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Application of thermal analysis for the characterisation of intercalated and grafted organo-kaolinite nanohybrid materials

Sadok Letaief · Christian Detellier

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Abstract Nanohybrid materials resulting from the intercalation of ionic liquids or from the grafting of aminoalcohols into the interlayer space of kaolinite pre-intercalated with dimethyl sulfoxide (DMSO), were successfully synthesized. Thermal analysis (TG and DTA) data, coupled with X-ray diffraction (XRD) data, and ^{13}C MAS-NMR spectroscopic analysis, as well as with hydrolysis reactions, were used for qualitative and quantitative characterisations. In the case of intercalated nanohybrid materials obtained by insertion of ionic liquids and of ethanolamine into the interlayer spaces of kaolinite upon displacement of DMSO, no major changes in the dehydroxylation temperature of the layer sheets could be observed. The stoichiometry of the intercalated organo-kaolinite materials was obtained from several independent measurements (TG, CHN) and theoretical calculation (THM). They were in good agreement. Grafted nanohybrid materials resulting from the formation of a covalent bond between the hydroxyl groups of diethanolamine and triethanolamine and the internal surfaces aluminol groups of kaolinite exhibited a significantly lower dehydroxylation temperature. A combined approach of hydrolysis reactions and TG analysis allows an unambiguous distinction between grafted and intercalated organo-kaolinite nanohybrid materials.

Keywords Kaolinite · Clay minerals · Ionic liquids · Intercalated nanohybrid materials · Grafted nanohybrid materials · Thermal analysis · Intercalation · Grafting

Introduction

The combination of mineral matrices and organic compounds (ionic, molecular, monomer, polymer or macromolecular) exhibits multiple and varied interests [1, 2]. From a chemical point of view, it allows the formation of bi-functional materials, combining the chemical properties of the two partners [2–7]. This combination leads to the modification of the physicochemical properties of the support mineral (properties of surface, property of adsorption, hydrophobicity, etc.). Functional organic species can be immobilized and stabilized. Among these nanohybrid materials, organo-clays constitute a versatile area of investigation, which is due in particular to the broad availability of natural clay minerals and their ability to incorporate a large variety of functional molecules, including polymers [8–16].

Kaolinite is an abundant clay mineral widely available. It is a 1:1 phyllosilicate, characterised by a dioctahedral structure, with the chemical composition $Al_2Si_2O_5(OH)_4$ [17–19]. Due to strong interactions between the tetrahedral and the octahedral sheets through H-bonds and dipolar interactions, direct intercalation of bulky compounds onto the interlayer space of kaolinite has not yet been reported. However, the compounds resulting from the intercalation of small dipolar compounds such as dimethyl sulfoxide (DMSO), *N*-methylformamide (NMF) or urea can be used as precursors for further intercalations of other organic molecules or polymers.

Organoclays resulting from the intercalation of organic molecules in the interlayer spaces of kaolinite could be mainly classified in three categories of materials: (i) intercalated nanohybrid materials [9, 13, 20–24], (ii) grafted nanohybrid materials [25–34] and (iii) nanocomposites: intercalated or delaminated [35, 36]. In the case of

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S. Letaief (✉) · C. Detellier
Center for Catalysis Research and Innovation and Department of Chemistry, The University of Ottawa, Ottawa, ON K1N6N5, Canada
e-mail: sletaief@uottawa.ca

intercalated nanohybrid materials, the interaction between the organic guests and kaolinite is due mainly to weak van der Waals interactions. These materials do not resist a treatment with water. Upon treatment with water, the guest is displaced from the interlayer spaces resulting in the formation of kaolinite hydrate [37]. In the case of the grafted nanohybrid materials, the organic moieties are covalently linked to the octahedral layers after reaction with the aluminol groups. These compounds strongly resist hydrolysis with water. These grafted nanohybrids have been reported for different compounds, such as polyols and alkoxysilanes [29, 33, 34]. Finally, in the case of delaminated nanocomposites, the individual layers of kaolinite are completely dispersed in the polymer matrix. They are randomly dispersed without any particular orientation [36].

In this article, thermal analysis (TG and DTA) data, coupled with X-ray diffraction (XRD) data and ^{13}C MAS-NMR spectroscopic analysis are used for qualitative and quantitative characterisations of various nanohybrid materials derived from the kaolinite clay mineral.

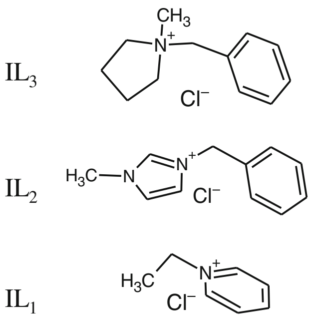
Sample preparation

Materials

Well-crystallized kaolinite (KGa-1b; Georgia) was obtained from the Source Clays Repository of the Clay Minerals Society, Purdue University, West Lafayette, IN, USA. The purification of KGa-1b was done according to the previously published procedures using standard sedimentation techniques and the <2 μm fraction was used in the following synthesis. Three ionic liquids, 1-ethylpyridinium chloride, 1-benzyl-3-methylimidazolium chloride and 1-benzyl-1-methylipyrrolidinium, were used in this study. They are labelled IL$_1$, IL$_2$ and IL$_3$, respectively (Scheme 1). IL$_1$ was purchased from Across Organics, it was used as received. IL$_2$ and IL$_3$ were synthesized according to the previously published procedures [38, 39]. DMSO, ethanolamine (EAO), diethanolamine (DEAO) and triethanolamine (TEAO) were purchased from Aldrich Chemicals and were used as received.

Dimethyl sulfoxide-kaolinite intercalate (DMSO-K)

10 g of kaolinite were 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 80 °C. The mixture was then allowed to stir for 5 days at room temperature. The resulting material was recuperated after two series of washing–centrifugation using first dioxane (2 × 50 mL), then isopropanol (2 × 50 mL). The product was finally dried at 50 °C.



Scheme 1 Chemical structures of the ionic liquids (IL$_1$, IL$_2$ and IL$_3$) used in the preparation of the nanohybrids using DMSO-K as precursor

Ionic liquid-kaolinite intercalates (IL-K)

IL-K (IL$_1$-K, IL$_2$-K, and IL$_3$-K) were prepared by a melt intercalation method using DMSO-K as starting material (Scheme 2). 1.6 g of the corresponding IL was added to 400 mg of DMSO-K at room temperature. The solid mixture was heated under a flow of nitrogen gas. The temperature was ramped up to 180 °C. The resulting suspension was then magnetically stirred at 180 °C during 2 h under a flow of nitrogen. The ionic liquid in excess was removed after four series of washing–centrifugation using isopropanol. The recuperated solid sample was dried at 60 °C overnight, grounded and stored for further characterisation.

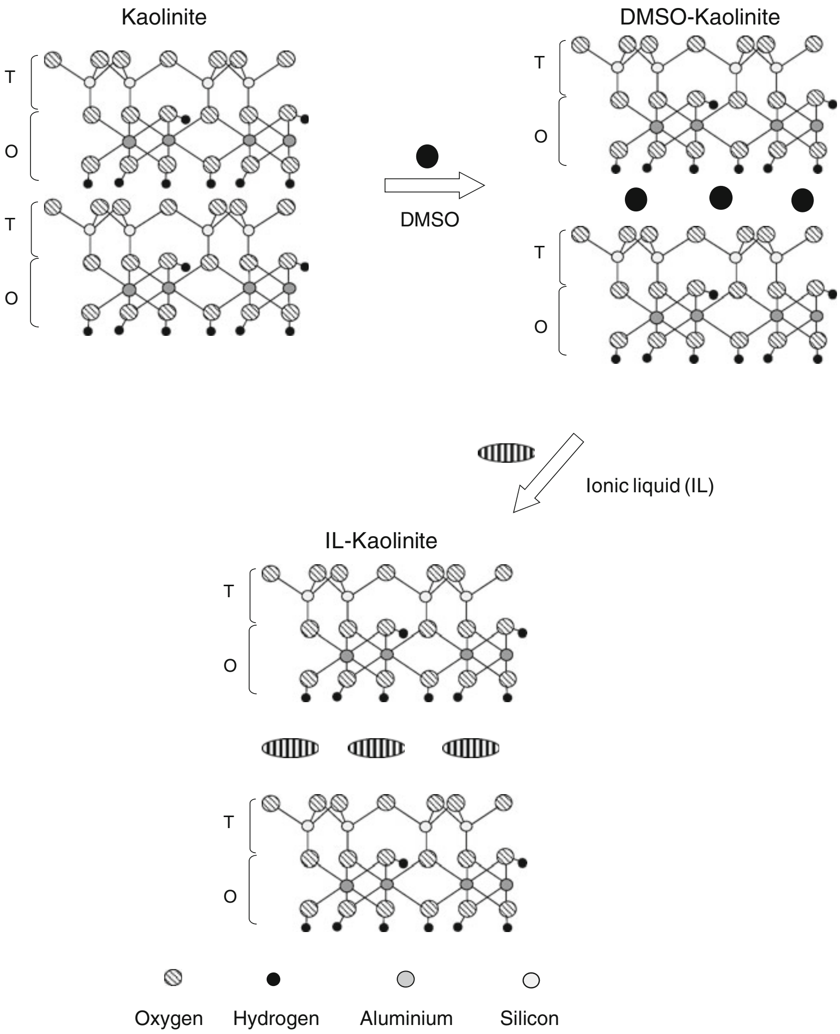
Intercalation or grafting of the aminoalcohols onto kaolinite (EAO-K, DEAO-K and TEAO-K)

DEAO and TEAO were grafted on the interlayer aluminol groups of kaolinite by a melt intercalation method using DMSO-K as starting material. One gram of DMSO-K was dispersed in 6 g of the aminoalcohol; the temperature of the mixture was then increased slowly from room temperature to 180 °C and maintained stable during 2 h. The resulting nanohybrid materials were recuperated after three series of centrifugation followed by washing with isopropyl alcohol (3 × 50 mL). The recovered solid samples (DEAO-K and TEAO-K) were dried at 60 °C overnight, grounded and stored for further characterisation. In the case of EAO, because the boiling point (170 °C) is lower than the ideal temperature of intercalation (180 °C), the reaction was done by refluxing for 2 h under N_2 a mixture containing 1 g of DMSO-K dispersed in 6 g of EAO.

Hydrolysis test

Hydrolysis test was used to confirm that the aminoalcohol molecules were grafted to the internal surfaces of kaolinite [31]. Half gram of the material resulting from the reaction

Scheme 2 Illustration of the intercalation process of ionic liquids into the interlayer space of kaolinite



of DMSO-K with the aminoalcohol was suspended in 100 mL of water and stirred for 48 h at room temperature. The solid sample was then separated by filtration, dried at 60 °C and stored for XRD characterisation.

Characterisation

XRD patterns were collected on a Philips PW 3710 instrument equipped with Ni-filtered and Cu K_α radiation ($\lambda = 0.15418$ nm) operating at 45 kV and 40 mA.

Differential thermal analyses (DTA) and thermal gravimetric (TG) analyses were recorded on a SDT 2960 Simultaneous DSC-TG instrument. Approximately 16 mg of clay was placed on the microbalance of the STA analyser, which was purged with nitrogen gas. The measurements were recorded from room temperature to 1,100 °C under nitrogen flow (100 mL min^{-1}) with an heating rate of 10 °C/min. Data analysis was performed using universal analysis 2000 software package.

Solid-state ^{13}C NMR CP/MAS spectra were collected on a Bruker AVANCE 500 NMR spectrometer operating at 125.77 MHz. Approximately 50 mg of sample were packed in 4 mm O.D. zirconia rotors which were spun at the magic angle at speeds between 10 and 14 kHz. A cross-polarization sequence was used. The ^{13}C chemical shifts were referenced to TMS at 0 ppm using the high frequency signal of adamantane at 38.4 ppm as a secondary standard.

Elemental analysis (CHN) was performed at Guelph Chemical Laboratories Ltd.

The ChemSketch program was provided by Advancement Chemistry Development Laboratories (ACD Labs).

Results and discussion

Ionic liquid-K nanohybrid materials

The intercalation of DMSO and of ionic liquids into kaolinite was followed by XRD techniques. The 001 reflection of kaolinite corresponds to an interlayer distance d_{001} of 0.71 nm (Fig. 1a). After intercalation of DMSO, a shift at lower angle of the 001 reflection of the DMSO-K intercalate can be observed, corresponding to an interlayer distance d_{001} of 1.10 nm (Fig. 1b). This increase of the interlayer space corresponds to the keying of one of the DMSO methyl groups in the siloxane rings of the tetrahedral sheets. The intercalation of the ionic liquids IL_1, IL_2 and IL_3 is also confirmed by a shift of the 001 reflection of the DMSO-K ($d_{001} = 1.10$ nm) to lower angles. The position of these reflections indicates an increase of the interlayer space upon displacement of DMSO and insertion of the ionic liquid. The increase of the interlayer space depends on the nature of the IL as well as on the size. The d_{001} of the interlayer space is 1.35, 1.53 and 1.40 nm, respectively, for the nanohybrids IL_1-K, IL_2-K and IL_3-K. Their oriented XRD patterns exhibit in general well developed 001 reflections (001, 002, 003 and 004) indicating that the kaolinite layer structure is preserved after the intercalation process. The intercalation ratio of these materials is very high, between 95 and 98%.

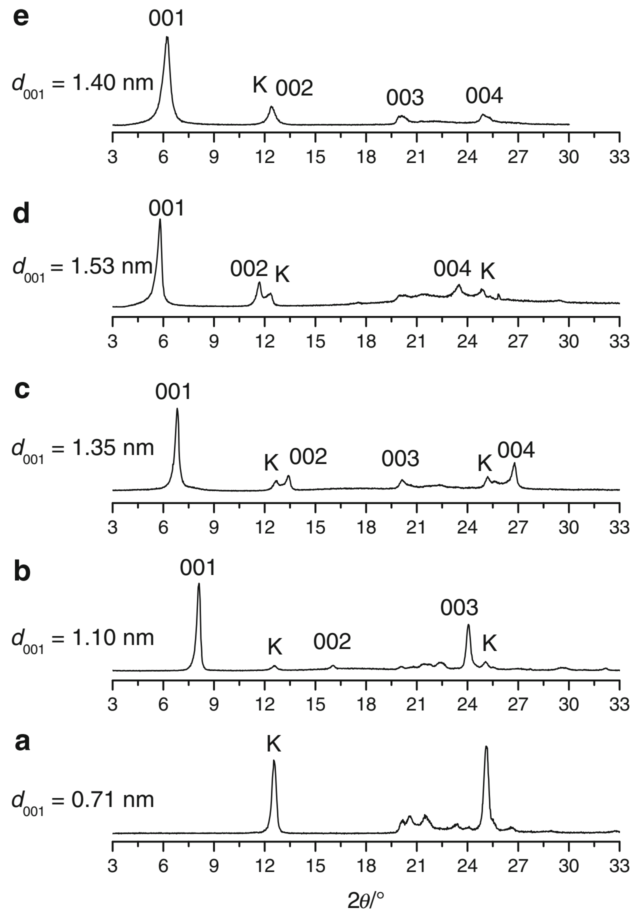


Fig. 1 XRD patterns ($2\theta = 3$–$33°$) of **a** pure kaolinite, **b** DMSO-K intercalate, **c** IL_1-K, **d** IL_2-K and **e** IL_3-K

^{13}C CP/MAS-NMR is a powerful technique that gives information on the structure of the intercalated species. DMSO-K spectrum is characterised by a doublet at 43.9 and 42.8 ppm due to the asymmetric location of DMSO within the interlayer spaces of kaolinite. The solid-state spectra of the ionic liquids–kaolinite intercalates are characterised by chemical shifts close to those of the starting organic salt in solution (Fig. 2b–d) [40–42]. This indicates that the ionic liquid moieties remain intact after the intercalation process. No doublet at 43.9 and 42.8 ppm corresponding to DMSO was observed, which confirms that DMSO was completely displaced by the ionic liquid from the interlayer spaces of kaolinite and removed from the solid during the washing process.

Unlike diffraction techniques and solid-state NMR spectroscopy that provide local and global information concerning the disposition of the guest (ionic liquid) inserted in the structure of the host (kaolinite), thermal analysis (TG–DTA–DTG) techniques provide qualitative and quantitative informations on the material, offering information on its thermal stability. The evolution of the thermal behaviour of the modified clay mineral is generally compared to the one of the starting clay mineral (unmodified host). In general, these differences are strongly related to the organization at the nanoscale of the nanohybrid materials resulting from a chemical modification. The TG–DTG traces of kaolinite show one mass loss at 512 °C (maximum on the DTG curve) corresponding to the dehydroxylation of the structure (Fig. 3). This mass loss (14% by mass) is due to the loss of the structural water of kaolinite during the transformation of kaolinite to metakolinite ($Al_2Si_2O_5(OH)_4 \rightarrow Al_2Si_2O_7 + 2H_2O$). It is associated in the DTA with an endothermic peak centred at 518 °C. The presence of an exothermic solid–solid transformation at 998 °C without variation of mass is also observed on the DTA curve, due to the crystallization of γ-Al_2O_3 [43–45].

After intercalation of DMSO, three mass losses were observed (Fig. 4). The first loss was observed below 100 °C, corresponding to the removal of externally adsorbed water, followed by a second loss at 179 °C, attributed to the removal and decomposition of DMSO, while the third one at 511 °C is due to the dehydroxylation of the layers. Once DMSO is removed, the behaviour of the remaining structure is essentially identical to what was observed in the case of pure kaolinite: (i) the dehydroxylation of the layer sheets takes place at approximately the same temperature and (ii) the exothermic peak due to the transition metakaolinite–mullite is also observed near 1,000 °C. Taking into account the molecular weight of kaolinite, the molecular weight of DMSO and the total mass loss observed during thermal treatment of DMSO-K (29.7%), it is possible to calculate the total amount of DMSO loaded on 1 unit

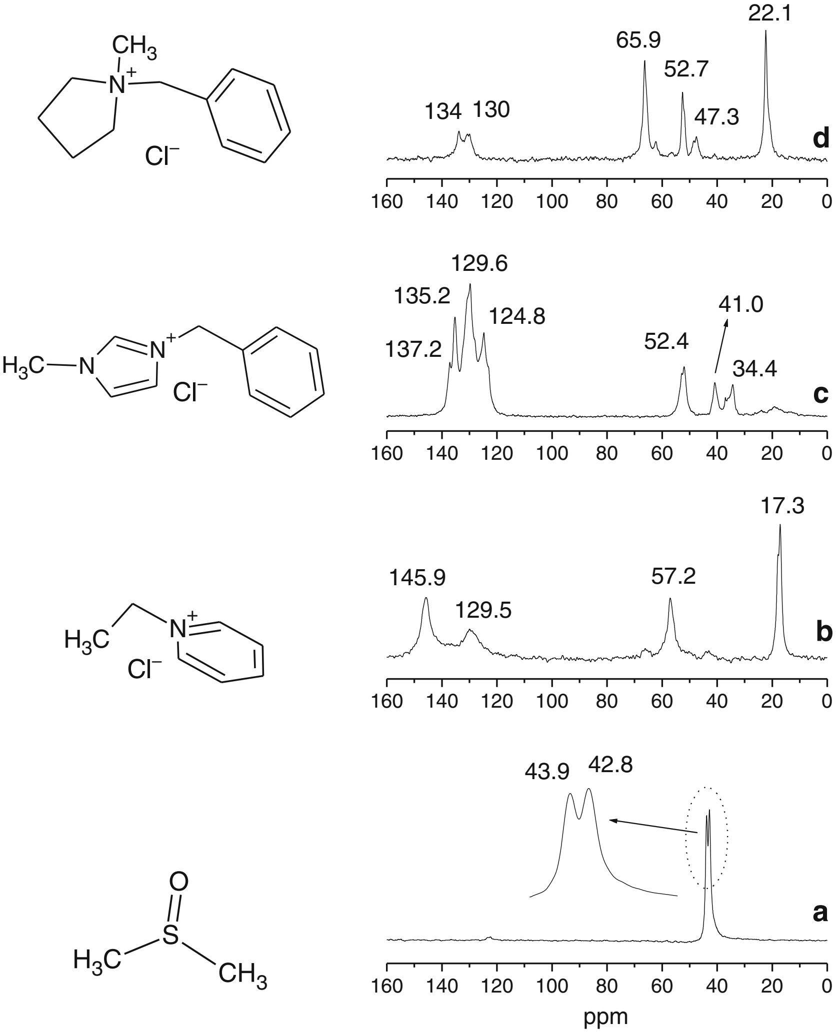


Fig. 2 Solid-state ^{13}C CP/MAS-NMR spectra of **a** DMSO-K intercalate, **b** IL_1-K, **c** IL_2-K and **d** IL_3-K

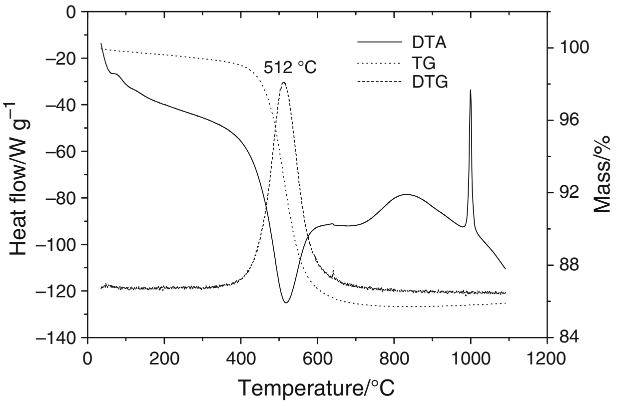


Fig. 3 DTA–TG curves (25–1,100 °C) for pure kaolinite

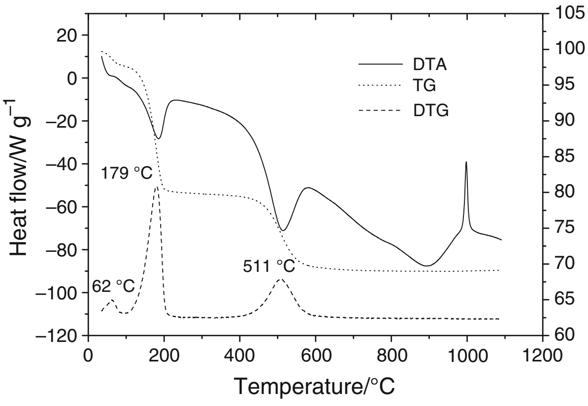


Fig. 4 DTA–TG curves (25–1,100 °C) of DMSO-K

structure of kaolinite. It corresponds to 0.75 mol of DMSO per unit structure of kaolinite. This value is in good agreement with the one calculated using CHN analysis.

The TG–DTG traces of IL_1-K, IL_2-K and IL_3-K are presented in Fig. 5a–c. Except the mass loss due to the physisorbed water observed at 76, 59, and 64 °C, respectively, for the nanohybrids IL_1-K, IL_2-K and IL_3-K, no mass loss was observed below 190 °C which indicates a complete elimination of the DMSO molecules from the interlayer space of kaolinite. This result corroborates those

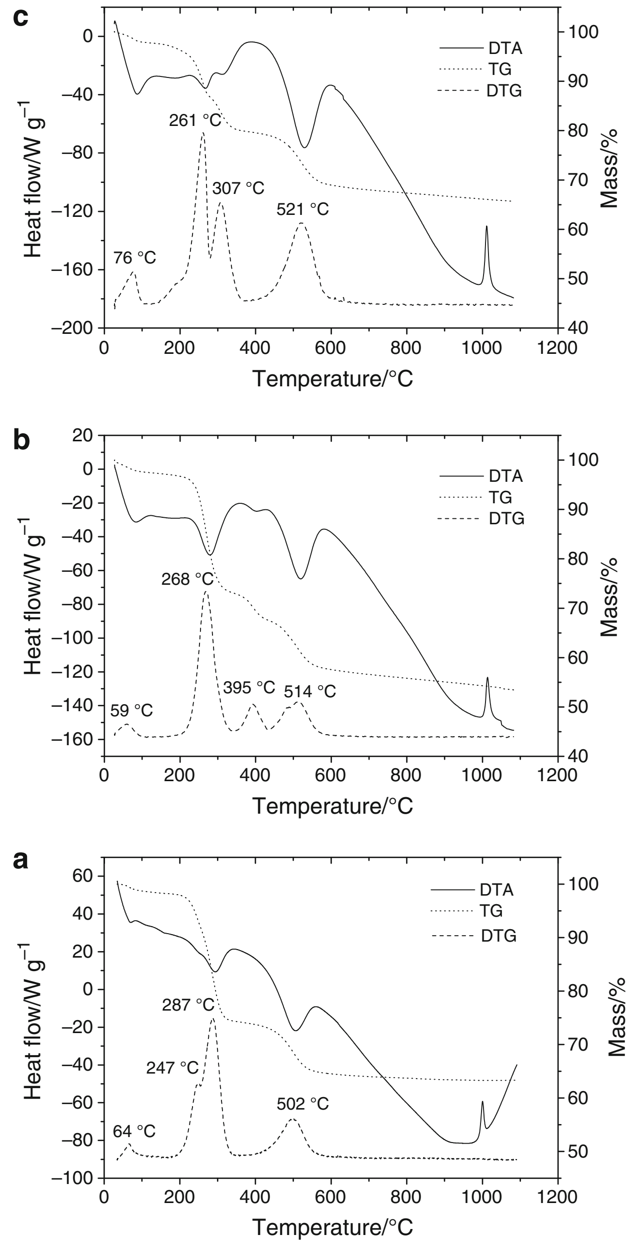


Fig. 5 DTA–TG curves (25–1,100 °C) of **a** IL$_1$-K, **b** IL$_2$-K and **c** IL$_3$-K

Table 1 Organic material content of the nanohybrid materials (number of moles of the IL per kaolinite structural unit $Al_2Si_2O_4(OH)_4$) calculated from TG analysis (n_{TG}), elemental analysis (n_{CHN}) and a theoretical model (n_{CHN})

	n_{TG}	n_{CHN}	n_{THM}
IL$_1$-K	0.58	0.52	0.57
IL$_2$-K	0.48	0.58	0.40
IL$_3$-K	0.38	0.32	0.36

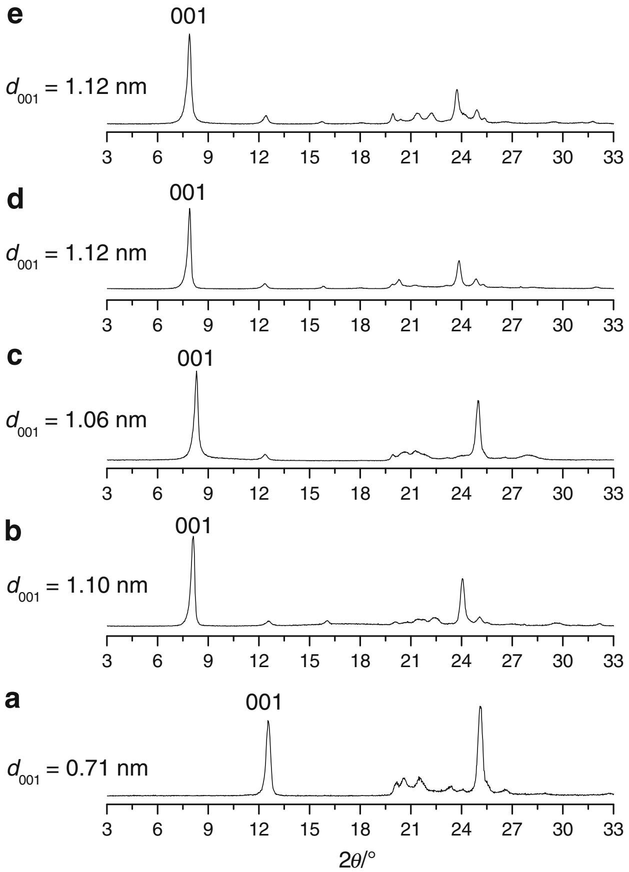


Fig. 6 XRD patterns ($2\theta = 3$–$33°$) of **a** pure kaolinite, **b** DMSO-K intercalate, **c** EAO-K, **d** DEAO-K and **e** TEAO-K

obtained from XRD and ^{13}C NMR analysis. TG–DTG traces show that ILs are removed from the interlayer spaces of kaolinite and are decomposed at high temperatures, between 240 and 400 °C. This observed relatively high thermal stability plausibly results from the strong interactions between the IL and the surface Al–OH (aluminol) groups through H–π interactions. After elimination of the organic material from the interlamellar space of kaolinite, the evolution of the DTA and TG curves of the modified kaolinite is identical to the non-treated kaolinite, indicating that the clay lattice was not modified during the intercalation process. This means that there was only intercalation, with no evidence of grafting reactions between the organic moieties and the aluminol groups. This conclusion was confirmed by the hydrolysis test. XRD results (patterns not shown) indicate that the materials subjected to the hydrolysis test were identical to hydrated kaolinite (main peak at 0.84 nm) [37], in which the ionic liquid was replaced by water.

The amounts of ILs loaded into the interlayer space were determined from the total mass loss during the thermal treatment of the nanocomposites. The amounts of IL loaded per 1 unit structure of kaolinite (n_{THA}) were calculated and were compared to those obtained by CHN analysis (n_{CHN}) and theoretical model (n_{THA}) using the

ChemSketch program (Table 1). There is a good agreement between the values obtained by different techniques.

Aminoalcohol-K nanohybrid materials

XRD patterns of the EOA-K, DEOA-K and TEOA-K are presented on Fig. 6c–e. They are characterised by an intense 001 reflection corresponding to an interlayer distance d_{001} of 1.06 nm for the EAO-K and 1.12 nm for both nanohybrid materials DEOA-K and TEOA-K. Contrary to the case of bulky ionic liquids, where it is possible to confirm the intercalation from the position of the 001 reflection, in the case of aminoalcohols, since the d_{001} of the nanohybrid material is very close to the d_{001} of DMSO-K (1.10 nm), XRD patterns cannot provide direct indications on the replacement of DMSO by the aminoalcohol. This could, however, be demonstrated by the ^{13}C MAS-NMR spectra (figure not shown) and also by thermal analysis. In the case of EOA-K, DEOA-K and TEOA-K no peaks corresponding to the removal of DMSO were detected around 180 °C like in the case of DMSO-K (Fig. 4), which indicates that DMSO was completely

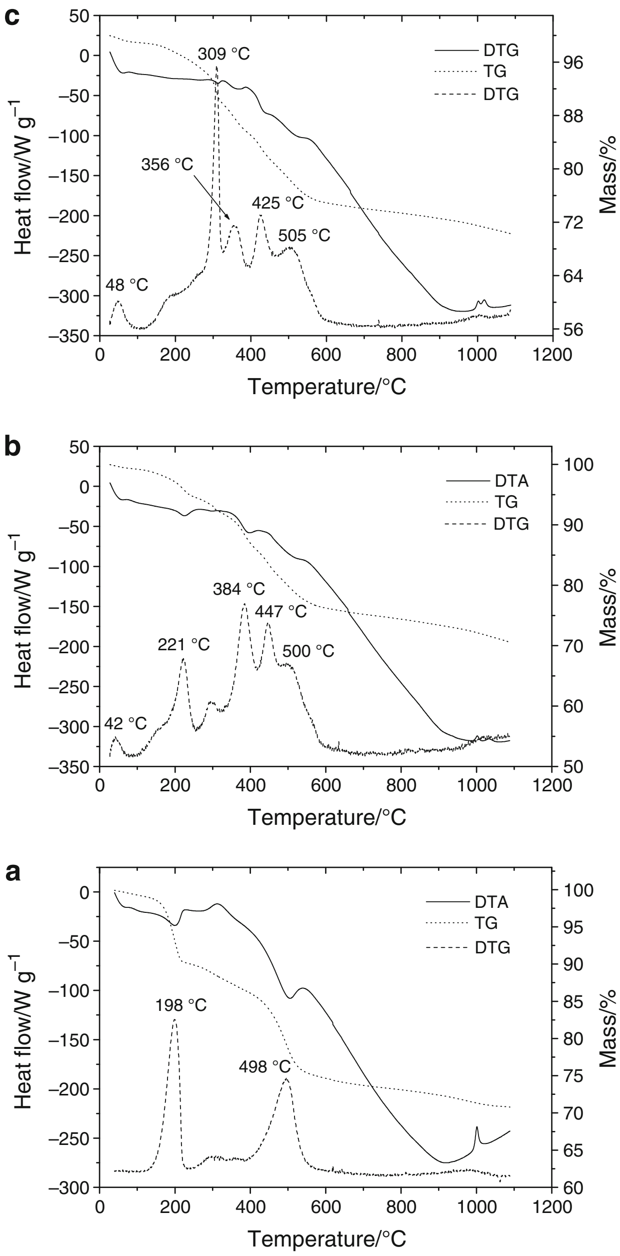


Fig. 7 DTA–TG curves (25–1,100 °C) of **a** EAO-K, **b** DEAO-K and **c** TEAO-K

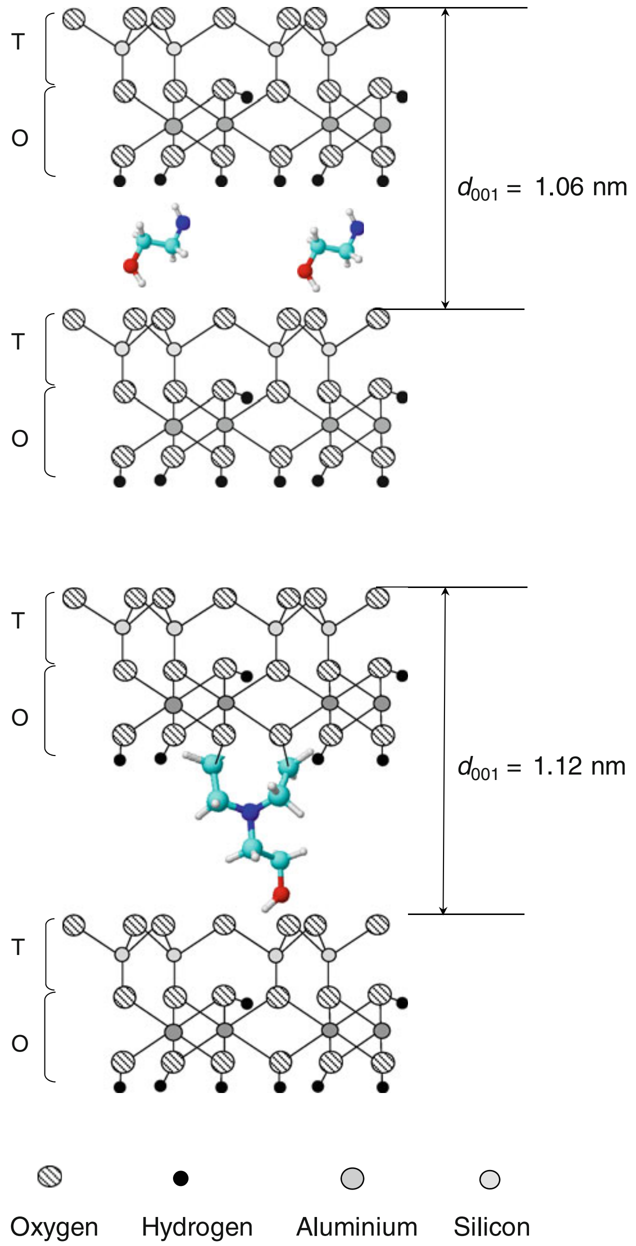


Fig. 8 Illustration of the structure of the nanohybrid materials resulting from **a** intercalation of EAO and **b** grafting of TEAO

removed from the interlayer space during the reaction with the aminoalcohol. EOA was removed and decomposed at a lower temperature, 198 °C, compared to the DEOA and TEOA which are more temperature resistant. They are decomposed at temperatures higher than 350 °C. One could observe that the dehydroxylation of the layer sheets occurs at 498 °C in the case of EAO-K. This temperature is close to the one of pure kaolinite and DMSO-K, an indication that EAO is intercalated, not grafted into the interlayer space as shown in Fig. 8a. This observation was confirmed by an hydrolysis test (see below). In the case of DEOA-K and TEOA-K (Fig. 7b, c) the dehydroxylation of kaolinite takes place at lower temperatures, 447 and 425 °C, respectively. This behaviour was observed also by Gardolinsky and Lagaly [35] in the case of the grafting of alcohols and polyols in the interlayer space of kaolinite. This confirms that DEOA and TEOA are covalently grafted to the aluminol groups of kaolinite (Fig. 8b).

An hydrolysis test was used to confirm the nature of the nanohybrid material: intercalated or grafted. In the case of EOA-K, EOA was displaced by washing with water during 1 h and the original kaolinite was recovered. One could conclude that EOA-K is not resistant to hydrolysis. Whereas, in strong contrast, the grafted derivatives (DEOA-K and TEOA-K), resulting from esterification of the aluminol surfaces, are stable towards extensive washing (48 h). The two 001 peaks were slightly shifted to lower values, corresponding to a d_{001} of 1.07 and 1.08 nm, respectively. [31] This experiment gives good support to the results obtained by thermal analysis. The two aminoalcohols with higher local hydroxyl group concentrations have reacted with the internal aluminol surfaces, whereas the EAO is only intercalated without any reaction with the aluminol groups.

Conclusions

Based on the results of characterisation from thermal analysis of a series of nanohybrid derivatives of kaolinite and taking into account the dehydroxylation temperature of the pristine clay (typically 510 °C), the nature of nanohybrid materials obtained by modification of kaolinite can be predicted. In particular, a clear distinction can be made between materials obtained by intercalation of organic molecules in the interlayer spaces of kaolinite and materials obtained by their intercalation followed by covalent grafting on the kaolinite internal surfaces. An hydrolysis test can be used to differentiate: grafted materials are resistant while intercalates will result in the formation of hydrated kaolinite. In addition to this test, TG analysis will provide additional bias for discrimination: not only will the organic moieties be generally decomposed at higher temperatures in the case of the grafted materials, but while the dehydroxylation of intercalates will take place at temperatures close to the one of the pristine kaolinite mineral (near 510 °C), the dehydroxylation of the grafted nanohybrid materials will occur at quite lower temperatures, typically in the range 400–460 °C.

This combined approach, hydrolysis reaction and TG analysis, allows an unambiguous distinction between grafted and intercalated materials.

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