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KAOLINITE INTERCALATION PRECURSORS

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Abstract—The preparation and characterization of intercalated kaolinite is important for industries such as those using nanocomposites, but the number of compounds that can be intercalated into these clay minerals is rather limited. The purpose of this study was to expand the range of possible intercalants by developing intercalation precursors using both single and multiple (co-intercalation) precursor agents. Characterization of the resulting precursors was by X-ray powder diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA), and differential thermal analysis (DTA). The results show that the most successful single intercalation agent was DMSO and, among the co-intercalation agents, the DMSO/CH_3OH system was the best. The preparation and characterization of kao-DMSO-KAc showed that the displacement reaction is the most efficient way to expand the interlayer spacing of kaolinite. At the same time, the lateral-bilayer arrangement of the Ac^- in the interlayers was proven by study of de-intercalation of kao-KAc under high temperature.

Key Words—Arrangement, Co-intercalation Agents, De-intercalation, Guest-Displacement Reaction, Intercalation Precursor, Kaolinite, Lateral-bilayer, Single Intercalation System, Thermal Decomposition, X-ray Analyses.

Terminology—DMF: dimethyl formamide; DMSO: dimethyl sulfoxide; HAc: acetic acid; KAc: potassium acetate; NaAc: sodium acetate; NH_4Ac: ammonium acetate.

INTRODUCTION

Intercalation is well known as a means of forming inorganic-organic nanocomposites under mild conditions and clay minerals are common host materials for intercalation chemistry. Kaolinite is one of the most ubiquitous clay minerals on Earth, commonly found in soils, sediments, and sedimentary rocks, and is one of the most important industrial raw materials. Kaolinite has a 1:1-type layered structure with high crystallinity and unique structure: one side of the interlayer space is covered with hydroxyl groups of the $Al_2(OH)_4$ octahedral sheets and the other side is covered by oxygens of the SiO_4 tetrahedral sheets (Benco *et al.*, 2001). Because of the hydrogen-bonding between its layers, kaolinite has often been classified as non-expandable, while only a limited number of polar organic compounds such as dimethylsulfoxide (DMSO), deuterated dimethylsulfoxide (Martens *et al.*, 2002), formamide (Horváth *et al.*, 2005), N-methylformamide, dimethylformamide, acetamide, potassium acetate (Frost *et al.*, 1999), octadecylamine, and methanol (Cabedo *et al.*, 2004) can be intercalated directly. In recent years, intercalation reactions of kaolinite have been extended by the so-called "guest displacement" method (Komori *et al.*, 1999) where kaolinite intercalation compounds can be replaced by a new guest species.

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Millions of tons of kaolinite are used each year in a large variety of applications, such as ceramics, paper coating, paper filling, paint extender, rubber filler, plastic filler, cracking catalysts, and cements (Bundy and Ishley, 1991; Murray *et al.*, 1993; Murray, 2000). Improvement of the properties of kaolinite by the intercalation method is difficult, however, because of the high passivity of the material. Increasing interest in possible new applications of kaolinite as a natural, common, and cheap material justifies a systematic study of the intercalation process.

Six pre-requisites need to be satisfied if guest molecules are to be intercalated successfully into kaolinite: (1) the hydrogen bonds must be broken; (2) the *d* spacing of the clay has to be expanded; (3) the organophilicity of kaolinite has to be modified; (4) the intercalation guest must have strong polarity; (5) the intercalation guest monomer must be of an appropriate size; and (6) the intercalated organic molecule should be bound with some functional group in the clay such as an hydroxyl of $Al_2(OH)_4$ octahedral sheets, an oxygen atom of a SiO_4 tetrahedron, or both (Zhang *et al.*, 2007).

Intercalation of a large number of solvents has been tested but little information about the effect of synthesis parameters on the intercalation process has been reported. The aim of the present work was to study the synthesis parameters that affect the process of preparing the precursors, using a single intercalation agent and using several co-intercalation agents. With a versatile and effectively benign approach based on displacing the

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intercalation guest, the kao-KAc (K_2) was prepared by the guest displacement reaction between KAc and DMSO. The synthesis parameters of the intercalation process and the arrangement of the organic molecules (Ac^-) in the interlayer region are also discussed.

EXPERIMENTAL SECTION

Chemicals and instrumentation

The natural clay mineral used in this work was kaolinite supplied by the China-kaolinite Company, Wuhan, with a particle size of 5−10 μm. Hydrochloric acid was supplied by the Beijing-Chemical Plant, Beijing. The DMSO, methanol, ethanol, HAc, KAc, NaAc, NH_4Ac, DMF, and urea used in this study, without further purification, were manufactured by the Fuchen-Chemical reagent Factory, Tianjin, China. All were of analytical reagent grade.

Wide-angle X-ray analyses were carried out using an XRD-6000 equipped with a vertical goniometer and a curved graphite diffracted-beam monochromator. The radiation applied was CuKα (λ = 1.54 Å) from a long, fine-focus Cu tube, operating at 40 kV and 30 Ma from 2 to 80º2θ. Thermal decomposition of the precursors was carried out using a Perkin-Elmer, TGA-7 type thermogravimetric analyzer at a heating rate of 10ºC/min from room temperature to 800ºC under an atmosphere of N_2. The thermal degradation temperature was taken as the minimum of the first derivative of the weight loss with respect to time (this point corresponds to the maximum weight-loss rate). The DTA data were collected using a Dupang-1090 DTA Instrument in an air atmosphere, the heating rate was 10ºC/min, and Al_2O_3 was used as a reference. Fourier-transform infrared spectra of these precursors' surfaces were recorded in the range 4000−350 cm^{-1} in a 670-type infrared Fourier transform spectrometer, using the KBr pellet technique (KBr:sample = 100:1~2).

Preparation of samples

5 g of crude kaolinite was stirred in 60 mL of 5.0 mol/L hydrochloric acid at 80ºC. After stirring for 8 h, the mixture was filtered and washed five times with distilled water until the pH value of the mother liquor was 7, in order to ensure removal of any unwanted cations such as Ca^{2+}, Fe^{3+}, *etc*. The purified kaolinite (K_0) was dried at 100ºC under vacuum for 5 h (Cabedo *et al.*, 2004).

To prepare kaolinite precursors with a single intercalation agent (DMSO, KAc, NaAc, NH_4Ac, Urea, DMF), 5 g of purified kaolinite was stirred with 100.0 mL of organic liquid or solution under different conditions (see below). The intercalation mixture was filtered and washed three times with hot (~50ºC) ethanol or water in order to remove excess organic compound (Belver *et al.*, 2002; Olejnik *et al.*, 1970; Elbokl and Detellier, 2006).

To prepare the kaolinite precursor with co-intercalation agents, five organic agents were chosen as possible guest intercalates: DMSO/HAc, DMSO/CH_3OH, DMSO/H_2O, DMSO/NaAc, and DMSO/KAc. 5 g of purified kaolinite was stirred with 100.0 mL of DMSO and 10 mL of organic compound (HAc, CH_3OH, H_2O) or 10 mL of aqueous solution of the organic agent (NaAc,

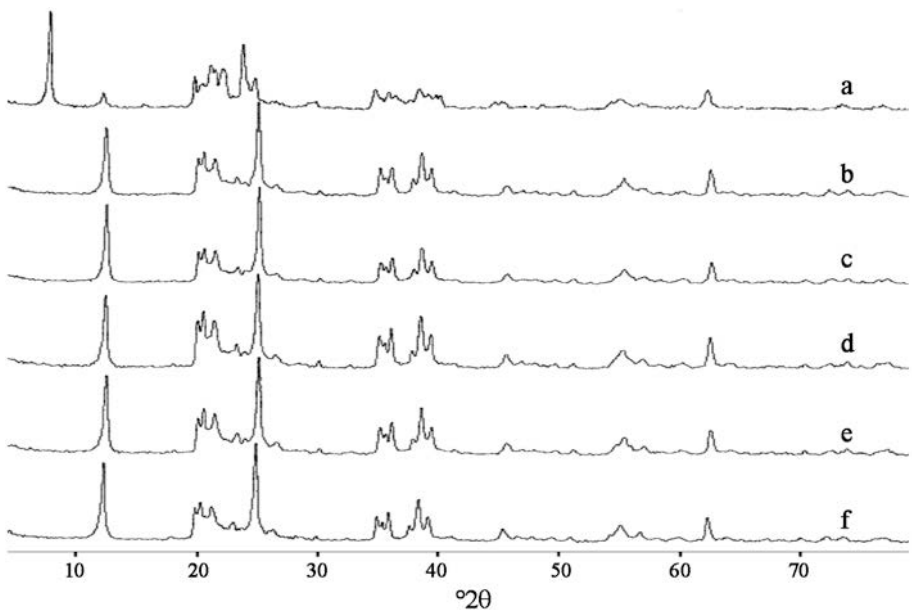


Figure 1. WXRD of kaolinite precursors with single intercalation agents: (a) Kao-DMSO; (b) Kao-KAc; (c) Kao-NaAc; (d) Kao-NH_4Ac; (e) Kao-Urea; and (f) Kao-DMF.

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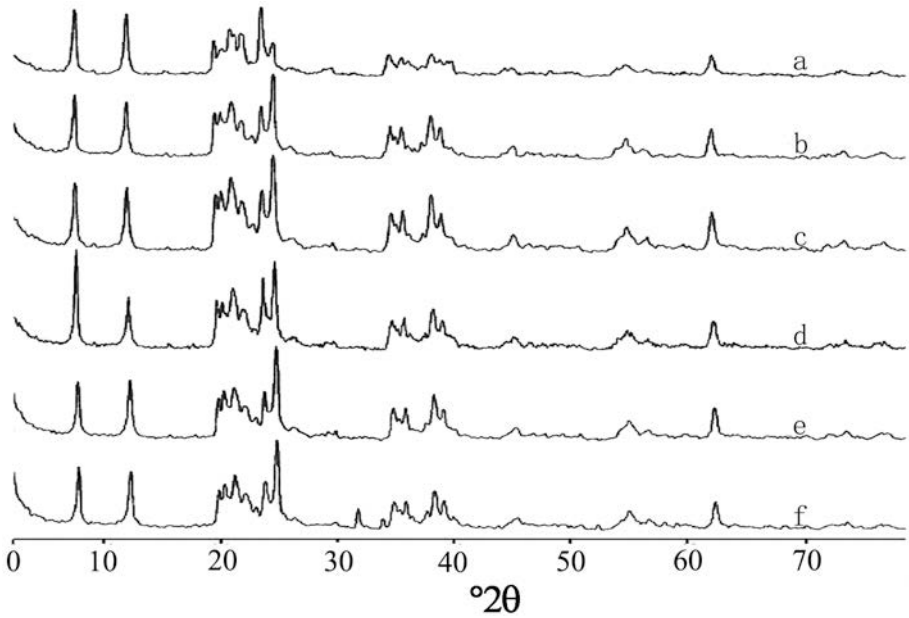


Figure 2. WXRD of kaolinite precursors with co-intercalation agents: (a) DMSO; (b) DMSO-HAc; DMSO/NaAc; (d) DMSO/H_2O; (e) DMSO/KAc; and (f) DMSO/CH_3OH.

KAc) at the concentration of 20 wt.% under different conditions (see below). The intercalation system was then filtered and washed three times with ethanol.

The kao-KAc precursor was prepared by the guest-displacement reaction between KAc and DMSO. The aqueous solution of KAc was stirred in with kao-DMSO/CH_3OH (K_1), and then the system was filtered and washed with hot (65ºC) water.

RESULTS AND DISCUSSION

Wide X-ray diffraction

The primary hydrogen bonds between the clays can be broken by a strong polar organic molecule (DMSO, μ = 3.9 D), and the new hydrogen bonds between the strong polar molecule and the tetrahedral or the octahedral sheet can be formed easily. The wide X-ray diffraction (WXRD) of kao-DMSO (Figure1a) shows that the d_{001} spacing of kao-DMSO was 1.118 nm compared to 0.72 nm of the raw kaolinite, the difference being due to the intercalation of DMSO in the kaolinite. The rate of intercalation was 87.72%. The intercalation rates (*IR*), given as percentages, were calculated as described by equation 1.

$$IR = (I_{i(001)}/(I_{k(001)} + I_{i(001)})) \times 100\% \quad (1)$$

where $I_{i(001)}$ is the peak intensity observed for the intercalate and $I_{k(001)}$ is the peak intensity observed for kaolinite. The basal spacing of the other precursors increased only slightly, according to the WXRD curves (Figure 1) of the precursors with a single intercalation agent. Their intercalation rates were negligible.

The lattice structure (Figure 2) and the reaction conditions and intercalation rates for different precursors with the co-intercalation agents (Table 1) show that the d_{001} spacing of kao-DMSO/CH_3OH is largest while the intercalated ratio of kao-DMSO/H_2O is the largest of these precursors. The d_{001} spacing of the precursor is fundamental to the intercalation of organic molecules in the future, and the intercalated ratio can be improved by temperature or reaction-time adjustment. The DMSO/CH_3OH agents were, therefore, chosen for this study.

The relationship between the ratio DMSO/CH_3OH and the amount of organic matter fixed in the solids and

Table 1. Summary of reaction conditions and intercalated ratio for different precursors with the co-intercalation agents.

Phase	Solvent	*T* (ºC)	*t* (h)	d_{001} (nm)	*IR* (%)
Kao-DMSO	–	90	48	1.118	51.90
Kao-DMSO/HAc	HAc	90	48	1.128	51.35
Kao-DMSO/NaAc	NaAc	90	48	1.123	51.02
Kao-DMSO/H_2O	H_2O	90	48	1.126	65.79
Kao-DMSO/KAc	KAc	90	48	1.125	49.22
Kao-DMSO/CH_3OH	CH_3OH	90	48	1.130	51.45

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Table 2. Summary of reaction conditions and intercalated ratio for the precursors with the DMSO/CH_3OH agents.

Sample	CH_3OH% (V%)	*T* (ºC)	*t* (h)	d_{001} (nm)	*IR* (%)
Kao-DMSO/ CH_3OH effect by concentration	0	80	48	1.118	51.38
	10	80	48	1.129	51.47
	20	80	48	1.128	54.00
	30	80	48	1.127	40.18
	40	80	48	1.127	30.65
	50	80	48	0.720	0
	70	80	48	0.720	0
Kao-DMSO/ CH_3OH effect by temperature	15	40	48	1.130	30.53
	15	60	48	1.125	43.94
	15	80	48	1.126	54.14
	15	90	48	1.126	53.38
	15	100	48	1.125	23.60
	15	120	48	1.127	7.50
Kao-DMSO/ CH_3OH effect by time	15	85	24	1.129	25.72
	15	85	48	1.127	53.97
	15	85	72	1.127	70.81
	15	85	96	1.126	88.50
	15	85	120	1.125	91.09
	15	85	144	1.128	90.73
	15	85	168	1.129	90.55

the basal spacing of the intercalated solids is significant. Seven samples were prepared at 80ºC for 48 h, with different DMSO/CH_3OH ratios. The basal spacings and the intercalated ratios of the precursors (tabulated in Table 2) revealed that the d_{001} spacing of the precursors prepared with co-intercalation agents of DMSO/CH_3OH is ~1.128 nm, while the basal spacing is 1.118 nm for a single system of DMSO. In the first case, the organic molecule (DMSO) and the solvent (CH_3OH) are actually intercalated together, while in the second case, only the fixation of DMSO occurs. The intercalated ratio first increased then decreased with increasing CH_3OH. The intercalation process stops when the amount of CH_3OH exceeds 50% (v/v). The results indicate that methanol

Table 3. Summary of reaction conditions and intercalated ratio for K_1-KAc.

Sample	C_{KAc} (mol/L)	*T* (ºC)	*t* (h)	d_{001} (nm)	*IR* (%)
K_1-KAc effect by concentration	2	30	72	1.414	75.76
	4	30	72	1.421	89.29
	6	30	72	1.413	88.50
	8	30	72	1.412	89.29
	10	30	72	1.423	89.29
	12	30	72	1.419	89.29
K_1-KAc effect by temperature	8	0	24	1.414	91.74
	8	20	24	1.411	91.74
	8	40	24	1.412	95.24
	8	60	24	1.408	95.24
	8	80	24	1.410	90.91
	8	90	24	1.424	89.29
K_1-KAc effect by time	5	50	2	1.423	94.34
	5	50	4	1.419	91.74
	5	50	6	1.396	90.09
	5	50	8	1.416	91.74
	5	50	12	1.430	94.34
	5	50	16	1.411	90.91
	5	50	20	1.415	91.74

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has an important role in the intercalation process of the co-intercalation agents. The strong polar organic molecules may be clustered to form aggregates through hydrogen bonds. Pure DMSO liquid is very viscous (η = 2.24 mPa·s 20ºC). The large aggregates and the great viscosity had a negative effect on the formation of the precursor. The aggregates and viscosity of DMSO were reduced by adding methanol (η = 0.6 mPa·s 20ºC). When the CH_3OH content was >50%, methanol intercalated into the clays first because too few sites were available for DMSO molecules and, consequently, the amount of DMSO fixed was insufficient to swell the clay efficiently. Intercalation is regarded as an equilibrium process between the cleavage of old hydrogen bonds and the formation of new hydrogen bonds. The process of forming hydrogen bonds is exothermic; high temperature restrains the process, as reflected in the intercalation rates of the kao-DMSO/CH_3OH, which is

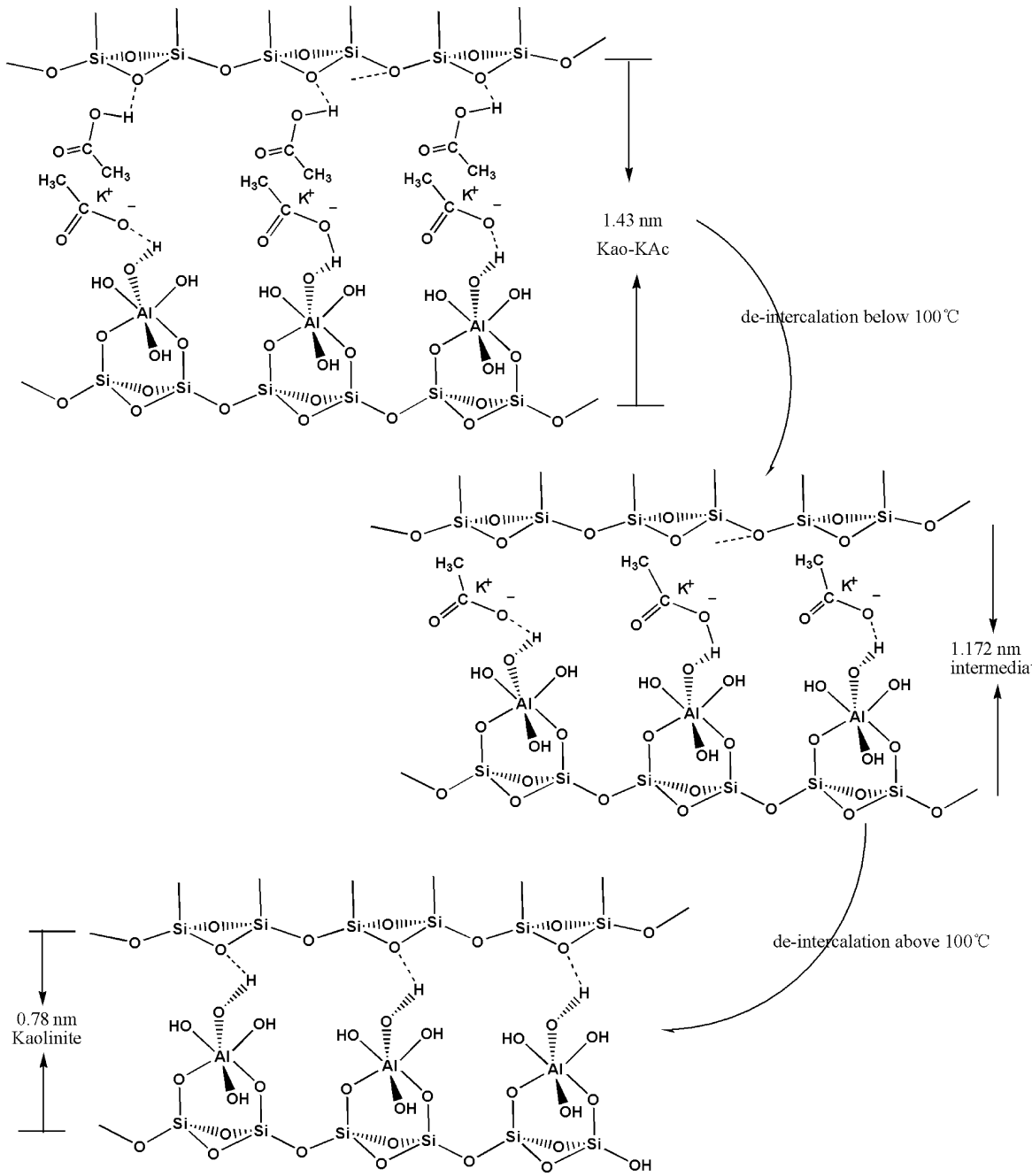


Figure 3. Illustration of the de-intercalated process of K_2.

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close to 54.14% at 80ºC and only 7.5% at 120ºC. The time allowed for intercalation plays an important role in this process, the intercalation rates increase almost linearly with respect to reaction time and then level off above 120 h.

The reactivity of DMSO/CH_3OH-treated kaolinite toward KAc was also investigated. The KAc molecules penetrate rapidly and easily even under ambient conditions (low concentration, room temperature, and short time), and the ratio of intercalated precursors prepared with KAc under different reaction conditions is high (Table 3). Intercalation of DMSO weakens the cohesion energies of the kaolinite stacking, and incorporation of DMSO transforms the surfaces of the clays from natural organophobic to organophilic. Comparing the synthesis conditions for kao-KAc and kao-DMSO/CH_3OH-KAc samples, pre-intercalation with the DMSO/CH_3OH agents followed by a displacement reaction between KAc and DMSO is much more effective than a single agent for intercalating the clay.

The *d* spacing of K_2 in this study was 1.43 nm, while a spacing of 1.16 nm was reported by Ledoux and White (1996). The observed 1.43 nm *d* spacing corresponds to a 0.71 nm expansion compared to the original kaolinite. The one CH_3COO^- group is 0.406 nm long, so even if the KAc is vertical to the siloxane surface, it falls 0.304 nm short of accounting for the observed expansion of the layers. The arrangement of the Ac^- in the interlayers is, therefore, considered to be lateral-bilayer (model shown in Figure 3), and this hypothesis is proved by WXRD of the de-intercalated samples (Figure 4) prepared at different temperatures. The de-intercalated K_2 was investigated because the intercalation is a dynamic equilibrium; the intercalated guest could be de-intercalated under certain conditions. The bonds in the lateral-bilayer are weak and can be destroyed by high temperature. The process of de-intercalation and the XRD spectrum of the de-intercalated samples (Figures 3 and 4, respectively) disclosed that new d_{001} peaks = 1.172 nm and 0.78 nm appeared when K_2 was treated at temperatures below 100ºC, and the d_{001} peak = 1.172 nm disappeared above 250ºC. The d_{001} peak = 1.172 nm, therefore, could be an indication of the transition state of a K_2 de-intercalated compound when it was treated at high temperature. The loss of one of the HAc molecular layers in the lateral-bilayer caused the decrease in the *d* spacing of ~0.258 nm, and the loss of the other layer caused a decrease of 0.392 nm (approximate length of the CH_3COO^- group).

According to these observations, optimal results are obtained when: K_1 is prepared at 85ºC for 120 h with the methanol concentration in the range ~10−15%; K_2 is prepared at 50ºC for 10 h with the KAc concentration at 5 mol/L.

When the precursors of K_1 and K_2 were prepared under optimal conditions, the lattice structure (Figure 5) of K_0 (a), K_1 (b), and K_2 (c) revealed that up to 93.6% of

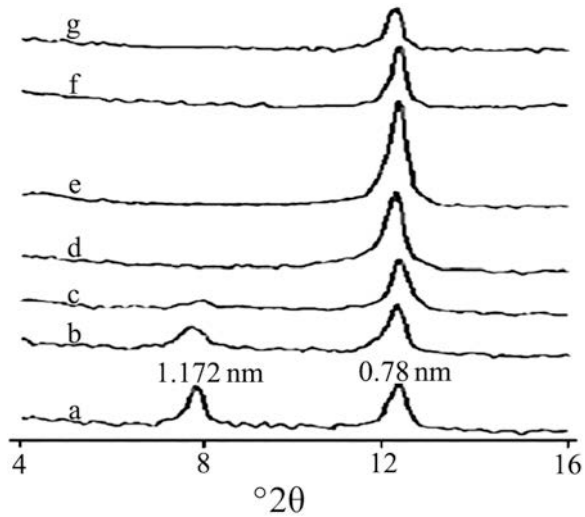


Figure 4. WXRD of the de-intercalated samples: (a) 100ºC; (b) 150ºC; (c) 200ºC; (d) 250ºC; (e) 400ºC; (f) 400ºC; and (g) 500ºC.

K_1 and 94.1% of K_2 of the kaolinite were intercalated. The basal spacing d_{001} of K_1 expands from 0.72 to 1.13 nm, an increase of 0.41 nm. After treatment of the K_1 intercalation compound with KAc in water, the basal spacing expanded to 1.43 nm from that of K_1 (1.13 nm).

FT-IR spectra

Kaolinite is characterized by a signature O−H stretching pattern consisting of four bands at 3696, 3669, 3654, and 3621 cm^{-1} (Figure 6a). The attribution of these bands has been the subject of extensive study (Ledoux and White, 1996; Johnston and Stone, 1990; Van der Marel and Beutelspacher, 1976). The band at 3621 cm^{-1} has been assigned unambiguously to the stretching frequency of the internal hydroxyl group of kaolinite which is believed to be oriented almost parallel to the direction of the (001) layers, pointing in the direction of the octahedral vacancy. The inner-surface

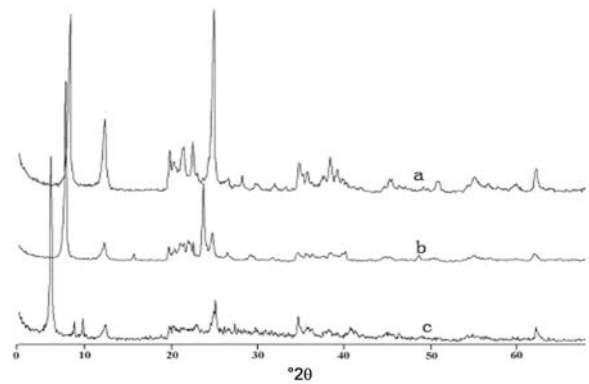


Figure 5. WXRD of raw kaolinite (a), Kao-DMSO/CH_3OH (b), and Kao-KAc (c).

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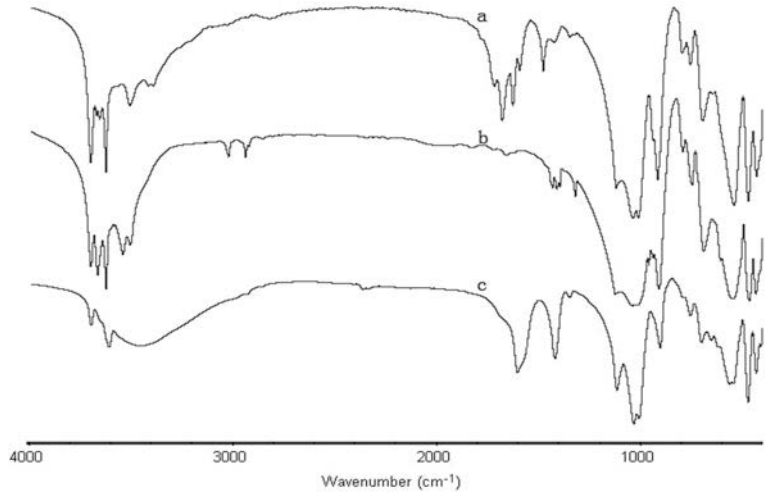


Figure 6. FTIR spectrum of raw kaolinite (a), Kao-DMSO/CH_3OH (b), and Kao-KAc (c).

hydroxyl groups associated with the remaining bands (3696, 3669, and 3654 cm^{-1}) are believed to make an angle of 60−73º with the (001) plane. The inner hydroxyl stretching band at 3621 cm^{-1} is not usually influenced very much by interlamellar modification reactions since it is separated from the interlamellar surface. In contrast, the three inner-surface hydroxyl stretching bands are very much influenced by interlamellar modifications, as was readily observed for K_1 (Figure 6b). The hydroxyl stretching bands at 3669 and 3653 cm^{-1} disappeared and new bands at 3663 and 3539 cm^{-1} appeared, which were assigned to hydrogen-bonding between DMSO and kaolinite. New peaks at 3022 and 2934 cm^{-1} could be assigned to C−H of DMSO. K_1 also showed deformation bands at 1431 and 1407 cm^{-1}. The results were consistent with previous reports and confirmed that intercalation between kaolinite and DMSO had taken place (Li *et al.*, 2003; Olejnik *et al.*, 1968). The IR spectra of K_2 (Figure 6c), which showed that the peak at 3539 cm^{-1} was assigned to hydrogen-bonding between DMSO and kaolinite, disappeared and new peaks at 3698 and 3610 cm^{-1} appeared, which were assigned to hydrogen-bonding between KAc and kaolinite. A further new peak at 1606 and 1418 cm^{-1} can be assigned to C=O of KAc. These results imply that KAc displaced DMSO and formed a kao-KAc intermediate, which was further supported by WXRD.

Thermogravimetric analyses

Thermogravimetric analyses of the raw kaolinite showed the loss of the water molecules in two steps, the first between room temperature and ~300ºC, and the second as a significant weight loss, beginning at 460ºC (Figure 7a). At the same time, in the high-temperature region, the differential thermal analyses (Figure 8a) showed three endothermal effects centered at 45, 220, and 510ºC, assigned to the removal of the water adsorbed on the surface of the kaolinite particles and the loss of the structural water of the kaolinite. As for K_0, in the low-temperature region, the DTA of K_1 showed three endothermal effects centered at 40, 180, and 510ºC (Figure 8b), assigned to the removal of the volatiles (water and methanol) adsorbed on the surface of the kaolinite particles and to the loss of the structural water of the kaolinite. In the DTA trace of K_2, an endothermic event with a broad peak at 80ºC and a very strong exothermic peak at 380ºC are noted (Figure 8c). The broad peak at 80ºC assigned to the removal of the water adsorbed on the surface of the kaolinite particles and to the strong exothermic peak at 380ºC were probably due to the pyrolytic decomposition of the organic component (Ac^-), overlapping the weight-loss trace of K_2 (Figure 7c). The absence of the broad peak at 510ºC in the case of K_2 (Figure 8c) was possibly due to a phase change at 380ºC, which was caused by the extended interlayer spacing because of the intercalated KAc.

CONCLUSIONS

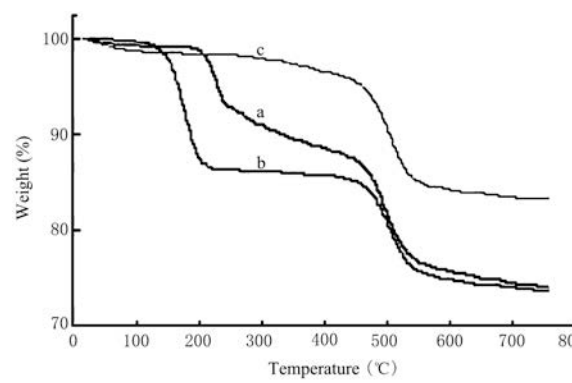


Figure 7. TGA trace of raw kaolinite (a), Kao-DMSO/CH_3OH (b), and Kao-KAc (c).

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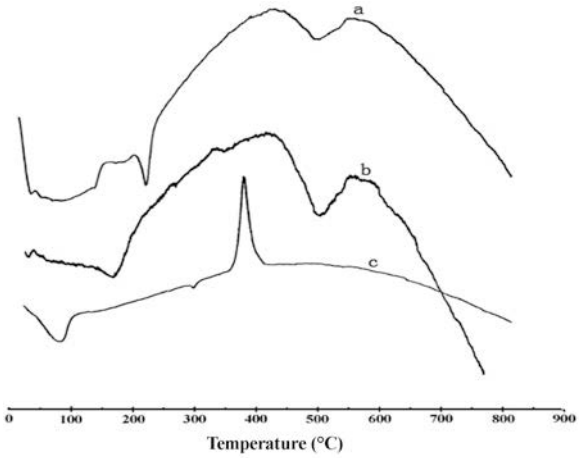


Figure 8. DTA curves of raw kaolinite (a), Kao-DMSO/CH_3OH (b), and Kao-KAc (c).

Kaolinite intercalation precursors have been prepared with a single intercalation agent and with co-intercalation agents by varying the temperature, concentration, and intercalation time used in the reaction process. The co-intercalation agents influence the process, especially in the DMSO/CH_3OH system; a certain amount of CH_3OH is necessary to accelerate the intercalation reaction. K_2 was prepared by a displacement reaction between KAc and DMSO, and the guest displacement reaction is an effective means of achieving the intercalation process. The lateral-bilayer arrangement of the organic molecules (Ac^-) in the interlayer region was also highlighted.

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