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A thermogravimetric investigation of alkylammonium intercalation into rectorite

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ABSTRACT

This study focuses on elucidating the structural detail of intercalated hexadecyltrimethylammonium (HDTMA) and dodecyltrimethylammonium (DDTMA) in rectorite using thermogravimetric (TG), Fourier transform infrared (FTIR) spectroscopy, and powder X-ray diffraction (XRD) analyses. The results showed that the majority of the intercalated alkylammonium decomposed between 200 and 300 °C when the amount intercalated was much higher than the cation exchange capacity (CEC) of the mineral. However, about 0.5 CEC of the intercalated alkylammonium was thermally stable up to 400 °C. The presence of this amount of alkylammonium was verified by FTIR and XRD analyses after samples were heated to 300 °C. These results suggested that two types of interactions and/or two types of sorption sites were responsible for the two-step decomposition of intercalated alkylammonium. The alkylammonium held by hydrophobic interaction decomposed at the lower temperature, while that held by cation exchange decomposed at the higher temperature. The XRD and FTIR results revealed different interlayer configurations of the intercalated alkylammonium. At the intercalation maxima, HDTMA adopted a vertical arrangement with *all-trans* configuration as indicated by a *d*-spacing of 49.5 Å, while DDTMA took a horizontal pseudo-trilayer arrangement with extensive *gauche* configuration.

1. Introduction

Layered silicate clay minerals have large surface area and high cation exchange capacity and thus their modification by cationic surfactant for environmental application has been studied extensively [1–3]. Majority of these studies were focused on smectites due to their swelling properties in water and organic solvents, which enables these smectites to be intercalated with organic molecules of different sizes and shapes. Since the uptake of organic cations by clay minerals was attributed to a cation exchange process occurring in the clay interlayers, the levels of modifications by cationic surfactants were limited to the cation exchange capacity (CEC) of the clays. Although the amount of a cationic surfactant, such as hexadecyltrimethylammonium (HDTMA), used was more than the CEC of the clay minerals, the observed sorption plateau was reported only to the CEC or a little above it [2].

Detailed studies on alkylammonium adsorption beyond the CEC of swelling clays showed that both cation exchange and hydrophobic bonding were responsible for the uptake of alkylammonium [4,5]. Further studies were undertaken to investigate the surface and interlayer configurations of sorbed/intercalated alkylammonium on montmorillonite and kaolinite with an initial surfactant input much higher than the CEC of the minerals [6–10]. The configuration of intercalated alkylammonium was characterized by Fourier transform infrared (FTIR), X-ray diffraction (XRD), and transmission electron microscope (TEM) analyses [7–9,11,12].Thermogravimetric analyses (TG) to study the stability of organo-montmorillonite at an elevated temperature were also undertaken [6,8,13–17]. The onset decomposition temperature (T_{onset}) was considered an index for the thermal stability of the material concerned. In one study, it was found that the T_{onset} of organically modified layered silicates (OLS) was approximately 180 °C and the thermal decomposition of the organic substances between silicate layers was mainly in the range between 200 and 500 °C [13]. A two-step process was involved in the decomposition of OLS. The first process occurred at a maximum rate at about 200 °C and the second one between 300 and 400 °C [14]. Separately, several mass loss steps associated with pyrolysis of octadecyltrimethylammonium (ODTMA)-modified montmorillonite were also observed [9]. The first step was attributed to the exchange of organic cations with Na^+ ions and the electrostatic interaction between the surfactant and clay mineral surface. The second step was due to surfactant surface adsorption, while the third step to surfactant interactions with van der Waals forces [9].

Decomposition products analyzed by GC–MS coupled to TG instrumentation indicated that the gases evolved during OLS degradation at 200 and 220 °C were the same as that of pure stearyltrimethyl ammonium (same as ODTMA) chloride [14]. However, the products detected at 300 and 400 °C were different from that of the pure organic compound [14]. High resolution TG

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analyses of HDTMA-modified clinoptilolite showed a 100 °C increase in HDTMA pyrolysis temperatures at HDTMA loadings less than 50% of the external CEC of the mineral, which was attributed to an increased stabilization of the HDTMA under direct tail interactions with the clinoptilolite surface at lower surfactant coverage [18].

Although extensive studies were conducted on alkylammonium intercalation with smectites, investigations of alkylammonium intercalation in illilte/smectite mixed-layered clays were limited. A separation of 9 Å in the smectite layers of regularly and randomly interstratified illite/smectite (I/S) was observed after being intercalated with aluminum chlorohydrate [19]. A vertical arrangement of HDTMA was adopted in the interlayer of the smectite component when rectorite, a 1:1 regular interstratified mixed layered clay mineral made of an illite-like and a smectite-like components, was intercalated with HDTMA at a loading level greater than 2.00 CEC [20]. In this study, we determined the thermal behavior of rectorite intercalated with different amounts of HDTMA and dodecyltrimethylammonium (DDTMA) together with XRD and FTIR analyses, in order to further elucidate the interlayer configuration of intercalated alkylammonium in rectorite.

2. Experimental

2.1. Materials

The rectorite was obtained from Zhongxiang, Hubei, China, with its clay fraction separated by sedimentation followed by centrifugation. Scanning electron microscope (SEM) observation and XRD analyses showed a pure rectorite [21]. It has a CEC of 410 mmol$_c$ kg^{-1}, with Ca^{2+} contributes to 95% of the exchangeable cations, indicating that the smectite-like component is Ca-rich [21]. The alkylammonium was HDTMA and DDTMA bromides (from Aldrich, Milwaukee, WI).

2.2. Alkylammonium intercalation

To each 50 mL centrifuge tube, 0.5 or 1.00 g of rectorite and 20 mL of alkylammonium solution at initial concentrations of 5, 15, 25, 30, 35, and 50 mmol L^{-1} were combined in 50 mL centrifuge tubes. The mixtures were shaken at 150 rpm for 24 h, centrifuged and the supernatant analyzed for equilibrium surfactant and counter-ion bromide solution concentrations, as counter-ions might accompany surfactant sorption at higher surfactant inputs [22]. The initial inputs correspond to 25, 75, 125, 175, 300, and 500% CEC of the mineral. The experiment was performed in duplicate.

2.3. Chemical analyses

Alkylammonium solution concentrations were analyzed by an HPLC method using a Shimadzu 9-A autoinjector, a Supelco C-18 column, and a Linear 100 UV–vis detector at a wavelength of 254 nm. The mobile phase was 5 mM *p*-toluenesulfonate in 45% water and 55% methanol. At a flow rate of 1 mL min^{-1} the retention time was 2.2 and 3.2 min for DDTMA and HDTMA, respectively. A dilution at 1/10 ratio was made for concentrations greater than 2 mmol L^{-1}.

Bromide analysis was performed by another HPLC system using a Shimadzu 9-A autoinjector, a Hamilton PRP-X100 anion chromatographic column, and an Alltech electric conductivity detector. The mobile phase was 2 mM potassium phthalate with pH 6 adjusted by NaOH. At a flow rate of 2 mL min^{-1} the retention time was 3.1 min. A 1/10 dilution was made for concentrations greater than 10 mmol L^{-1}. The amount of surfactant and bromide adsorbed was determined by the difference between the initial and equilibrium concentrations.

2.4. Instrumental analyses

The TG analysis was performed on a Thermal Analysis model TGA 2950. The heating rate was 20 °C min^{-1} under an ambient air condition. An open platinum pan was used for holding the sample with the initial mass between 7 and 15 mg.

FTIR spectra were acquired on a Perkin Elmer Spectra One Spectrometer equipped with a diamond Attenuated total reflection (ATR) accessory. The spectra were obtained by accumulating 256 scans at a resolution 4 cm^{-1}.

Powder XRD analysis was performed on a Rigaku D/Max-IIIa diffractometer with Ni-filtered Cu Kα radiation at 35 kV and 20 mA. Oriented samples were collected from 2° to 15° 2θ at a scanning rate of 2° min^{-1} and scanning step of 0.01°.

3. Results and discussion

3.1. Alkylammonium sorption

Sorption of alkylammonium and counter-ion bromide on rectorite is plotted in Fig. 1. At an initial input of 0.25 CEC, the input HDTMA and DDTMA were completely sorbed onto rectorite while no counter-ion bromide sorption occurred. As the initial surfactant input increased, the sorption of bromide started to show up. An HDTMA sorption plateau of 1200 mmol kg^{-1}, corresponding to 3.20 CEC, was determined by the Langmuir sorption isotherm. At the HDTMA sorption plateau, the counter-ion bromide sorption reached to 700 mmol kg^{-1}, slightly larger than 50% of HDTMA sorbed (Fig. 1(a)). On the contrary, the DDTMA sorption plateau

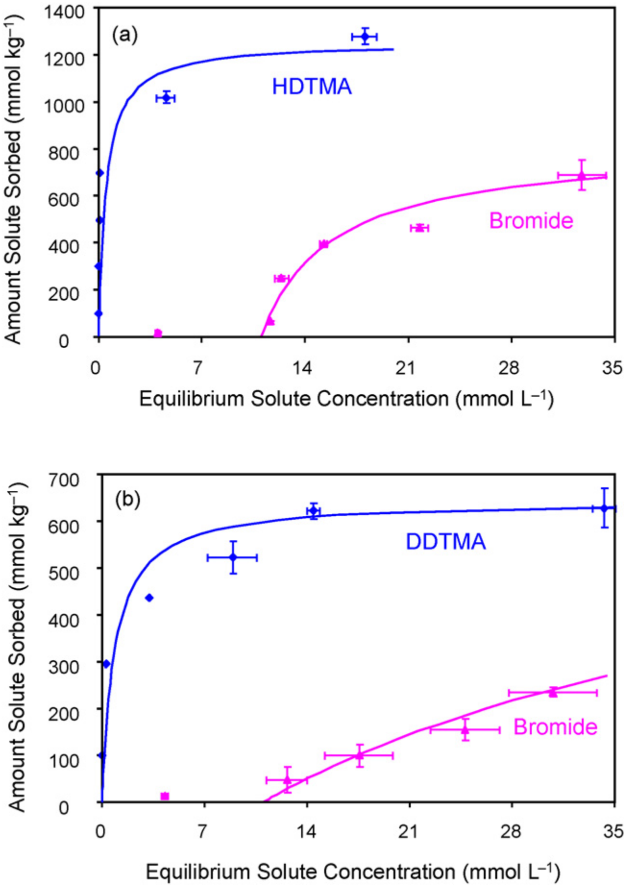

Fig. 1. Sorption of HDTMA (a) and DDTMA (b) (◆) and counterion bromide (▲) on rectorite. Horizontal and vertical error bars are shown only when they are larger than the symbols. Lines are Langmuir fits to the observed data.

Table 1
Percentage of mass loss at several characteristic temperatures for HDTMA intercalated rectorite.

HDTMA intercalated	Step 1 mass loss		Step 2 mass loss		Step 3 mass loss		Total mass loss (%)	HDTMA mass loss (%)
	°C	%	°C	%	°C	%		
Raw rectorite	150	8.4	–	–	–	–	12.4	
0.25 CEC	–	4.5	–	0	433	7.2	11.7	7.2
0.75 CEC	–	2.8	272	4.0	433	5.9	12.7	9.9
1.25 CEC	–	3.0	243	11.1	422	5.4	19.5	16.5
1.75 CEC	–	1.8	236	18.1	422	4.5	24.4	22.6
2.54 CEC	–	2.1	236	20.2	422	4.6	26.9	24.8
3.20 CEC	–	2.1	230	24.4	422	4.5	31.0	28.9
HDTMA solid	–	0	233, 251	95	–		100	100

Table 2
Percentage of mass loss at several characteristic temperatures for DDTMA intercalated rectorite.

DDTMA intercalated	Step 1 mass loss		Step 2 mass loss		Step 3 mass loss		Total mass loss (%)	DDTMA mass loss (%)
	°C	%	°C	%	°C	%		
Raw rectorite	150	8.4	–	–	–	–	12.4	
0.25 CEC	–	5.4	–	0	445	6.1	11.5	6.1
0.74 CEC	–	2.1	285	4.2	445	4.5	10.8	8.7
1.09 CEC	–	2.1	256	6.3	424	5.6	14.0	11.9
1.31 CEC	–	2.1	256	7.9	424	5.5	15.5	13.4
1.56 CEC	–	2.1	256	8.9	424	5.3	16.3	14.2
1.67 CEC	–	2.1	256	11.1	424	4.9	18.1	16.0
DDTMA solid	–	0	239, 256	95	–		100	100

was 600 mmol kg^{-1} while that of counter-ion bromide was only 300 mmol kg^{-1}, much less than that of HDTMA (Fig. 1(b)). The exact amount of HDTMA and DDTMA adsorbed/intercalated is given in Tables 1 and 2. The different trend in surfactant and counter-ion bromide sorption suggests that surfactant chain length played an important role for their sorption and intercalation [23].

3.2. TG analyses of pure HDTMA and DDTMA

The TG and derivative of thermogravimetric (DTG) curves of HDTMA and DDTMA were plotted in Fig. 2. The procedural initial decomposition temperature, also called onset temperature (T_{onset}), is defined as the intercept of the tangents of the plateau and the main slope of the TG curves (Fig. 2). For HDTMA and DDTMA the T_{onset} is 215 °C. The temperatures corresponding to a maximum decomposition rate (T_{peak}) are 251 and 256 °C for HDTMA, and DDTMA, respectively (Fig. 2, Tables 1 and 2). In addition, there is a small peak before the main peak on each of the DTG curves, and the T_{peak} values for those small peaks are 233 and 239 °C for HDTMA and DDTMA, respectively.

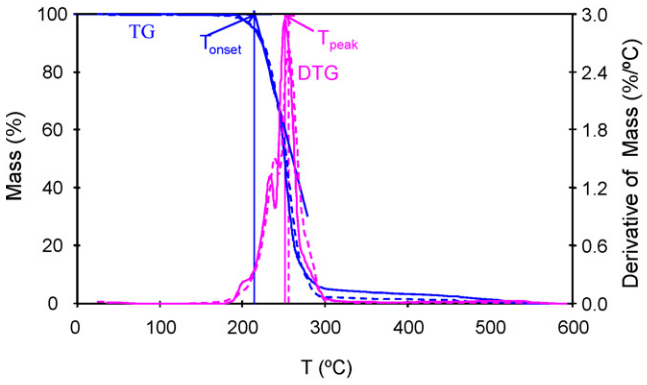

Fig. 2. TG and DTG curves for HDTMA (solid) and DDTMA (dashed). The vertical lines are temperature corresponding to initial mass change (T_{onset}) and to maximum mass change (T_{peak}).

3.3. TG analyses of intercalated alkylammonium

To compare the oxidative decomposition to pyrolysis (in the absence of oxygen under nitrogen environment) of intercalated alkylammonium, samples were heated under air and ultra pure nitrogen conditions for rectorite intercalated with 0.25 and 3.20 CEC of HDTMA (Fig. 3). Both the T_{onset} and T_{peak} for rectorite modified with 3.20 CEC of HDTMA were the same (at 199 and 232 °C, respectively). Similar results were found for samples intercalated with 0.25 CEC of HDTMA. The intermediate and pathway could be different for oxidative decomposition vs. pyrolysis, but the amount of mass loss remained the same (less than 0.3% difference). Thus, in the subsequent TG and DTG analyses, air was used for oxidative decomposition.

The TG and DTG curves of rectorite intercalated with different amounts of alkylammonium are presented in Figs. 4 and 5. The change in mass involved in three steps: less than 150 °C, 170–320 °C, and 370–500 °C. For rectorite, a T_{peak} is found at 150 °C (Fig. 5) and a mass loss of 8% occurred at 170 °C (Fig. 4). This amount of mass loss was attributed to the removal of adsorbed water as determined

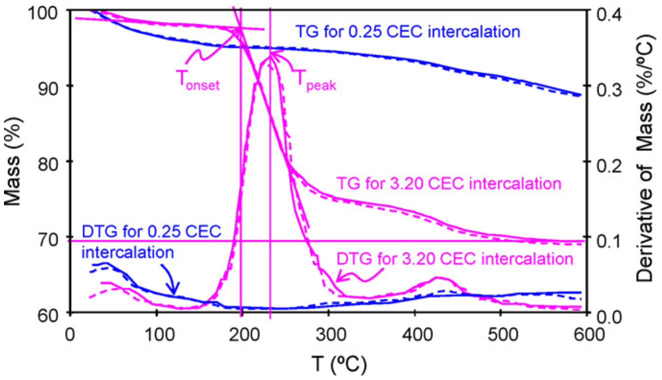

Fig. 3. TG and DTG curves for HDTMA-intercalated rectorite at amounts of 0.25 and 3.20 CEC combusted in air (solid lines) and pyrolyzed under nitrogen condition (dashed lines).

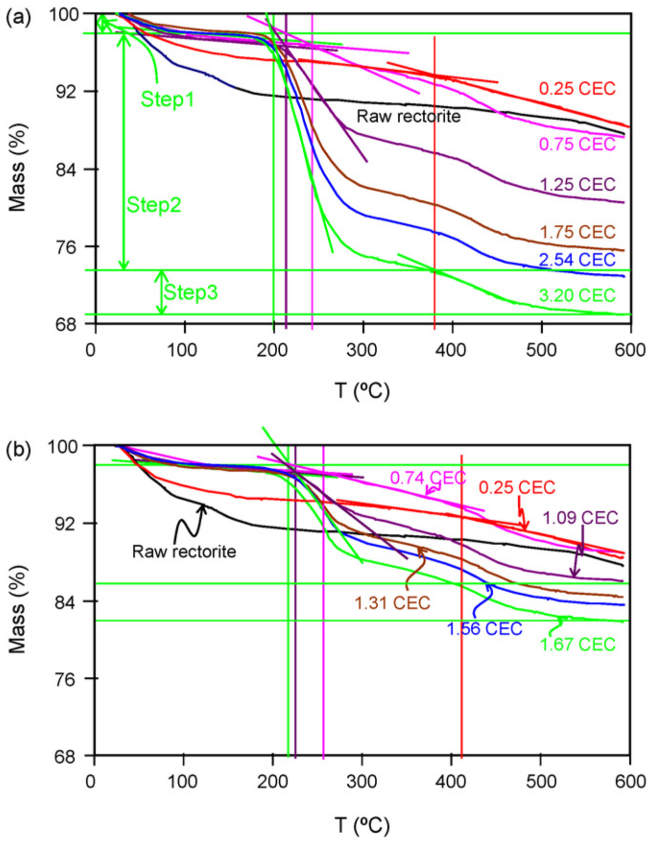

Fig. 4. TG analyses of rectorite intercalated with different amounts of HDTMA (a) and DDTMA (b).

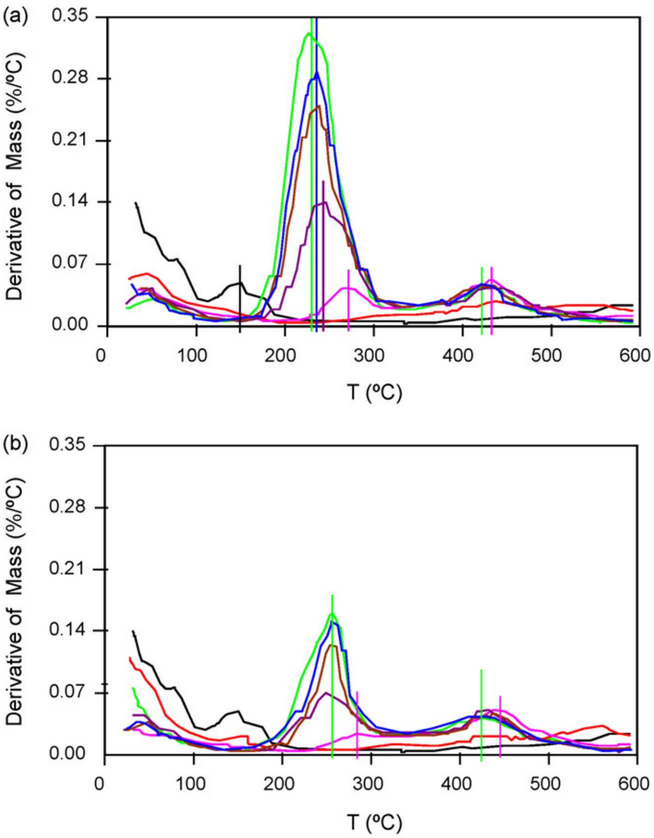

Fig. 5. DTG analyses of rectorite intercalated with different amounts of HDTMA (a) and DDTMA (b).

by GC/TOFMS analysis attached to the TG instrumentation [14]. At an alkylammonium intercalation of 0.25 CEC, the mass loss due to removal of adsorbed water accounted only for 4.5–5.5%. When the amount of intercalated alkylammonium reached to 0.75 CEC, the amount of mass loss due to the removal of adsorbed water was further reduced to 2.1–2.8% and remained at 2% at the alkylammonium intercalation level greater than the CEC of the mineral (Tables 1 and 2). In contrast, the mass losses of HDTMA and DDTMA at 150 °C were negligible (Fig. 2).

For rectorite intercalated with 0.25 CEC of HDTMA or DDTMA, the second step of mass loss was missing and while the third step mass loss occurred after 400 °C (Fig. 4), with the percentage of mass losses corresponding to 7.2 and 6.1% (Tables 1 and 2). The T_{peak} values of the third step mass loss were at 433 and 445 °C for HDTMA and DDTMA, respectively (Fig. 5). Meanwhile, the percentage of mass loss at this temperature range remained more or less constant regardless of the amount of HDTMA or DDTMA intercalated (Tables 1 and 2).

When the amount of intercalated alkylammonium was above 0.75 CEC, the second step of mass loss appeared at the temperature between 200 and 300 °C. It is interesting to note that the percentage of mass loss in this temperature range was proportional to the amount of alkylammonium intercalated with a threshold corresponding to 0.75 CEC, similar to the observation of alkylammonium intercalation into montmorillonite [13]. In addition, the rate of mass loss at the T_{peak} showed a monotonic increase as the amount of intercalated HDTMA and DDTMA increased (Fig. 5). The T_{peak} decreased from 272 to 233 °C as HDTMA intercalation increased from 0.75 CEC to 3.20 CEC and from 285 to 256 °C as DDTMA intercalation increased from 0.74 CEC to 1.67 CEC (Tables 1 and 2). When the amount of intercalated alkylammonium was greater than the CEC of rectorite the T_{peak} in this temperature range was comparable to that of the oxidative decomposition of HDTMA and DDTMA solid (Tables 1 and 2).

The third step of mass loss occurred between 400 and 470 °C, but the rate of mass loss was invariable with respect to the amount of alkylammonium intercalated except at the very lowest amount of 0.25 CEC (Fig. 5). The mass loss in this temperature range was found for samples with alkylammonium intercalation and was absent for HDTMA, DDTMA, and raw rectorite. Thus, the mass loss in the third step is different from that of the second step. It was associated with alkylammonium intercalation into rectorite, but irrelevant to the amount intercalated. In contrast, the second step of mass loss occurred only when the intercalated alkylammonium was above 0.75 CEC and was proportional to the amount of alkylammonium intercalated. The TG and DTG analyses showed that the intercalated surfactant molecules could be present in two distinct states: the one associated with stronger interaction and thus required a higher temperature to decompose and the one with weaker interaction whose decomposition temperature was about the same as that of pure alkylammonium.

Results similar to the aforementioned observations were previously found for alkylammonium intercalated montmorillonite [13–15,24]. For example, a T_{onset} at 151 and 143 °C and T_{peak} at 223–224 °C for the first decomposition temperature, and a T_{onset} at 258 and 259 °C and T_{peak} at 384 and 368 °C for the second decomposition temperature were determined for a montmorillonite intercalated with DDTMA and ODTMA, respectively [13]. Separately a T_{onset} of 200 °C and T_{peak} of 250 °C for the second step of mass loss and a T_{peak} of 440 °C for the third step of mass loss were found for montmorillonite intercalated with stearyltrimethyl ammonium chloride (same as ODTMA) [14]. A Brazilian bentonite intercalated with 1.2 CEC of HDTMA also showed two T_{peak} values at 230 and 420 °C [15]. Also, a T_{onset} temperature at 230 °C, corresponding to the second mass loss step in this study, was seen for a smectite treated with HDTMA to 2.5 CEC, but was absent for

HDTMA modification to 1.2 CEC [6]. In a different study, the HDTMA combustion peak occurred at 202 °C for HDTMA-modified montmorillonite [24], compared to 250 °C in this study. In addition, at 0.5 CEC treatment, there was just one T_{peak} at 365 °C, while three peaks at 254, 317, and 368 °C appeared for 0.7 CEC treatments [24]. Furthermore, these peaks changed to 218, 281, and 380 °C at 1.5 CEC treatment and to 205, 278, and 380 °C at 2.5 CEC treatment [24]. In contrast, the study conducted by Zhu et al. [25] had the decomposition temperature of 254 °C for HDTMA, in agreement with our study.

In addition to the variation of T_{onset} and T_{peak} as affected by the surfactant loading and surfactant chain length, the peak height of the third step mass loss in DTG curves was more or less constant regardless of the amount of alkylammonium intercalated (Fig. 5). This reflects that the rate of decomposition at T_{peak} is the same for the third step mass loss and is not affected by the amount of alkylammonium intercalated. Similar results were found for montmorillonite modified with four types of alkyl trimethylammonium of different chain lengths [13]. Their results also showed that the rate of decomposition of surfactant molecules held by hydrophobic bonding varied with surfactant chain length. In contrast, the rate of decomposition of surfactant molecules held by cation exchange remained the same regardless of the surfactant chain length.

A detailed analysis of the structure of ODTMA exchanged clays using XRD and TG methods suggested that a surfactant monolayer is formed in the montmorillonite interlayers at the surfactant loading up to 0.4 CEC, a lateral-bilayer arrangement is formed to surfactant loading up to 0.8 CEC, while a pseudo-trimolecular layer is formed with excess surfactant adsorbed on the clay surface when the surfactant loading was above 1.5 CEC [9]. In fact, the T_{peak} at 230 °C was absent at 0.4 CEC but showed up at 0.6 CEC treatment with ODTMA in their study, similar to the observation of this study. However, since the surfactant Xi et al. [9] used contains 18C in the tail group compared to 16C for HDTMA, the thermal behavior of the surfactant may be slightly different. Their DTG curves revealed three peaks at $T < 425$ °C, corresponding to 179, 284, and 382 °C at the initial surfactant loading level of 4.00 CEC compared to two for HDTMA and DDTMA intercalated rectorite at an initial loading of 5.00 CEC. Furthermore, their ODTMA pyrolysis temperature was 200 °C compared to 250 °C for HDTMA in our study.

Based on the above discussion, it is speculated that the first state of presence of alkylammonium in rectorite is in the form of monomer intercalation involving in a *gauche* arrangement of intercalated surfactant molecules due to cation exchange of alkylammonium for Ca^{2+} in the interlayer of the smectite-like component. In contrast, the second state of presence of alkylammonium in rectorite is in the form of admicellar intercalation due to hydrophobic interaction of the surfactant tail group. The decrease in T_{peak} with an increase in surfactant intercalation may reflect a continuous increase in *trans* conformation. These results are in agreement with the FTIR study of intercalated HDTMA in rectorite [20] and with the trend in HDTMA intercalation in montmorillonite [7,8,12]. The gases evolved from ODTMA and ODTMA-modified montmorillonite showed same composition at 200 to 220 °C and different compositions at 300–400 °C [14]. This result further supported the conclusion derived from the TGA analyses for a two-stage decomposition of the alkylammonium intercalated clays.

3.4. FTIR studies

The vibration bands of the surfactant can be groups into two categories: those associated with methylene tails and those with alkylammonium head groups. The peak around 3018 cm^{-1} was assigned to the anti-symmetric stretching modes of the trimethylammonium head group of HDTMA [26,27]. For HDTMA and DDTMA two peaks were well resolved at 3032 and 3018 cm^{-1} and were assigned to anti-symmetric ν_{as} CH_3–N and symmetric ν_s CH_3–N stretching modes of the alkylammonium head group (Fig. 6). These two peaks were resolved only in the sample intercalated with 3.20 CEC of HDTMA. In addition, the ν_{as} CH_3–R and ν_s CH_3–R were located at 2944 and 2872 cm^{-1} and they were visible only for HDTMA intercalation at 3.20 CEC (Fig. 6). The appearance of these vibration bands confirms the conformational difference between the HDTMA intercalated at higher loading and the rest of the treatment.

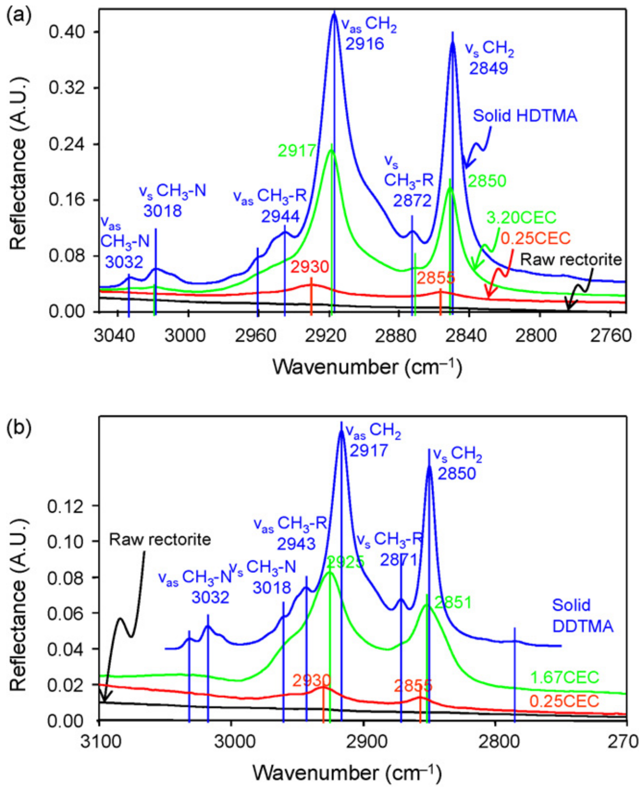

Fig. 6. FTIR spectra of the CH_2 stretching vibrations showing the peak shift after intercalated with 0.25 and 3.20 CEC of HDTMA (a) and 0.25 and 1.67 CEC of DDTMA (b).

The CH_2 stretching bands of the tail groups near 2917 and 2850 cm^{-1}, are sensitive to the *gauche*/*trans* conformer ratio of the hydrocarbon chains. At 0.25 CEC intercalation, the bands were located at 2930 and 2855 cm^{-1} for both HTDMA and DDTMA treatment, indicating that at this low surfactant intercalation the alkylammonium adopted a more *gauche*-like monolayer configuration regardless of the surfactant chain length (Fig. 6). At the maximum DDTMA loading of 1.67 CEC, the anti-symmetric vibration band was located at 2925 cm^{-1}, still much larger than that of 2917 cm^{-1} for solid DDTMA, revealing that the intercalated DDTMA had some degree of ordering of the tail group, but mainly taking *gauche*-like conformation. In contrast to the DDTMA intercalation, at the maximum HDTMA loading of 3.20 CEC, the band was at 2917 cm^{-1}, much closer to that of solid HDTMA, confirming an *all-trans* arrangement of the intercalated HDTMA in the interlayer of rectorite.

To verify that different sorption sites or different sorption mechanisms were responsible for the second and third step mass loss, the rectorite intercalated with 3.20 CEC HDTMA was heated to 300 and 550 °C and then analyzed by FTIR. The absorbance at 2917 and 2850 cm^{-1} was much reduced compared to that of the unheated counterpart (Fig. 7). Furthermore, the locations of these bands shifted from 2917 and 2850 cm^{-1} to 2930 and 2856 cm^{-1}, corresponding to the locations of intercalated HDTMA monomers with

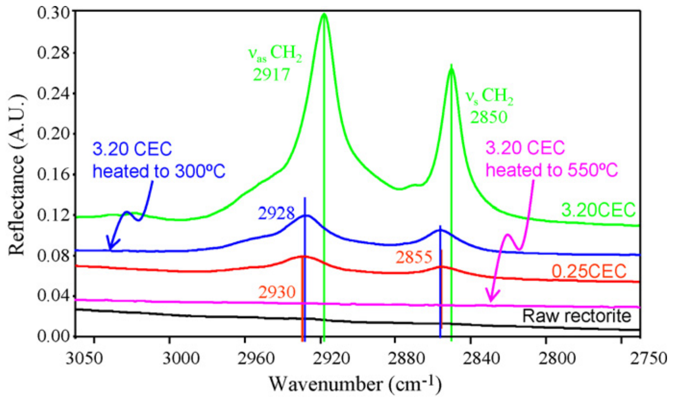

Fig. 7. FTIR spectra of rectorite heated to 300 and 550 °C after intercalated with 3.20 CEC of HDTMA. At 300 °C the HDTMA intercalated with *all-trans* configuration was decomposed while that with *gauche* configuration remained until heated to 550 °C.

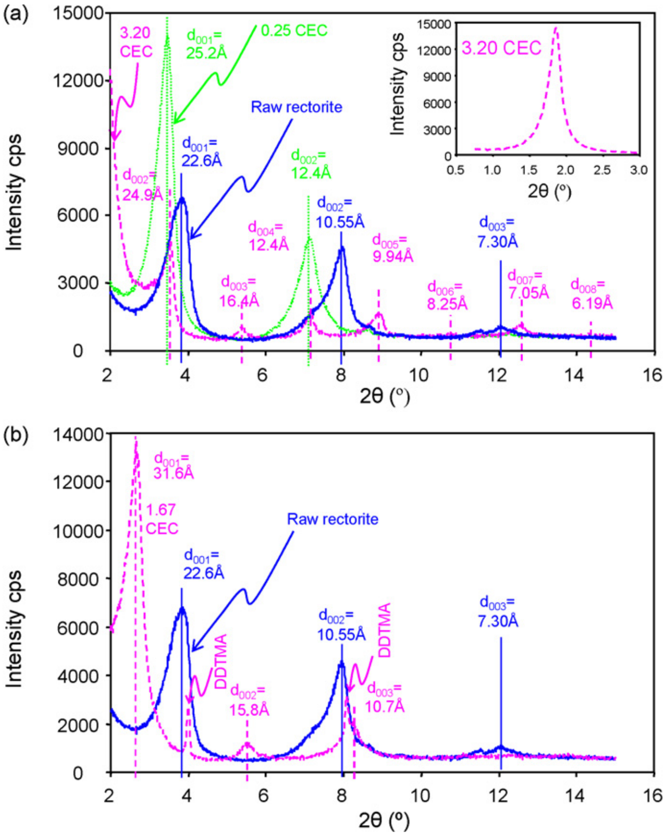

Fig. 8. XRD patterns of oriented and HDTMA intercalated at 3.20 and 0.25 CEC (a) and DDTMA intercalated at 1.67 CEC (b). The d_{001} peak of the HDTMA intercalated sample is missing due to a larger *d*-spacing, but can be seen with a wide angle XRD (insert). Separate DDTMA peaks showed up due to the presence of crystalline DDTMA after suspension was dried up.

a more *gauche* arrangement. The height of these two peaks was linearly proportional to the amount of HDTMA intercalated in rectorite [20]. The amount of residual HDTMA after heated to 300 °C determined from the peak height of 2930 and 2856 cm^{-1} vibration was about 0.5 CEC of the mineral, similar to that reported by Xi et al. [9]. The variations in peak location and peak height from the FTIR observation further confirmed the two sites for HDTMA and DDTMA intercalation in rectorite as revealed by the TG and DGT data. The FTIR absorption at 2930 and 2856 cm^{-1} disappeared after the samples were heated to 550 °C, similar to an observation after ODTMA-intercalated montmorillonite was heated to 500 °C [14]. Again, the FTIR results confirmed that the third step mass loss in TG and DTG analyses was due to decomposition of the strongly held HDTMA molecules via cation exchange process.

3.5. XRD analyses

The XRD patterns of the raw and alkylammonium intercalated rectorite to their maximum loading are given in Fig. 8. The d_{001} value of the raw rectorite was 22.7 Å, and it expanded to 25.2 Å at HDTMA intercalation of 0.25 CEC. At the maximum HDTMA intercalation of 3.20 CEC, the (0 0 1) peak was missing due to the limited 2θ scanning range of the employed Rikagu instrument. However, the XRD pattern clearly showed well-defined (0 0 2), (0 0 3), (0 0 4), (0 0 5), and (0 0 7) reflections (Fig. 8(a)) and minor (0 0 6) and (0 0 8) reflections. The calculated d_{001} value based on these seven peaks is 49.5 ± 0.2 Å. The coefficient of variance is 0.36%, lower than 0.75%, satisfying the definition of a regularly interstratified clay [28]. At this basal spacing, the 2θ for the (0 0 1) reflection would be 1.87°, which explains why the (0 0 1) reflection was missing. However, when the sample was scanned from 2θ 0.5° using a wide angle XRD (Brukers), a strong and symmetric peak was indeed observed at 1.87° (Fig. 8(a) insert). Contrast to HDTMA intercalation, when rectorite was intercalated with maximum DDTMA loading of 1.67 CEC, the d_{001} was 31.6 Å. while the d_{002} and d_{003} were 15.8 and 10.7 Å, respectively (Fig. 8(b)), showing significant difference between HDTMA and DDTMA intercalation.

To confirm the two step decomposition observed by TG, DTG, and FTIR, rectorite intercalated with 0.25 and 3.20 CEC was analyzed by XRD after they were heated to 300 °C for half an hour (Fig. 9). The d_{001} of rectorite intercalated with 0.25 CEC HDTMA was slightly reduced from 25.2 Å to 23.9 Å. On the contrary, a significant reduction of d_{001} was found for rectorite intercalated with 3.20 CEC HDTMA, changing from 49.5 Å to 23.9 Å. The fact that the same d_{001} spacing was reached after samples were heated to 300 °C with completely different HDTMA loading may indicate that an approximate same amount of intercalated HDTMA was still present after the samples were heated to 300 °C (Fig. 9), similar to the observation obtained by FTIR (Fig. 7). In addition, the d_{001} of 23.9 Å could be considered as a flat monolayer of HDTMA (3.5 Å) plus an illite layer (10 Å) and a dehydrated smectite-like layer (10 Å). The XRD results further confirmed the observation from TG, DTG, and FTIR that most of the intercalated HDTMA decomposed at temperature between 200 and 300 °C, but certain amount of intercalated HDTMA was still stable at temperature greater than 300 °C.

Studies of intercalation of alkylammonium into smectite showed that a flat-lying orientation was adopted with a surfactant chain length less than eight carbons, resulting in an expansion

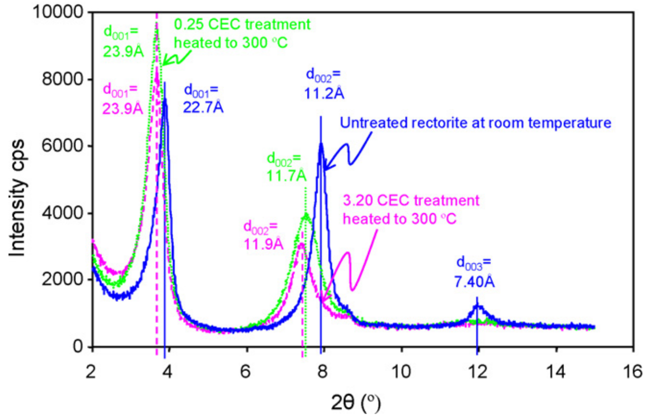

Fig. 9. XRD patterns of untreated and HDTMA rectorite intercalated at 3.20 and 0.25 CEC after heated to 300 °C.

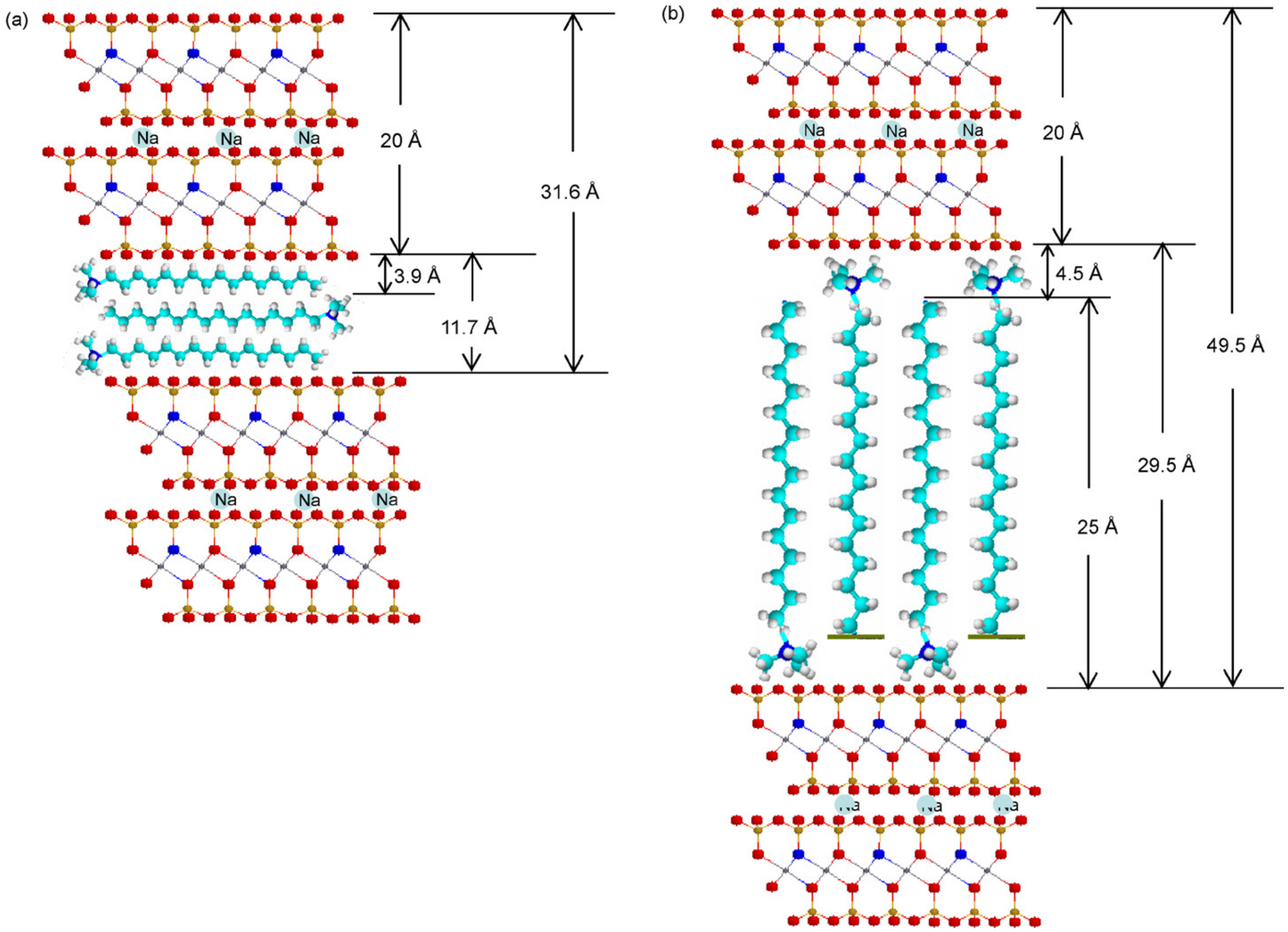

Fig. 10. Illustration of interlayer configuration of intercalated DDTMA (a) and HDTMA (b) molecules in the interlayer space of smectite component in rectorite.

of *d*-spacing to 13.5 Å, made of a dehydrated montmorillonite layer (same as an illite layer) of 10 Å together with the flat-lying monolayer of 3.5 Å [11,23]. As the surfactant loading increased, the intercalated alkylammonium could adapt horizontal bilayer and pseudo-trilayer, resulting in a *d*-spacing of 17 and 21.5 Å, respectively, for the smectites [9,23]. A *d*-spacing of 21 Å was achieved when an alkylammonium with 12 carbons on the tail group was intercalated into a vermiculitic material [29]. A pseudo-trilayer formation of DDTMA intercalated into montmorillonite with a CEC of 1450 $\mathrm{mmol_c\,kg^{-1}}$ resulted in a *d*-spacing of 21.5 Å [30]. If an additional illite layer of 10 Å is added to the pseudo-trilayer intercalated DDTMA in the montmorillonite, the *d*-spacing would be 31.6 Å such as the case in DDTMA intercalated rectorite in this study (Fig. 10(a)). This would be the case for rectorite with maximum intercalation of DDTMA. As intercalation of three layers of alkyl chain is only observed in clay minerals with high layer charges [31], the results suggest that the studied rectorite have a higher layer charge, consistent with the result obtained by electron probe microanalysis [32].

Batch results showed that the amount of DDTMA intercalated was only 1.67 CEC even though the initial DDTMA input was 5.00 CEC. On the contrary, the HDTMA intercalation is totally different. At an initial HDTMA input of 5.00 CEC, the amount of HDTMA intercalated was 3.20 CEC, twice to that of DDTMA. In addition, the *d*-spacing, after such high amount of HDTMA intercalation, expanded to 49.5 Å. Subtracting 10 Å for illite and another 10 Å for dehydrated montmorillonite layer, the remaining 29.5 Å was due to HDTMA intercalation. For an HDTMA molecule the tail group is 21 Å while the head group is 4 Å [7]. A vertically oriented HDTMA surfactant bilayer intercalation in rectorite would require the tail plus two head groups with a total length being 29 Å and the overall *d*-spacing 49 Å (Fig. 10(b)).

Similar results were observed only for Ca-montmorillonite, but not for Na-montmorillonite. For example, a *d*-spacing was expanded to 40 Å, for SAz-1 at an initial HDTMA loading of 3.0 CEC [7] and for a Ca-montmorillonite at an initial HDTMA loading of 4.0 CEC [25]. A *d*-spacing of 38 Å was determined separately for a montmorillonite modified by HDTMA at an initial loading of 3.0 CEC [12]. Compared to these results, it is not surprising to see the gallery height of 29.5 Å for rectorite at HDTMA adsorption capacity of 3.20 CEC.

Additional examples of vertical arrangements of HDTMA can also be found for its sorption onto other minerals. Studies on perchloroethylene partitioning into adsorbed HDTMA bilayer on clinoptilolite revealed such an arrangement of HDTMA as a result of stronger lateral tail–tail hydrophobic interaction [33]. In a similar study a thickness of 28 Å was determined for the sorbed HDTMA-Br molecules with a vertical bilayer configuration on amorphous silica [34].

Regardless of the pseudo-trilayer configuration for DDTMA intercalation or vertical arrangement for HDTMA intercalation, only a portion of the surfactant (about 0.5 CEC) is held by cation exchange and the majority of it is held by hydrophobic interaction as revealed by the smaller mass loss in step three and large mass loss in step two in TG analysis. This is also confirmed by the batch study that significant counter-ion sorption occurred accompanying alkylammonium intercalation at higher surfactant input, by the FTIR analyses conducted at room temperature, 300 and 550 °C, and by XRD analyses before and after the samples were heated to 300 °C.

4. Conclusions

The intercalation of alkylammonium in rectorite is affected by surfactant chain length and initial surfactant input. When the input level was less than 0.5 CEC of the clay, the intercalation of both HDTMA and DDTMA was via cation exchange, resulted in a *gauche* interlayer configuration whose decomposition temperature was about 430–440 °C. Due to a shorter chain length and weaker hydrophobic interaction, maximum DDTMA intercalation was achieved at 1.67 CEC and the intercalated DDTMA molecules adopted a lateral pseudo-trilayer configuration with extensive *gauche* arrangement. On the contrary, maximum intercalation of HDTMA reached at 3.20 CEC, with the intercalated surfactant molecules adopted an *all-trans* vertical arrangement held by electrostatic interaction together with hydrophobic bonding in the interlayer of the smectite-like component in rectorite. The decomposition temperature for the alkylammonium held by hydrophobic bonding in an excess to 0.5 CEC of the mineral was 230–250 °C. Thus, the T_{peak} determined from TG and DTG analyses could be used to interpret the type of bonding of alkylammonium held in the interlayer of clays.

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References

[1] M.M. Mortland, S. Shaobai, S.A. Boyd, Clays Clay Miner. 34 (1986) 581–585.
[2] J. Lee, J.R. Crum, S.A. Boyd, Environ. Sci. Technol. 23 (1989) 1365–1372.
[3] L.J. Michot, T.J. Pinnavaia, Clays Clay Miner. 39 (1991) 634–641.
[4] S. Xu, S.A. Boyd, Langmuir 11 (1995) 2508–2514.
[5] S. Xu, S.A. Boyd, Environ. Sci. Technol. 29 (1995) 312–320.
[6] S.Y. Lee, S.J. Kim, Clay Miner. 38 (2003) 225–232.
[7] S.Y. Lee, W.J. Cho, P.S. Hahn, M. Lee, Y.B. Lee, K.J. Kim, Appl. Clay Sci. 30 (2005) 174–180.
[8] H.P. He, R.L. Frost, J. Zhu, Spectrochim. Acta A 60 (2004) 2853–2859.
[9] Y. Xi, Z. Ding, H. He, R.L. Frost, J. Colloid Interface Sci. 277 (2004) 116–120.
[10] Z. Li, L. Gallus, Colloid Surf. A 264 (2005) 61–67.
[11] R.A. Vaia, R.K. Teukolsky, E.P. Giannelis, Chem. Mater. 6 (1994) 1017–1022.
[12] H. Xue, H. He, J. Zhu, P. Yuan, Spectrochim. Acta A 67 (2007) 1030–1036.
[13] W. Xie, Z. Gao, W.P. Pan, D. Hunter, A. Singh, R. Vaia, Chem. Mater. 13 (2001) 2979–2990.
[14] J.M. Hwu, G.J. Jiang, Z.M. Gao, W. Xie, W.P. Pan, J. Appl. Polymer Sci. 83 (2002) 1702–1710.
[15] M.M.G.R. Vianna, J. Dweck, V.F.J. Kozievitch, F.R. Valenzuela-Diaz, P.M. Büchler, J. Therm. Anal. Cal. 82 (2005) 595–602.
[16] Y. Xi, W. Martens, H. He, R.L. Frost, J. Therm. Anal. Cal. 81 (2005) 91–97.
[17] C.B. Hedley, G. Yuan, B.K.G. Theng, Appl. Clay Sci. 35 (2007) 180–188.
[18] E.J. Sullivan, D.B. Hunter, R.S. Bowman, Clays Clay Miner. 45 (1997) 42–53.
[19] J. Sterte, Clays Clay Miner. 38 (1990) 609–616.
[20] Z. Li, W.-T. Jiang, H. Hong, Spectrochim. Acta A 71 (2008) 1525–1534.
[21] H.L. Hong, W.T. Jiang, X. Zhang, L. Tie, Z. Li, Appl. Clay Sci. 42 (2008) 292–299.
[22] Z. Li, R.S. Bowman, Environ. Sci. Technol. 31 (1997) 2407–2412.
[23] G. Lagaly, M.F. Gonzalez, A. Weiss, Clay Miner. 11 (1976) 173–187.
[24] Q. Zhou, R.L. Frost, H. He, Y. Xi, J. Colloid Interface Sci. 307 (2007) 50–55.
[25] R. Zhu, L. Zhu, J. Zhu, L. Xu, Appl. Clay Sci. 42 (2008) 224–231.
[26] T.C. Wong, N.B. Wong, P.A. Tanner, J. Colloid Interface Sci. 186 (1997) 325–331.
[27] R.A. Campbell, S.R. Parker, J.P.R. Day, C.D. Bain, Langmuir 20 (2004) 8740–8753.
[28] S.W. Bailey, G.W. Brindley, H. Kodama, R.T. Martin, Clays Clay Miner. 30 (1982) 76–78.
[29] D.A. Laird, A.D. Scott, T.E. Fenton, Clays Clay Miner. 37 (1989) 41–46.
[30] H. Heinz, R.A. Vaia, R. Krishnamoorti, B.L. Farmer, Chem. Mater. 19 (2007) 59–68.
[31] G. Lagaly, Clay Miner. 16 (1981) 1–21.
[32] H. Hong, X. Zhang, M. Wan, Y. Hou, D. Du, J. China Univ. Geosci. 19 (2008) 38–46.
[33] Z. Li, R.S. Bowman, Environ. Sci. Technol. 32 (1998) 2278–2282.
[34] A.R. Rennie, E.M. Lee, E.A. Simister, R.K. Thomas, Langmuir 6 (1990) 1031–1034.