above 200 °C caused a change in the sandwich layered structure, which is discussed below. The basal spacing of 1.69 nm for the hydrothermally treated, ion-exchanged montmorillonite at 150 °C is larger than that of aluminium hydroxide–montmorillonite (1.47 nm),[9] nickel hydroxide–montmorillonite (1.46 nm)[6] and magnesium hydroxide–montmorillonite (1.48 nm).[8] However, the basal spacing of 1.39 nm for the hydrothermally treated ion-exchanged montmorillonite at 200 °C is slightly smaller than the metal hydroxide–montmorillonites. Water adsorption isotherms (not shown) after degassing at 200 °C showed <5% water adsorption at a P/P_0 of 0.60 for the hydrothermally treated samples at 150 and 300 °C. These two samples showed surface areas of 28 and 32 $m^2\ g^{-1}$, respectively. These results show that interlayer space is not accessible for water after hydrothermal treatment.

For comparison with the ion-exchanged montmorillonite, the untreated montmorillonite was also hydrothermally treated. The montmorillonite showed different behavior from the ion-exchanged montmorillonite under hydrothermal conditions. The basal spacing of the montmorillonite decreased from 1.61 to 1.46 nm after the hydrothermal treatment at 100 °C, and remained almost constant beyond 100 °C in the temperature range studied (Fig. 2).

Chemical composition

The composition analysis results for the precursor, ion-exchanged and hydrothermally treated samples are given in Table 1. Almost all Na^+ and Ca^{2+} were removed from the montmorillonite by the ion-exchange treatments with $Li_xAl_n(OH)_m{}^{z+}$ complex ion solution. The content of both Li and Al increased after the ion-exchange treatment. This suggests that Li and Al can be inserted into the interlayer space of montmorillonite structure as a complex ion form of lithium aluminium hydroxide by the ion-exchange reaction. The Li/Si and Al/Si mol ratios of the hydrothermally treated samples at 100 and 150 °C (Mont-LiAl-Hy-100 and -150) are almost the same as the ion-exchanged sample (Mont-LiAl), indicating that there is almost no dissolution of Li and Al under hydrothermal conditions up to 150 °C. The Li/Si and Al/Si mol ratios of the hydrothermally treated samples at ⩾200 °C (Mont-LiAl-Hy-200, -250 and -300), however, decreased after hydrothermal treatment. This may be due to partial dissolution of lithium and aluminium under the hydrothermal conditions.

DTA–TG analysis

The untreated montmorillonite, the ion-exchanged sample and the hydrothermally treated samples show different DTA–TG curves (Fig. 3). The untreated montmorillonite showed endothermic peaks around 92 and 705 °C (Fig. 3, top) with corresponding weight losses (Fig. 3, bottom). The endothermic peaks around 92 °C can be assigned to evaporation of absorbed water and dehydration of crystal water from the interlayer space. The peak around 705 °C corresponds to dehydration of OH groups in the silicate layer.[7] After the ion-exchange treatment with the $Li_xAl_n(OH)_m{}^{z+}$ solution, two new endothermic peaks around 289 and 400 °C with corresponding weight losses were observed, and the endothermic peak, which corresponds to the dehydration of OH groups in the silicate layer, shifted to 626 °C (Fig. 3(b)). The endothermic peaks around 103 °C can be assigned to dehydration of absorbed water and crystal water from the interlayer space. The peaks around 289 and 400 °C can be assigned to dehydration of water coordinated to the $Li_xAl_n(OH)_m{}^{z+}$ ions and of the OH group of the complex ions, respectively, by comparison with $Li_xAl_n(OH)_m{}^{z+}$ ion-exchanged layered manganese oxide.[14]

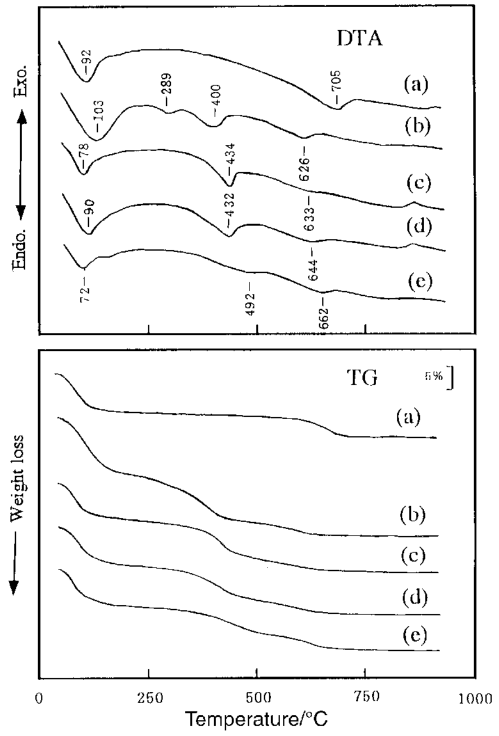

Fig. 3 DTA (top) and TG (bottom) curves for (a) montmorillonite used as starting material, (b) ion-exchanged sample with $Li_xAl_n(OH)_m{}^{z+}$ complex ions and hydrothermally treated samples at (c) 100, (d) 150 and (e) 200 °C for 1 day.

After the hydrothermal treatment at 100 and 150 °C, the peak around 289 °C disappeared and the peak which corresponds to the OH group of Li–Al–OH hydroxide shifted to higher temperature (*ca.* 432 °C, Fig. 3(c) and (d)). The content of crystal water in the interlayer space decreased significantly after the hydrothermal treatment. These facts suggest that the $Li_xAl_n(OH)_m{}^{z+}$ ions in the interlayer space

Table 1 Compositions of starting, ion-exchanged and hydrothermally treated samples

Sample	Al/Si	Li/Si	Na/Si	Ca/Si	K/Si
Precursor					
Montmorillonite	0.50	0.00	0.061	0.020	0.012
Ion-exchanged					
Mont-LiAl	0.90	0.081	0.003	0.001	0.011
Hydrothermally treated					
Mont-LiAl-Hy-100	0.89	0.080	0.00	0.001	0.009
Mont-LiAl-Hy-150	0.88	0.079	0.00	0.001	0.008
Mont-LiAl-Hy-200	0.84	0.062	0.00	0.001	0.007
Mont-LiAl-Hy-250	0.73	0.045	0.00	0.001	0.005
Mont-LiAl-Hy-300	0.78	0.047	0.00	0.001	0.004

polymerized to an $LiAl_2(OH)_6^+$ octahedral layer, and the polymerization reaction was accompanied by a dehydration of the crystal water from the interlayer space. These results are similar to the formation of lithiophorite under hydrothermal conditions.[14] After hydrothermal treatment at 200 °C, the endothermic peak which corresponds to the OH group of Li–Al–OH hydroxide became broad and shifted to higher temperature (492 °C) (Fig. 3(e)). This result is in accord with the XRD result, indicating that there is a structural change after hydrothermal treatment at $\geqslant$200 °C. DTA–TG analysis was also carried out for the hydrothermally treated montmorillonites without ion-exchange treatment up to 200 °C (not shown) with almost no change being observed after the hydrothermal treatment.

Heat treatment of $Li_xAl_n(OH)_m^{z+}$ ion-exchanged montmorillonite

Many studies[15–23] have been carried out on pillared montmorillonites and other clay compounds by heat treatment of metal hydroxy complex cations, such as $Al_{13}O_4(OH)_{24}^{7+}$ and $Zr_4(OH)_{14}^{2+}$, exchanged montmorillonite and clay compounds. The $Li_xAl_n(OH)_m^{z+}$ ion-exchanged montmorillonite was heat-treated in air to investigate the possibility of pillaring montmorillonite with $Li_xAl_n(OH)_m^{z+}$ ions. X-Ray diffraction patterns of heat-treated $Li_xAl_n(OH)_m^{z+}$–montmorillonite are shown in Fig. 4. The layered structure of the montmorillonite was retained, but the basal spacing decreased after the heat treatment up to 500 °C. The dependence of the basal spacing of the ion-exchanged montmorillonite on the heat treatment temperature is shown in Fig. 2. The dehydration of interlayer crystal water up to 200 °C was accompanied by a large decrease in the basal spacing. The dehydration of coordinated water and OH groups of $Li_xAl_n(OH)_m^{z+}$ ions in the temperature range 200–500 °C led to a small decrease in the basal spacing. The basal spacing is 1.49 nm after heat treatment at 500 °C, which is smaller than the basal spacing (1.7 nm) obtained using $Al_{13}O_4(OH)_{24}^{7+}$ ion as the intercalating ion.[15] The basal spacing of 1.49 nm after heat treatment at 500 °C is larger than that (1.36 nm) of the aluminium hydroxide–montmorillonite sandwich layered compound after heat-treatment at 500 °C.[8] This fact suggests that $Li_xAl_n(OH)_m^{z+}$ ion is different from the $Al_{13}O_4(OH)_{24}^{7+}$ ion and aluminium hydroxide, and $Li_xAl_n(OH)_m^{z+}$ ion can be used as an intercalation ion in the preparation of pillared clay compounds.

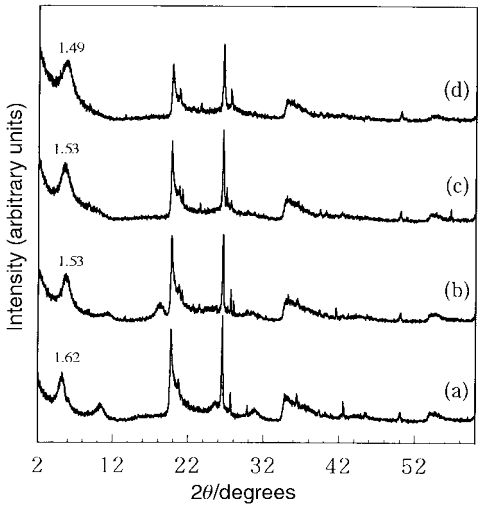

Fig. 4 X-Ray diffraction patterns of heat-treated $Li_xAl_n(OH)_m^{z+}$–montmorillonite at (a) 200, (b) 300, (c) 400 and (d) 500 °C for 2 h in air.

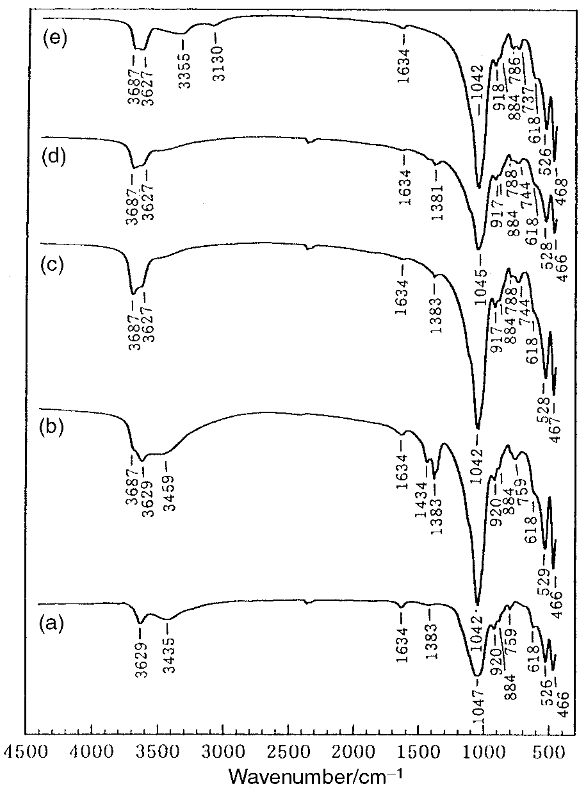

Fig. 5 IR spectra of (a) untreated montmorillonite, (b) ion-exchanged sample with $Li_xAl_n(OH)_m^{z+}$ complex ions and samples obtained by hydrothermal treatment of the ion-exchanged sample at (c) 100, (d) 150 and (e) 200 °C for 1 day.

IR spectra

The IR spectra of the untreated montmorillonite, $Li_xAl_n(OH)_m^{z+}$ ion-exchanged and hydrothermally treated montmorillonites are shown in Fig. 5. In the IR spectrum of the untreated montmorillonite (Fig. 5(a)), the bands at 3435 and 1634 cm^{-1} can be assigned to stretching and bending vibrations of OH groups of crystal and absorbed water molecules, respectively, and the band at 3629 cm^{-1} to the stretching vibration of the OH groups in the silicate layer.[7] The bands at 920 and 884 can be assigned to the OH bending modes of Al_2OH and $Fe^{III}AlOH$ groups, respectively.[7,24] The distinguishing feature in the ion-exchanged montmorillonite is the appearance of new bands at 3687 and 1434 cm^{-1}. The band at 3687 cm^{-1} can be assigned to the OH stretching vibration of the $Li_xAl_n(OH)_m^{z+}$ ion in the interlayer space. After hydrothermal treatment at 100 and 150 °C, a significant decrease in the intensity of the band at 3459 cm^{-1}, disappearance of the band at 1434 cm^{-1}, and splitting of the band at 759 cm^{-1} into bands at 788 and 744 cm^{-1} were observed. The decrease in the intensity of the band at 3459 cm^{-1} is due to dehydration of interlayer water by the polymerization of $Li_xAl_n(OH)_m^{z+}$ ions to $LiAl_2(OH)_6^+$ layers in the interlayer space. Since the disappearance of the band at 1434 cm^{-1} corresponds to the disappearance of the endothermic peak at 289 °C in the DTA curve of the ion-exchanged montmorillonite (Fig. 3), the band at 1434 cm^{-1} may be assigned to a vibration of $Li_xAl_n(OH)_m^{z+}$ ion in the interlayer space, probably an OH bending vibration of a water molecule coordinated to the $Li_xAl_n(OH)_m^{z+}$ ion. Two new bands were observed at 3355 and 3130 cm^{-1} in the hydrothermally treated sample at 200 °C (Fig. 5(e)). These bands can be assigned to stretching vibrations of OH groups. Since almost no change was observed in the spectra of hydrothermally treated montmorillonite without ion-exchange treatment (Fig. 6), the appearance of these new bands suggests that a structural change occurs under the hydrothermal

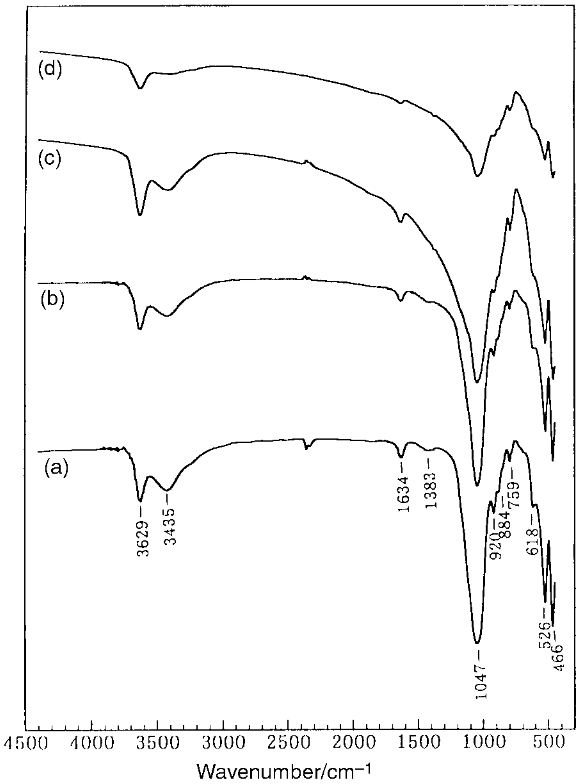

Fig. 6 IR spectra of (a) untreated montmorillonite and samples obtained by hydrothermal treatment of the montmorillonite at (b) 100, (c) 150 and (d) 200 °C for 1 day.

conditions. The results of the IR study are in agreement with the results of XRD and DTA–TG studies.

Formation reaction of the sandwich layered compound

The formation reaction of the sandwich layered structure of $LiAl_2(OH)_6^+$–montmorillonite can be described by a reaction model as shown in Fig. 7. In the first step, ion exchangeable metal ions in the interlayer space are exchanged with $Li_xAl_n(OH)_m^{z+}$ ions, and the basal spacing expands from 1.61 to 1.97 nm. In the second step, $Li_xAl_n(OH)_m^{z+}$ ions become unstable under the hydrothermal conditions in the temperature range 100–150 °C, and polymerize to form $LiAl_2(OH)_6^+$ octahedral sheets between the silicate layers by hydrolysis of $Li_xAl_n(OH)_m^{z+}$ and dehydration of crystal water from the interlayer space of the layered structure. The basal spacing collapses from 1.97 to 1.70 nm, accompanying the dehydration of the crystal water.

To make up a perfect double layered hydroxide structure in the interlayer space, a mol ratio of the aluminium content in the interlayer to the content of metal ions in the octahedral sites in the silicate layer will be about one. However, the mol ratio of the aluminium content in the sample hydrothermally treated at 150 °C is 0.76 (calculated from data in Table 1). The lower aluminium content in the interlayer suggests that the interlayer space is partially filled by $LiAl_2(OH)_6^+$. The crystal water can occupy vacant spaces in the $LiAl_2(OH)_6^+$ layer. The Li/Al mol ratio (0.21) of the lithium aluminium hydroxide in the interlayer space for the hydrothermally treated samples at 150 °C is smaller than the theoretical value (0.5) for the ideal $LiAl_2(OH)_6^+$ layer, indicating the presence of lithium vacancies in the $LiAl_2(OH)_6^+$ octahedral sheet. The basal spacing of 1.70 nm for the $LiAl_2(OH)_6^+$-montmorillonite obtained by hydrothermal treatment in the temperature range 100–150 °C corresponds to the basal spacing (1.46 nm) of 'normal' double layered hydroxide–montmorillonite sandwich compounds plus one sheet of crystal water molecules. This fact suggests that one sheet of crystal water molecules may exist in the interlayer space between the silicate layers.

After hydrothermal treatment at 200 °C, the basal spacing of 1.70 nm collapses to 1.39 nm. This fact could be interpreted by migration of Li^+ from the $LiAl_2(OH)_6^+$ layer to vacant octahedral sites in the clay silicate layer. It is well known that the clay silicate layer has one-third vacant octahedral cation sites, and small interlayer cations, such as Li^+, Mg^{2+} and Ni^{2+} can migrate into such sites through the 6-membered oxygen ion rings of the silicate layers.[7,24–26] The migration of Li^+ to the silicate layer will cause a decrease in the charge densities of silicate and $LiAl_2(OH)_6^+$ layers, and decrease in the hydration ability of the sandwich compound. Therefore, the basal spacing collapses to 1.39 nm, with the accompanying loss of one sheet of crystal water from the interlayer space. The presence of the OH stretching bands at 3355 and 3130 cm^{-1} in the hydrothermally treated sample at 200 °C (Fig. 5(e)) may be due to a strong interaction between the silicate layer and the $Al_2(OH)_6$ layer after the basal spacing collapsed to 1.39 nm to form a chlorite-like phase.

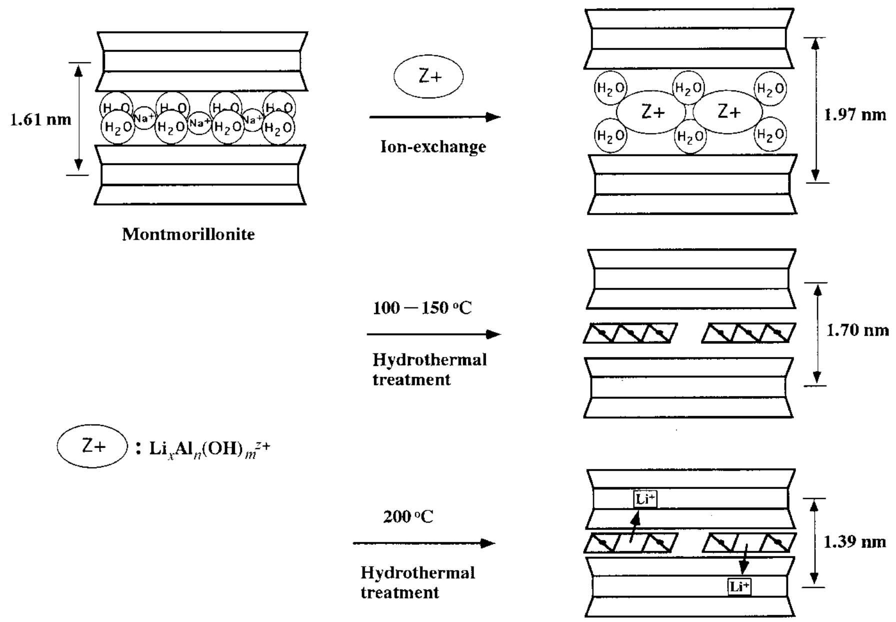

Fig. 7 A model of the formation reaction of the $LiAl_2(OH)_6^+$ intercalated montmorillonite.

Conclusion

Metal ions in the interlayer space of the montmorillonite can be exchanged with $Li_xAl_n(OH)_m^{z+}$ complex ions. $Li_xAl_n(OH)_m^{z+}$ complex ions can polymerize to form $LiAl_2(OH)_6^+$ layers between the interlayer spaces of the montmorillonite upon low temperature hydrothermal treatment. Li^+ ions in the $LiAl_2(OH)_6^+$ layer can migrate into vacant octahedral sites in the silicate layer under high temperature hydrothermal conditions, and form a 1.39 nm chlorite-like phase.

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Paper a904918e