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FUNCTIONALIZATION OF THE INTERLAYER SURFACES OF KAOLINITE BY ALKYLAMMONIUM GROUPS FROM IONIC LIQUIDS

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Abstract—The objective of this study was to design new, functional, nanostructured materials from the abundant clay mineral kaolinite, in spite of development problems with the interlayer chemistry of kaolinite because of its non-swelling properties. A particular goal of this work was to graft, in a controlled way, alkylammonium groups onto the aluminol interlayer surfaces of kaolinite. This was successfully achieved by soft-chemical approaches, more specifically by the melting intercalation process of alkylammonium ionic liquids which were synthesized for this purpose. The resulting nanohybrid materials were characterized chemically and structurally by X-ray diffraction analysis, thermal analysis (TG/DTA), ^{13}C cross polarization magic angle spinning nuclear magnetic resonance spectroscopy, and Fourier-transform infrared spectroscopy. The amount of grafted organic material was quantified from TGA results. Alkylammonium salts with a short alkyl chain were grafted directly using a melting reaction at 180ºC under N_2 involving the *in situ* displacement of dimethylsulfoxide (DMSO) from a DMSO-kaolinite pre-intercalate; for longer alkyl chains, the grafting was done in two steps. In the first step, the corresponding amino-alcohol was grafted into the kaolinite by displacement of DMSO from the interlayer space. The second step consisted of quaternarization of the grafted material by reaction with iodomethane or iodoethane.

Key Words—Alkylammonium, Choline, Aluminosilicate, Clay Mineral, Grafting, Intercalation, Ionic Liquids, Kaolinite, Layered Materials, Nanohybrid Materials, Organo-clay.

INTRODUCTION

During the past decade, nanosized hybrid materials, prepared by controlled intercalation of organic entities into the interlayer spaces of layered inorganic materials, have received considerable attention (Pinnavaia and Beall, 2000; Ruiz-Hitzky *et al*., 2004; Gómez-Romero and Sanchez, 2004). The resulting nanometric assemblies benefit from the structural and textural properties of the inorganic matrix as well as from the specific functionalities of the guest organic entities (Yariv and Cross, 2002; Ajjou *et al*., 1997; Fujinami *et al*., 1998; Letaief and Detellier., 2005; Letaief *et al*., 2006; Ruiz-Hitzky and Van Meerbeeck, 2006).

Among the layered inorganic materials, clay minerals are particularly interesting as host materials. They are available, abundant, cheap, and largely non-toxic. In addition to their use in chemical syntheses, in separation processes, and as catalysts, or as sensors, clay minerals can also be used in environmental applications (Chakrabarty and Sarkar, 2002; Penieres-Carrillo *et al*., 2003; Yadav and Rai, 2006; Selvam and Swaminathan, 2007).

Kaolinite is a 1:1 layered dioctahedral aluminosilicate with the theoretical formula $Al_2Si_2O_5(OH)_4$ giving a molecular weight of 258.07 (Newman and Brown, 1987; Bailey, 1988; Bergaya *et al*., 2006). The silicon oxide tetrahedral sheets (SiO_4) are linked to a gibbsite-like octahedral sheet (Al(O,OH)) of an adjacent layer through hydrogen bonds between the aluminol groups of the octahedral sheet on one side and the siloxane macrorings of the tetrahedral sheets on the other side. The layered 1:1 structure results in large superposed dipoles, which, in conjunction with the network of interlayer H-bonds, result in the large cohesive energy of the mineral. Consequently, the intercalation of molecular guests into the interlayer spaces of kaolinite is not as easily achieved as in the case of the minerals of the smectite family. Kaolinite pre-intercalated with a selected group of dipolar molecules has, however, been used successfully for further intercalations of a variety of organic entities and of polymers.

Chemical modification of the interlayer surfaces of kaolinite could be achieved through covalent grafting reactions between the interlayer surface aluminol groups (hydroxyl groups on the octahedral sheet) and some organic reagents. This was achieved using alcohols (Tunney and Detellier, 1993, 1994; Komori *et al*., 2000; Murakami *et al*., 2004; Gardolinski and Lagaly, 2005; Janek *et al*., 2007; Letaief and Detellier, 2008a), polyols (Elbokl and Detellier, 2005), amino-alcohols (Tunney and Detellier, 1997; Letaief and Detellier, 2007b), and alkoxysilane (Tonle *et al*., 2007). Barrer and MacLeod (1955) were the first to show the creation of porosity by the intercalation of tetra-alkylammonium groups in montmorillonite. Lagaly and Weiss (1969) pioneered

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the incorporation of long-chain alkylammonium groups into the interlayer space of montmorillonites for the determination of the interlayer charge of 2:1 phyllosilicates. This method was improved by Stanjek and Friedrich (1986), Ghabru *et al*. (1989), Olis *et al*. (1990), Stanjek *et al.* (1992), and Mercier and Detellier (1994), among others. Other organic salts were also incorporated into clay minerals of the smectite family for various purposes (Vansant and Uytterhoeven, 1973; Gilman *et al*., 2002; Yariv and Cross, 2002; Bergaya *et al*., 2006).

While there are numerous examples of intercalation of alkylammonium cations in smectites, mainly through ion exchange, reports on the intercalation of alkylammonium salts into the interlayer spaces of kaolinite are extremely scarce (Weiss *et al.*, 1963). The adsorption of alkylammonium salts onto kaolinite external surfaces has, however, been reported (Gonzalez *et al*., 1989; Saada *et al*., 1995; Hu *et al*., 2003). The difficulty with intercalation of ammonium groups is the lack of swelling in kaolinite. Recently, the intercalation of molten salts derived from pyridinium, pyrrolidinium, and imidazolium cations into kaolinite was reported using melting-intercalation processes (Letaief *et al*., 2006; Letaief and Detellier, 2005, 2007a, 2008b). A similar approach was tested for the intercalation in kaolinite of ionic liquids based on ammonium derivatives. The nature of the ammonium salts is crucial in determining whether the intercalation will succeed. The majority of the ammonium salts used in the modification of smectites (*e.g.* cetyltrimethylammonium bromide, known as CTAB) exhibit such a high melting point that they decompose before melting, which renders the melt-intercalation process impossible. For this reason, ammoniums salts were synthesized. They are characterized by lower melting points (<100ºC). Four ammonium salts belonging to the choline family were synthesized by reacting triethanolamine or dimethydiethanolamine with iodomethane or iodoethane. The resulting ammonium salts were then used for the intercalation process.

In the present study, soft-chemical approaches are reported in order to functionalize the interlayer surfaces of kaolinite either by performing direct grafting of ammoniums salts or by grafting aminoalcohols first, followed by quaternarization using alkyl halides. Samples were characterized using X-ray diffraction (XRD), thermal analysis (DTA-TG), Fourier-transform infrared (FTIR) spectroscopy, and ^{29}Si and ^{13}C MAS NMR.

MATERIALS AND METHODS

Materials

Well crystallized kaolinite (KGa-1b, Georgia) was obtained from the Source Clays Repository of The Clay Minerals Society (located at Purdue University, West Lafayette, Indiana, USA). The purification of KGa-1b and the preparation of the dimethylsulfoxide-kaolinite pre-intercalate (DMSO-K) were carried out according to previously published procedures (Letaief *et al*., 2006; Letaief and Detellier, 2005, 2007a, 2007b, 2008a, 2008b). The ionic liquid, labeled Am-1, was synthesized using a different approach from that used by Hayashi *et al.* (1987), whereas Am-2, Am-3, and Am-4 (Figure 1) are reported here for the first time. Am-1, Am-2, and Am-3 are solids at room temperature. Their melting points are 29, 33, and 131ºC, respectively, whereas Am-4 is liquid at room temperature. Iodomethane, iodoethane, butyldiethanolamine, triethanolamine, and N-methyldiethanolamine were purchased from Aldrich Chemicals (Sigma-Aldrich, St. Louis, Missouri, USA) and were used as received. Dodecyldiethanolamine was purchased from ABCR (Karlsruhe, Germany).

Synthesis and characterization of ionic liquid compounds

Am-1. Iodomethane (3.1 mL, 50 mmol) was added dropwise to 5 g of triethanolamine (34 mmol). The mixture was first stirred at room temperature for 20 min, then at 60ºC for 48 h under N_2. The excess iodomethane was removed by washing with diethyl ether. After drying, a yellowish solid (melting point of 29ºC) was obtained with 95% yield. Analysis by ^{1}H NMR gave the following results: δ 3.25 ppm (s, 3 H, (HO-CH_2-CH_2)$_3$$N^+$-$CH_3$); 3.95 ppm (m, 6 H, (HO-CH_2-CH_2)$_3$$N^+$-$CH_3$), and 4.3 ppm (m, 4 H, (HO-CH_2-CH_2)$_3$$N^+$-$CH_3$). Analysis by ^{13}C NMR gave: 51.3 ppm ((HO-CH_2-CH_2)$_3$$N^+$-**C**$H_3$); 56.0 ppm ((HO-$CH_2$-**C**$H_2$)$_3$$N^+$-$CH_3$), and 65.1 ppm ((HO-**C**H_2-CH_2)$_3$$N^+$-$CH_3$). Electrospray mass spectrometry (*A*: cation; *B*: anion): A^+ peak at 164.1, with a regular series of $[A(AB)_n]^+$ peaks observed at 164.1 + $n \times 291.0$.

Am-2. Iodomethane (3.1 mL, 50 mmol) was added dropwise to 5 g of N-methyldiethanolamine (42 mmol). The mixture was first stirred at room temperature for 20 min, then at 60ºC for 48 h under N_2. The excess iodomethane was removed by washing with diethyl ether. After drying, a yellowish solid (melting point 33ºC) was obtained with 95% yield. Analysis by ^{1}H NMR gave the following results: δ 3.11 ppm (s, 6 H, (HO-CH_2-CH_2)$_2$$N^+$-($CH_3$)$_2$); 3.48 ppm (m, 4 H, (HO-CH_2-CH_2)$_2$$N^+$-($CH_3$)$_2$); and 3.95 ppm (m, 4 H, (HO-CH_2-CH_2)$_2$$N^+$-($CH_3$)$_2$). Analysis by ^{13}C NMR gave: 52.6 ppm ((HO-CH_2-CH_2)$_2$$N^+$-(**C**$H_3$)$_2$); 55.7 ppm ((HO-$CH_2$-**C**$H_2$)$_2$$N^+$-(**C**$H_3$)$_2$); and 66.5 ppm ((HO-**C**H_2-CH_2)$_2$$N^+$-($CH_3$)$_2$). Electrospray mass spectrometry (*A*: cation; *B*: anion): A^+ peak at 134.1, with a regular series of $[A(AB)_n]^+$ peaks observed at 134.1 + $n \times 261.0$.

Am-3. Iodoethane (4.80 mL, 60 mmol) was added dropwise to 7.46 g of triethanolamine (50 mmol). The mixture was first stirred at room temperature for 20 min, then at 60ºC for 48 h under N_2. The excess iodoethane

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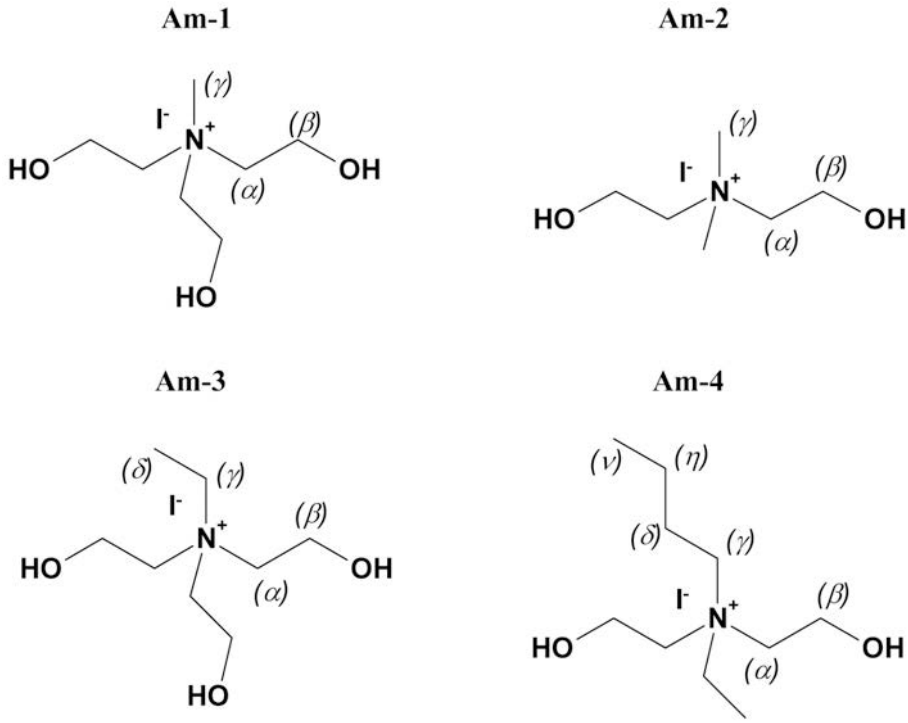


Figure 1. Chemical structures of the ammonium iodide ionic liquids used in the preparation of the grafted nanohybrid materials derived from kaolinite.

was removed by washing with diethyl ether. After drying, a yellowish solid (melting point 131ºC) was obtained at 90% yield. Analysis by ^{1}H NMR gave the following results: δ 1.2 ppm (t, 3 H, (HO-CH_2-CH_2)$_3$$N^+$-$CH_2CH_3$); 3.5 ppm (m, 8 H, (HO-$CH_2$-$CH_2$)$_3$$N^+$-$CH_2CH_3$); and 3.9 ppm (m, 6 H, (HO-CH_2-CH_2)$_3$N-CH_2CH_3). Analysis by ^{13}C NMR gave: 7.7 ppm (HO-CH_2-CH_2)$_3$$N^+$-$CH_2$**C**$H_3$); 55.3 ppm (HO-$CH_2$-$CH_2$)$_3$$N^+$-**C**$H_2CH_3$); 56.7 ppm (HO-$CH_2$-**C**$H_2$)$_3$$N^+$-$CH_2CH_3$); and 60.6 ppm (HO-**C**H_2-CH_2)$_3$$N^+$-$CH_2CH_3$). Electrospray mass spectrometry (*A*: cation; *B*: anion): A^+ peak at 178.1, with a regular series of $[A(AB)_n]^+$ peaks observed at 178.1 + $n \times 305.0$.

Am-4. Iodoethane (3.2 mL, 40 mmol) was added dropwise to 4.8 g of N-butyldiethanolamine (30 mmol). The mixture was first stirred at room temperature for 20 min, then at 60ºC for 48 h under N_2. The excess iodoethane was removed by washing with diethyl ether. After drying, a reddish liquid was obtained at 85+% yield. Analysis by ^{1}H NMR gave the following results: δ 0.85 ppm (t, 3 H, C**H**$_3$$CH_2$-$CH_2$-$CH_2$-$N^+$-); 1.26 ppm (m, 5 H, CH_3C**H**$_2$-CH_2-CH_2-N^+-CH_2-C**H**$_3$); 1.7 ppm (m, 2 H, CH_3CH_2-C**H**$_2$-CH_2-N^+-), 3.35 ppm (m, 2 H, CH_3CH_2-C**H**$_2$-CH_2-N^+-); 3.50 ppm (m, 6 H, CH_3CH_2-CH_2-C**H**$_2$-N^+-(C**H**$_2$-$CH_2OH)_2$); and 3.95 ppm (m, 4 H, -N^+-(CH_2-C**H**$_2$$OH)_2$). Analysis by ^{13}C NMR gave: 7.3 ppm (**C**H_3CH_2-CH_2-CH_2-N^+-); 13.0 ppm (CH_3CH_2-CH_2-CH_2-N^+-CH_2-**C**H_3); 19.2 ppm (CH_3**C**H_2-CH_2-CH_2-N^+-CH_2-CH_3); 23.3 ppm (CH_3CH_2-**C**H_2-CH_2-N^+-CH_2-CH_3); 55.0 ppm (CH_3C**H**$_2$-CH_2-**C**H_2-N^+-**C**H_2-CH_3); 59.5 ppm (CH_3CH_2-CH_2-CH_2-N^+-(**C**H_2-$CH_2OH)_2$); and 59.6 ppm (CH_3CH_2-CH_2-C**H**$_2$-N^+-(CH_2-**C**$H_2OH)_2$). Electrospray mass spectrometry (*A*: cation; *B*: anion): A^+ peak at 190.1, with a regular series of $[A(AB)_n]^+$ peaks observed at 190.1 + $n \times 317.0$ (Figure 2).

Intercalation reaction

Dimethyl sulfoxide-kaolinite pre-intercalate (DMSO-K). 10 g of kaolinite was added to a mixture of 60 mL of DMSO and 5 mL of H_2O. The suspension was maintained under magnetic stirring for 10 days at 80ºC. The mixture was then stirred for 5 days at room temperature. The resulting material was recovered after two series of washing-centrifugation, first using dioxane (2 × 50 mL), then isopropanol (2 × 50 mL). The product was finally dried at 50ºC, ground, and stored for further modification.

Grafting reaction

The synthesized ammonium salts (Am-1-*n*; n = 1−4) as well as butyldiethanolamine and dodecyldiethanolamine were grafted into kaolinite by a melt intercalation method using DMSO-K or Urea-K as the starting material. Typically, 2 g of the ammonium salt was added to 400 mg of DMSO-K (Am-*n*/DMSO-K = 5/1 w/w) at room temperature. The mixture was heated under a flow of N_2 gas. The temperature was ramped up to 180−190ºC and the suspension was maintained at this temperature for 2 h with magnetic stirring and under a flow of N_2. The excess

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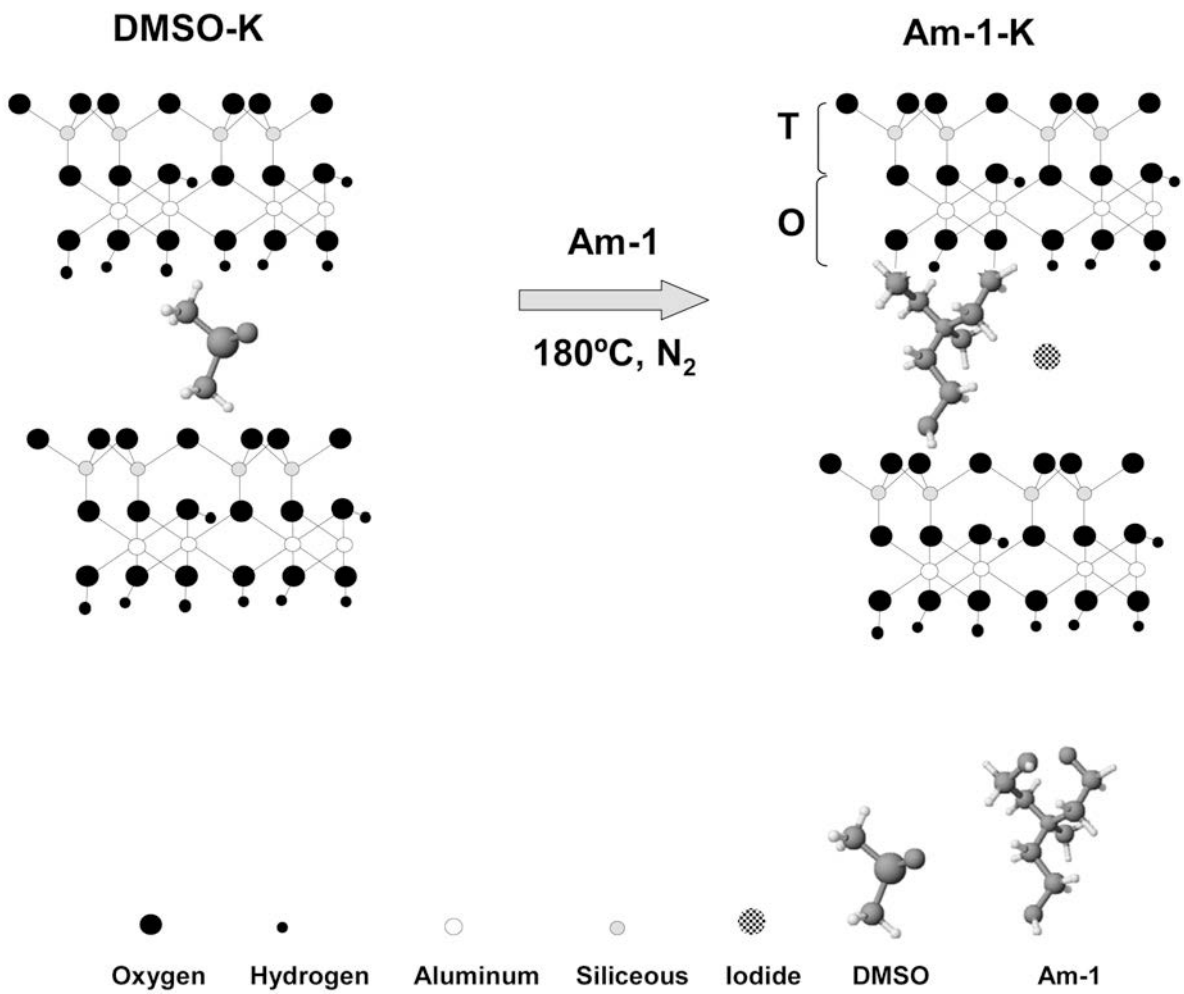


Figure 2. Illustration of the procedure of grafting ammonium ionic liquids onto the interlayer surfaces of kaolinite.

molten salt was removed after four series of washing-centrifugation, using deionized water. The solid sample recovered was dried at 60ºC overnight, ground, and suspended again in water and stirred for 72 h to remove residual DMSO and to confirm the grafting (Letaief and Detellier, 2007b).

Quaternarization reaction

0.5 g of kaolinite grafted with butyldiethanolamine or dodecyldiethanolamine was suspended in 5 mL of of iodomethane and iodoethane, respectively. The mixture was stirred for 72 h at 50ºC. The excess iodomethane or iodoethane was removed by filtration and the resulting functionalized kaolinite was recovered after a series of washings using isopropanol. The two quaternarized nanohybrid materials were labeled Am-5-K and Am-6-K.

Characterization

X-ray diffraction (XRD) patterns were obtained using a Philips PW 3710 instrument equipped with Ni-filtered Cu-Kα radiation (λ = 0.15418 nm) operating at 45 kV and 40 mA. Differential thermal analyses (DTA) and thermal gravimetric analyses (TGA) were recorded using an SDT 2960 Simultaneous DSC-TGA instrument under N_2 flow (100 mL/min) at a heating rate of 10ºC/min. Infrared spectra were collected using a Thermo Nicolet Nexus 670 FTIR E.S.P. spectrometer under dry air with 128 scans at a resolution of 4 cm^{-1}. The spectra were recorded using KBr pellets (95/5 (w/w)). Before recording a spectrum, a flow of hot air was circulated in the room containing the pellet for 30 min to remove any water molecules physically adsorbed on the sample. The ^{1}H and ^{13}C NMR spectra in solution were recorded using a Bruker 400 MHz spectrometer. Solid-state ^{13}C NMR CP/MAS spectra were collected using a Bruker AVANCE 500 NMR spectrometer operating at 125.77 MHz. The ^{13}C NMR chemical shifts were referenced to TMS at 0 ppm using the high-frequency signal of adamantane at 38.4 ppm as a secondary standard. ^{29}Si CP/MAS spectra were collected using a

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Bruker AVANCE 500 NMR spectrometer operating at 99.35 MHz. The ^{29}Si NMR chemical shifts were referenced to TMS at 0 ppm using the high-frequency signal of tetrakis(trimethylsilyl) silane at 29.9 ppm as a secondary standard.

RESULTS AND DISCUSSION

XRD

The d_{001} values of pure kaolinite, of kaolinite intercalated with DMSO, and of the nanohybrid materials obtained after treatment of DMSO-K with the ammonium salts (Am-1, Am-2, Am-3) followed by water washing for 72 h were deduced from the position of the 001 reflection observed on the XRD patterns (Figure 3). After intercalation of DMSO into the interlayer space of kaolinite (Figure 3b), a shift in the 001 reflection to a lower angle was observed due to the separation of the layers. The d_{001} value was 1.10 nm, similar to those reported previously (Letaief and Detellier, 2008a; Elbokl and Detellier, 2009). The intercalation ratio was >95%, an approximation based on the respective intensities of the 001 reflections of kaolinite and DMSO-K. In the case of the nanohybrid materials obtained by the reaction of DMSO-K with Am-1, Am-2, or Am-3, well defined 00l reflections were obtained, as well as the presence of the kaolinite 060 reflection, demonstrating the persistence of the *a,b* structure of kaolinite during the intercalation process (Rich, 1957). The d_{001} distances were in the range 1.12−1.16 nm for the nanohybrids Am-1-K, Am-2-K, and Am-3-K. The separation of the layers was close to the typical value of DMSO-K (1.10 nm) but different from the starting kaolinite (0.71 nm). The fact that the compounds resulting from the grafting process were not DMSO-K was confirmed by the hydrolysis treatment. The treatment of DMSO-K with water resulted in the displacement of DMSO from the interlayer space to produce a hydrate characterized by a d_{001} spacing of

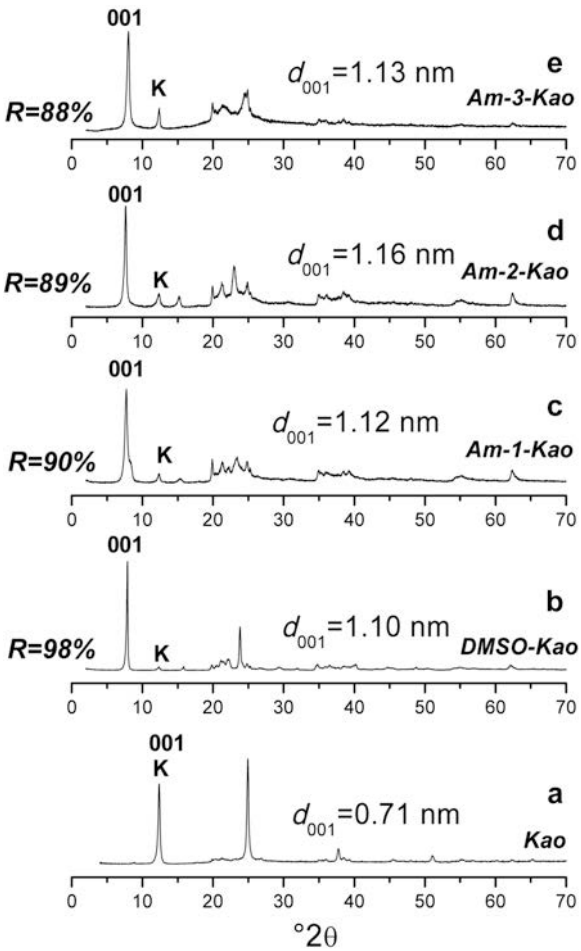


Figure 3. XRD patterns of: (a) pure kaolinite; (b) kaolinite intercalated with DMSO (DMSO-K); (c) kaolinite grafted with Am-1 (Am-1-K); (d) kaolinite grafted with Am-2 (Am-2-K); (e) kaolinite grafted with Am-3 (Am-3-K); K: reflection of kaolinite at 0.71 nm.

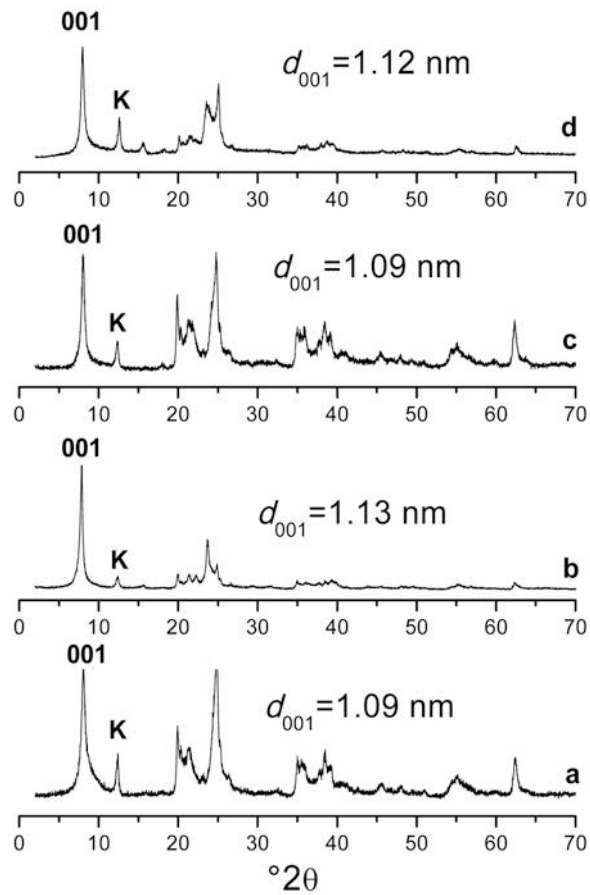


Figure 4. XRD patterns of: (a) kaolinite grafted with butyldiethanolamine; (b) sample a quaternarized by iodoethane (Am-5-K); (c) kaolinite grafted with dodecyldiethanolamine; (d) sample c quaternarized by iodomethane (Am-6-K).

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0.84 nm (Wada *et al*., 1987), while the nanohybrid materials Am-1-K, Am-2-K, and Am-3-K resisted the water treatment. The hydrolysis procedure is a good test of the success of the grafting procedure (Letaief and Detellier, 2007b). In the case of the sample prepared by treatment of DMSO-K with Am-4, the intercalation did not succeed. X-ray diffraction of the samples obtained after washing with isopropanol (without water treatment for 72 h) exhibited a 001 reflection close to 0.72 nm, indicating that DMSO was removed from the interlayer space of kaolinite during the intercalation attempt without concurrent intercalation of the ammonium salt. In a previous work, the successful intercalation of a series of various alkyl-substituted imidazolium salts into kaolinite was reported (Letaief and Detellier, 2007a). The intercalation was successful only when the number of carbon atoms in the aliphatic chain was <3, a conclusion reached in the present study also.

In another approach, the grafting of Am-4 was attempted in two steps: (1) grafting of butyldiethanolamine into the interlayer space of kaolinite; and (2) treatment by iodoethane. The resulting nanohybrid material obtained was named Am-5-Kao. The same procedure was followed by treating DMSO-K with dodecyldiethanolamine followed by functionalization with iodomethane. The resulting nanohybrid material was labeled Am-6-Kao. The d_{001} values obtained from the XRD patterns of the corresponding nanohybrid materials (Figure 4) indicated that the grafting of alkyldiethanolamine with >4 carbon atoms in the alkyl group resulted in an increase of the interlayer space of ~0.4 nm compared to the pristine kaolinite. This corresponds to an orientation in which the alkyl chain was maintained parallel to the individual kaolinite layers. Upon quaternarization with iodomethane and iodoethane, the d_{001} values remained essentially identical, suggesting that the orientation of the alkyl chain was not altered during the quaternarization process. The success of the quaternarization was corroborated by the observation of a signal at 52 ppm on the ^{13}C CP/MAS NMR spectra, as observed previously (Letaief *et al*., 2008).

^{13}C NMR

In the case of DMSO-K, the two peaks clearly observed on the ^{13}C CP/MAS NMR spectrum at 43.9 and 42.8 ppm (Figure 5a) were characteristic of the asymmetrical configuration of DMSO within the interlayer space (Hayashi, 1997). After grafting of the ammonium salts, they disappeared completely, confirming the

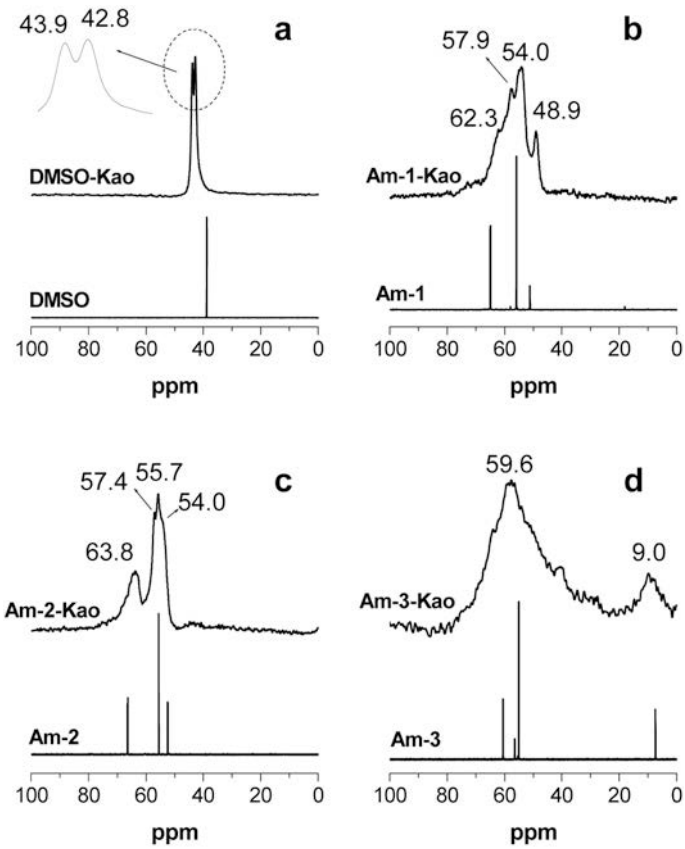


Figure 5. ^{13}C NMR spectra in solutions of: (a) DMSO; (b) Am-1; (c) Am-2; and (d) Am-3, and solid-state ^{13}C CP/MAS NMR spectra of the nanohybrid materials: (a') DMSO-K; (b') Am-1-K; (c') Am-2-K; and (d') Am-3-K.

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Table 1. ^{13}C NMR chemical shifts (ppm) of the ammonium ionic liquids and of the nanohybrid materials.

	$\delta_{C(\alpha)}$	$\delta_{C(\beta)}$	$\delta_{C(\gamma)}$	$\delta_{C(\delta)}$	$\delta_{C(\eta)}$	$\delta_{C(\nu)}$
Am-n[a]						
n = 1	55.9	64.9	51.1	–	–	–
n = 2	56.0	66.4	52.5			
n = 3	56.6	60.5	54.9	7.5		
n = 4	55.5	59.6	55.0	19.2	13.0	7.3
Am-n-K[b]						
n = 1	54–57.9	62.3	48.9			
n = 2	55.7–57.4	63.8	54.0			
n = 3	———	50–68	———	9.0		

a: Ammonium ionic liquids in solution (D_2O)
b: nanohybrid materials (solid state)

complete removal of DMSO. The ^{13}C CP/MAS NMR spectra clearly showed that the ammonium moiety remained intact after the grafting process. The solid-state spectra were characterized by chemical shifts close to those of the starting molecules in solution (see the Experimental section and Table 1).

TGA-DTG

A typical TG analysis of pure kaolinite (Figure 6a) showed that heating kaolinite results in a dehydroxylation of kaolinite with a maximum weight loss at 483ºC. The experimental weight loss was ~14% (w/w) corresponding to the theoretical weight loss (13.9%) during the transformation of kaolinite ($Al_2Si_2O_5(OH)_4$) to metakolinite ($Al_2Si_2O_7$). Upon intercalation of DMSO, three weight losses were observed (Figure 6b). The first, at 59ºC, corresponded to the removal of water physically adsorbed on the external surfaces. The second, with a maximum close to 154ºC, corresponded to the de-intercalation and decomposition of DMSO. The third, which occurred at 485ºC, corresponded to the dehydroxylation of the layers at a temperature close to that of kaolinite (483ºC). After grafting of the ammonium salts into the interlayer space of kaolinite, the TG-DTG traces of the resulting nanohybrids showed a marked difference from those of the pristine kaolinite and DMSO-K intercalate. At lower temperatures, the removal of water physically adsorbed on the external surfaces was observed. Further heating at temperatures >290ºC (from 294ºC to 390ºC) resulted in the decomposition of the organic moieties. The decomposition of the nanohybrid materials took place at greater temperature than the decomposition of materials prepared by intercalation of ammonium salts into montmorillonite (Hedley *et al.*, 2007). After decomposition of the ammoniums salts, the DTG traces showed two additional weight losses with a maximum between 430−450ºC and 498−511ºC. Both corresponded to the dehydroxylation of kaolinite. The number of ammonium salts grafted per structural unit of kaolinite, $Al_2Si_2O_4(OH)_4$, was calculated from the TGA analysis, taking into account the weight loss of water during the transformation of kaolinite to metakaolinite and the molecular weight of the ammonium salts. The stoichiometry of the various nanohybrids is summarized in Table 2.

FTIR

The FTIR spectrum of kaolinite exhibited four bands at 3695, 3670, 3653, and 3621 cm^{-1} in the region 4000−3200 cm^{-1} (Figure 7a). Those at 3695, 3670, and 3653 cm^{-1} corresponded to the interlayer hydroxyl stretching modes while that at 3621 cm^{-1} corresponded to the stretching vibrations of the internal hydroxyl group (Balan *et al.*, 2001). The intercalation of organic

Table 2. Total weight loss and number of moles of the ammonium salts grafted per kaolinite structural unit calculated from TG analysis.

Am-n-K	Total loss (%)	Stoichiometry
Am-1-K	28.85	$Al_2Si_2O_9H_{3.80}(C_{12}O_2H_{17}N^+I^-)_{0.20}$
Am-2-K	32.90	$Al_2Si_2O_9H_{3.70}(C_6OH_{15}N^+I^-)_{0.30}$
Am-3-K	32.37	$Al_2Si_2O_9H_{3.78}(C_8O_2H_{19}N^+I^-)_{0.22}$
Am-5-K	25.56	$Al_2Si_2O_9H_{3.86}(C_9OH_{21}N^+I^-)_{0.14}$
Am-6-K	35.5	$Al_2Si_2O_9H_{3.78}(C_{17}OH_{37}N^+I^-)_{0.22}$

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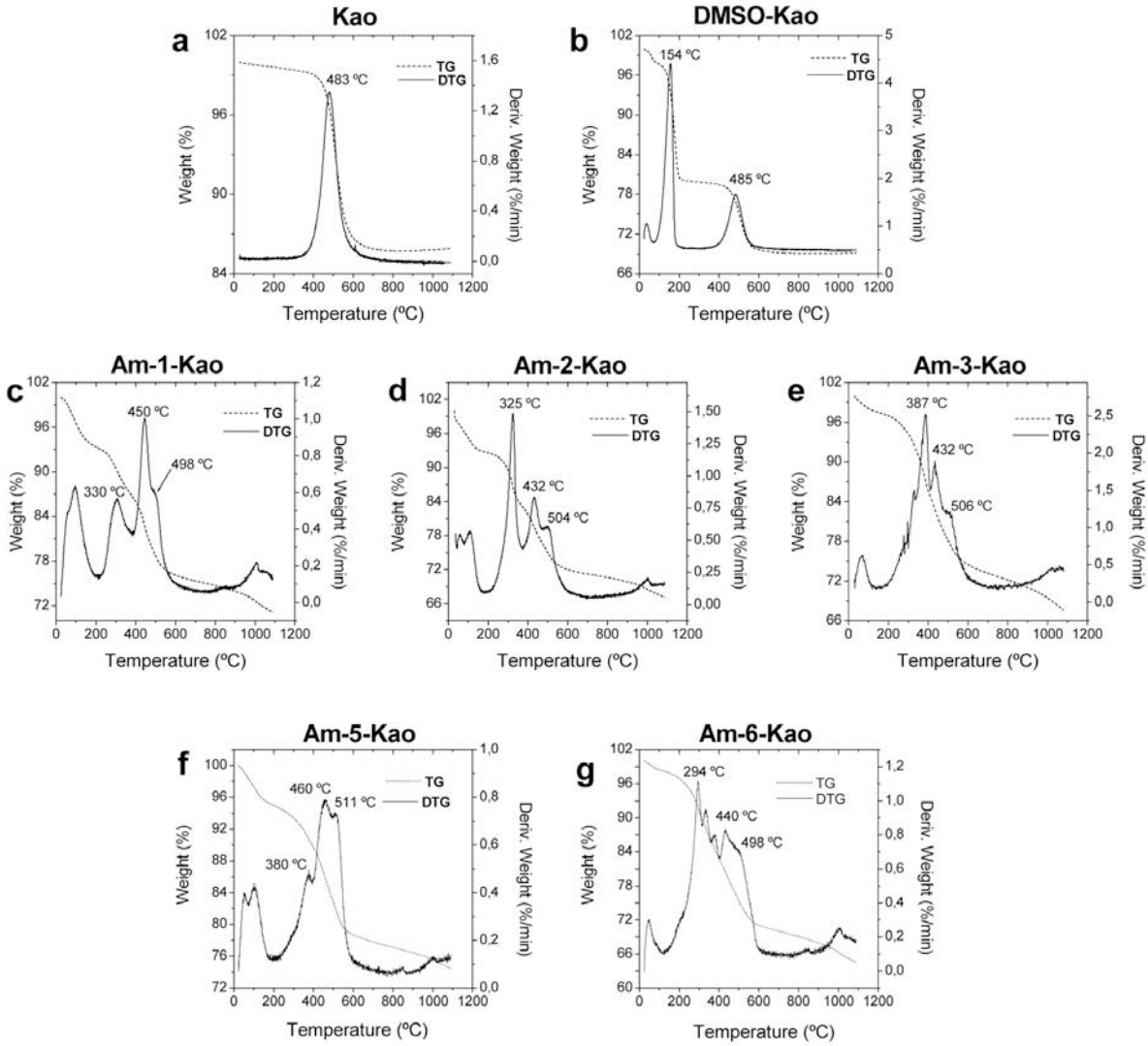


Figure 6. TG and DTG patterns of: (a) pure kaolinite (K); (b) kaolinite intercalated with DMSO (DMSO-K); kaolinite grafted with ammonium salts in one step; (c) kaolinite grafted with Am-1 (Am-1-K); (d) kaolinite grafted with Am-2 (Am-2-K); (e) kaolinite grafted with Am-3 (Am-3-K), and kaolinite grafted with ammonium salts in two steps; (f) Am-5-K and (g) Am-6-K.

entities into kaolinite broke some hydrogen bonds between the octahedral and tetrahedral sheets of adjacent layers, with the formation of a new hydrogen bond network resulting from the interaction of surface hydroxyl groups with the intercalated molecule. The evolution of the hydroxyl vibration modes gives information on the structural modifications taking place in the interlayer space. After intercalation of DMSO, the 3670 and 3653 cm^{-1} peaks disappeared completely (Figure 7a) and new peaks appeared at 3664, 3538, and 3503 cm^{-1}. The band at 3620 cm^{-1} remained unperturbed, which confirmed its attribution to the stretching of the inner hydroxyls. The two bands at 3538 and 3503 cm^{-1} could be attributed to the perturbed inner-surface hydroxyl groups, hydrogen bonded to the DMSO (Olejnik *et al*., 1968; Ledoux and White, 1967). After grafting of the ammonium salts, the FTIR spectra (Figure 7c,d) showed two shoulders at ~3666 and 3650 cm^{-1}, similar to those observed in the pristine kaolinite, revealing that the interlayer structure of kaolinite was less perturbed by the presence of the grafted moieties than by the intercalated DMSO. In the case of DMSO-K, one methyl group was keyed into the siloxane macro-ring, whereas in the nanohybrid materials of this study the side chain was plausibly not pointed into the siloxane macro-ring.

CONCLUSIONS

The first observations of the direct intercalation in kaolinite of potassium acetate and urea, made by Wada (1961) and Weiss (1961), respectively, were followed by

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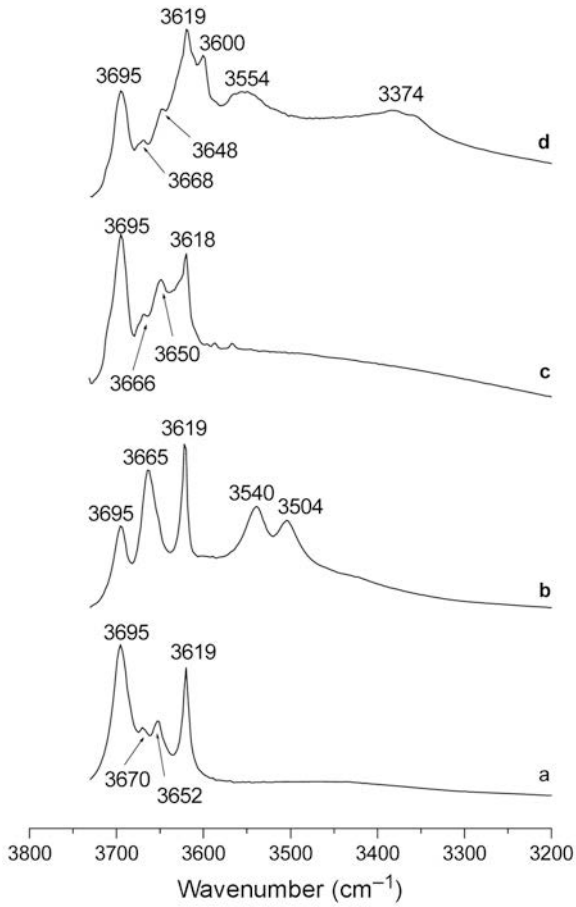


Figure 7. FTIR spectra (3730–3200 cm^{-1}) for: (a) kaolinite, (b) DMSO-K, (c) Am-3-K, and (d) Am-5-K.

the finding that a limited number of dipolar molecules or salts of organic anions could be intercalated directly into kaolinite. These intercalates could serve as pre-intercalates for the subsequent intercalation of a variety of relatively small organic molecules. More recently, a few examples of polymer intercalations were given, as well as the intercalation of salts of organic cations based on ionic liquids. In some cases, the intercalated molecules could be grafted by reaction with the aluminol groups of the interlayer surfaces.

In the present study, for the first time, tetra-alkylammonium derivatives were grafted directly onto the interlayer surfaces of kaolinite by the concurrent replacement of the pre-intercalated DMSO molecules. The intercalation and the grafting reaction were made possible by the use of ammonium-based ionic liquids, which, in a melt approach, allowed the use of the ammonium derivatives themselves as solvents. The direct grafting was successful in the cases of relatively short alkylammonium chains (*i.e.* <4 methylene, $-CH_2-$, units). For longer chains (butyl and dodecyl in this work), the corresponding aminoalcohol was intercalated and grafted in a first step, and the quaternarization was achieved in a subsequent step using alkyl-iodides.

New possibilities for the interlayer chemistry of kaolinite were described by demonstrating the functionalization of the grafted moieties and by creating new opportunities for controlled organic reactions in the confined, asymmetric, interlayer spaces of kaolinite. Even though, after 40 y, the interlayer chemistry of kaolinite is still poorly understood, the present work has shown the potential for creating new complexes and for the internal structuring of this remarkable clay mineral.

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