IONIC LIQUIDS-KAOLINITE NANOSTRUCTURED MATERIALS. INTERCALATION OF PYRROLIDINIUM SALTS

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Abstract—Ionic liquids intercalated in kaolinite constitute a novel class of nanostructured material. Kaolinite-pyrrolidinium halide intercalates have been prepared successfully by reacting the pyrrolidinium salts with kaolinite which was preintercalated with dimethyl sulfoxide (DMSO) using the melt condition under N_2. X-ray diffraction, ^{13}C magic angle spinning nuclear magnetic resonance, differential thermal analysis (DTA)-thermal gravimetric analysis, and Fourier transform infrared spectroscopy confirm the displacement of DMSO during the intercalation process. Based on results from the various characterization techniques, a structural model is proposed in which one mole of the pyrrolidinium salt covers two or three structural units of kaolinite, depending on the structure and size of the salt. The thermal stability was improved remarkably after intercalation of the pyrrolidinium salts, compared to the pre-intercalate. The DTA-TGA data show that the largest number of organic units released and decomposed, occurs under N_2 flow, at temperatures ranging from 260 to 340ºC, depending on the nature of the intercalated organic salts.

Key Words—^{13}C CP/MAS NMR, FTIR, Intercalation, Ionic Liquids, Kaolinite, Nanohybrid Materials, Nanostructured Materials, Pyrrolidinium, ^{29}Si CP/MAS NMR, TGA, XRD.

INTRODUCTION

The design, synthesis, and characterization of nanohybrid materials for various applications constitute a great challenge, involving a large interdisciplinary community. An example of these nanohybrid materials is the intercalation of functional organic molecules in the interlamellar spaces of kaolinite.

Kaolinite is one of the most representative of the 1:1 phyllosilicate clays; each non-expandable layer consists of an octahedral sheet linked to a tetrahedral sheet (Bailey, 1988). The ideal chemical composition of kaolinite is $Al_2Si_2O_5(OH)_4$. Kaolinite is interesting as a mineral precursor due to its unique asymmetric layered structure with $(SiO)_6$ macro-rings on one side and aluminol groups on the other side. This asymmetry creates large superposed dipoles in the lamellar structure, resulting in a large cohesive energy. Kaolinite can intercalate some organic molecules, but with difficulty, compared to swelling clays such as smectites (Lagaly *et al.*, 2006; Frost and Kristof, 2004). The surface modification of kaolinite can be achieved through the grafting of alcohol or diols onto the aluminol surface (Tunney and Detellier, 1993, 1994, 1996a, 1996b; Komori *et al.*, 1999; Gardolinski *et al.*, 2000; Itagaki *et al.*, 2001; Brandt *et al.*, 2003; Itagaki and Kuroda, 2003; Murakami *et al.*, 2004; Elbokl and Detellier, 2005, 2006; Gardolinski and Lagaly, 2005a, 2005b; Letaief and Detellier, 2007a).

Ionic liquids are organic salts that are usually liquids below 100ºC. They are attractive solvents, as they are non-volatile, non-flammable, have high thermal stability, and are relatively inexpensive to manufacture. They are currently receiving considerable attention as a new alternative reaction medium for chemical and biocatalytic reactions, and are qualified as ''green solvents'' (Earle and Seddon, 2000; Yang and Pan, 2005; Winterton, 2006). They could potenially be used in organic synthesis, extraction, catalysis, nanofiltration, and separation (Branco *et al.*, 2002a, 2002b; Sekhon *et al.*, 2006). Due to their high decomposition temperature, ~350ºC, they have been incorporated into porous membranes to form so-called ''functional supported ionic liquid membranes'', and have also been used for high-temperature sensing (Yu *et al.*, 2005; Buzzeo *et al.*, 2004). Pyrrolidinium salts have significant ionic conductivity, 7×10^{-3} S cm^{-1}, in their solid state (Sun *et al.*, 2001), which has led to much interest in terms of using them as electrolytes in electrochemistry applications (Wang *et al.*, 2005).

The present authors were able to synthesize, easily and economically, modified kaolinite nanohybrid materials by intercalation of pyridinium and imidazolium salts (Letaief and Detellier, 2005; Letaief *et al.*, 2006; Letaief and Detellier, 2007b). In this paper, we report the intercalation of pyrrolidinium salts in kaolinite by using the dimethyl sulfoxide-kaolinite (DMSO-K) pre-intercalate as a starting material. To the best of our knowledge, this is the first report of the intercalation of pyrrolidinium salts into the interlayer spaces of kaolinite. The prepared nanohybrid materials were characterized using various techniques such as X-ray diffraction

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(XRD), Fourier transform infrared (FTIR) spectroscopy, and magic angle spinning nuclear magnetic resonance (MAS NMR), as well as elemental and thermal analyses.

EXPERIMENTAL

Materials

Well crystallized kaolinite (KGa-1b; Georgia) was obtained from the The Clay Minerals Society Source Clays Repository, located at Purdue University, West Lafayette, Indiana, USA. The purification of KGa-1b and the preparation of the DMSO-K were carried out according to previously published procedures (Letaief and Detellier, 2005; Letaief *et al.*, 2006). Three pyrrolidinium salts were synthesized using variations of published procedures (Zhou *et al.*, 2004, 2006). Their structures are presented in Table 1 and their ^{13}C NMR chemical shifts are listed in Table 3.

Intercalation reaction

The pyrrolidinium salts were intercalated into kaolinite by a melt-intercalation method, using DMSO-K as the starting material. Typically, 1.6 g of the pyrrolidinium salt were added to 400 mg of DMSO-K (Im/DMSO-K w/w = 4/1) at room temperature. The mixture was heated under a flow of N_2 gas. The temperature was ramped up to 180ºC. During the heating, the modified clay (DMSO-K) was well dispersed in the melt. The suspension was then stirred magnetically at 180ºC for 2 h under a flow of N_2. The excess molten salt was removed using isopropanol, after

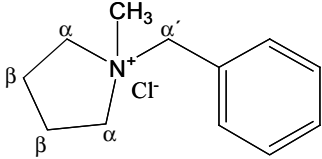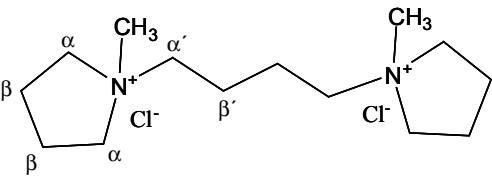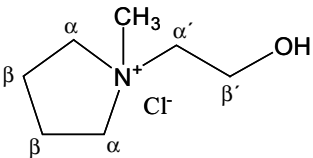four series of washing and centrifugation. The recuperated solid sample was dried at 60ºC overnight.

CHARACTERIZATION

Powder XRD patterns were obtained on a Philips PW 3710 diffractometer (CuKα radiation; λ = 1.54059 Å), using a generator voltage of 45 kV and current of 40 mA. Differential thermal analysis (DTA) and thermal gravimetric analysis (TGA) was recorded using an SDT 2960 instrument under N_2 flow (100 mL/min) with a heating rate of 10ºC/min. Infrared spectra were acquired on a Thermo Nicolet Nexus 670 FT-IR ESP spectrometer under dry air using 128 scans with a resolution of 4 cm^{-1}. The spectra were recorded using KBr pellets. The ^{1}H and ^{13}C NMR spectra in solution were recorded using a Bruker 300 MHz spectrometer. Solid-state ^{13}C CP/MAS NMR spectra were collected using a Bruker AVANCE 500 NMR spectrometer operating at 125.77 MHz for [13]C. ^{29}Si CP/MAS NMR spectra were collected using a Bruker AVANCE 500 NMR spectrometer operating at 99.35 MHz for [29]Si.

RESULTS

The oriented XRD patterns of the starting DMSO-K pre-intercalate and of the nanohybrid materials, are shown in Figure 1. In general, they exhibit a well developed 00*l* reflection (001, 002, 003, and 004), indicating that the kaolinite layer structure is preserved after the intercalation process. In all cases, the d_{060}

Table 1. Chemical structures of the ionic liquids used in the preparation of the nanohybrid materials derived from kaolinite.

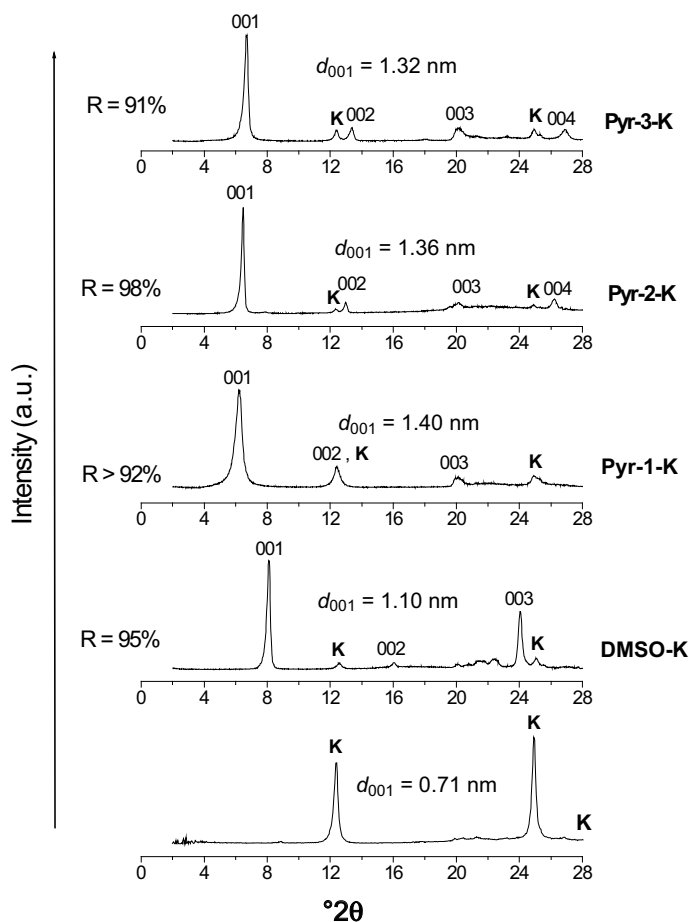| Ionic liquid	Structure	State at room temperature
Pyr-1		liquid
Pyr-2		solid-hygroscopic
Pyr-3		liquid

Figure 1. Oriented XRD patterns of kaolinite intercalated with DMSO (DMSO-K) and of kaolinite intercalated with pyrrolidinium salts (Pyr-*n*-K, *n* =1−3).

reflection of kaolinite (not shown) remains at 1.49 Å, characteristic of a dioctahedral clay mineral, also showing that the structure of the layers of kaolinite is largely unaffected by the intercalation process. The intercalation of pyrrolidinium salts into the interlamellar spaces of kaolinite is clearly observed by a shift of the 001 reflection to lower angles, upon displacement of DMSO (the d_{001} of DMSO-K is 1.10 nm). The values of d_{001}, of Δd_{001} (obtained by subtracting the kaolinite c spacing, 0.71 nm, from the observed d_{001}), of the intercalation ratio, R (obtained as an approximation, from the relative intensities of the d_{001} peaks of the intercalate and of the non-intercalated kaolinite), and of two independent determinations of the organic content of Pyr-*n*-K, n_{TGA}, and n_{EA}, obtained from the TGA analysis and the elemental analysis, respectively, are indicated in Table 2. The d_{001} expansion (Δd_{001}) values are between 0.6 nm (Pyr-2, Pyr-3) and 0.7 nm (Pyr-1). The intercalation ratio varies in the range 92−98%, values expected on the basis of previous intercalation studies in kaolinite (Gardolinski *et al.*, 2000; Itagaki *et al.*, 2001; Brandt *et al.*, 2003; Itagaki and Kuroda, 2003; Murakami *et al.*, 2004; Elbokl and Detellier, 2005, 2006;

Gardolinski and Lagaly, 2005a; Tunney and Detellier, 1997; Deng *et al.*, 2002). The XRD peak characteristic of DMSO-K is removed completely in all cases, indicating a complete replacement by Pyr-*n* (*n* = 1−3) of the DMSO-intercalated molecules.

The ^{13}C CP/MAS NMR spectra of the nanohybrid materials obtained by intercalation of the pyrrolidinium salts are shown in Figure 2, along with a spectrum for the starting material. In DMSO-K the two peaks

Table 2. Basal spacing (d_{001}), interlamellar expansion (Δd_{001}), intercalation ratio (R), and organic material content of the nanohybrid materials (number of moles of the pyrrolidinium derivative per kaolinite structural unit, $Al_2Si_2O_4(OH)_4$), calculated from (a) TGA analysis, and (b) elemental analysis.

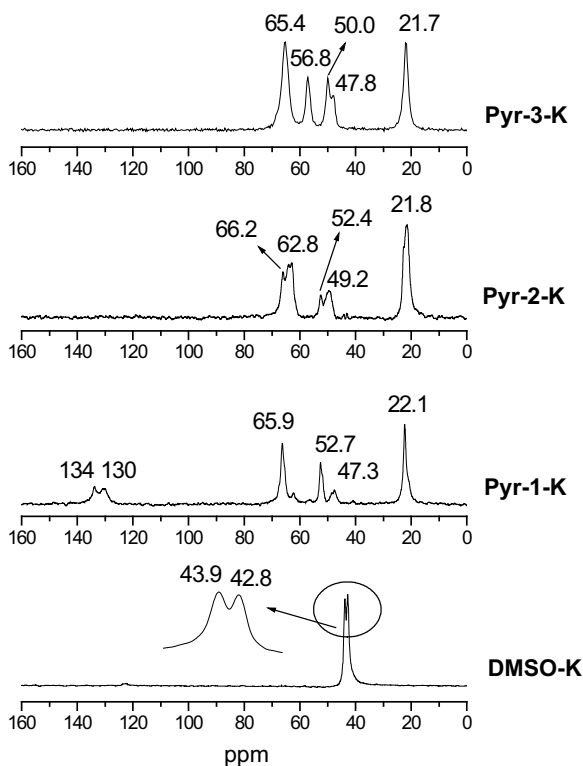|	d_{001} (nm)	Δd_{001} (nm)	R (%)	n_{TGA}[a]	n_{EA}[b]
Pyr-1-K	1.40	0.69	>92	0.38	0.32
Pyr-2-K	1.36	0.65	98	0.26	0.21
Pyr-3-K	1.32	0.61	91	0.53	0.60

Figure 2. Solid-state ^{13}C CP/MAS NMR spectra for the starting material (DMSO-K) and kaolinite intercalated with pyrrolidinium salts (Pyr-*n*-K, *n* =1−3).

characteristic of the asymmetric location of DMSO within the interlamellar spaces of kaolinite are clearly observed at 43.9 and 42.8 ppm (Hayashi, 1997). These peaks are absent in spectra of Pyr-*n*-K, confirming the complete removal of DMSO upon intercalation of the pyrrolidinium salts. The ^{13}C NMR spectra clearly show that the pyrrolidinium moiety remains intact after the intercalation process. The solid-state spectra are characterized by chemical shifts close to those of the starting molecules in solution. For example, the ^{13}C NMR of Pyr-3-K showed signals at 21.7, 47.8, 50.0, 56.8, and

65.4 ppm, assigned to the CH_3, CH_2 (β), CH_2 (α′), CH_2 (β′), and CH_2 (α) groups, respectively (Table 3). In the case of Pyr-1-K and Pyr-2-K, the ^{13}C NMR signals are also in agreement with the pyrrolidinium structures presented in Table 1 (see Table 3).

The thermal decomposition of the nanohybrids was studied by conventional thermal methods (TGA, DTA) as well as by XRD, after heating at various temperatures (pattern not shown). The DTA-TG analysis showed results similar to those observed in the case of intercalates of pyridinium (Letaief and Detellier, 2005; Letaief *et al.*, 2006), and of imidazolium (Letaief and Detellier, 2007a) salts. Typically, a first loss is observed below 100ºC, corresponding to the removal of externally adsorbed water. Loss of material at ~180ºC, which would correspond to the decomposition of DMSO, was not observed. This confirms that all the DMSO molecules were replaced during the intercalation process. The removal of the organic salts takes place in a number of steps, similar to the removal of imidazolium salts (Figure 3). The release and the pyrolysis of the pyrrolidinium salts take place between 260 and 440ºC. The loss of material observed between 440 and 525ºC is attributed to the decomposition of the remaining organic units concurrently with dehydroxylation of kaolinite. In the case of Pyr-2-K, the dehydroxylation temperature is less than in kaolinite, as is usually observed for intercalated kaolinite derivatives, whereas for the Pyr-1-K, the dehydroxylation temperature is slightly greater. In all cases, the solid-solid exothermic transformation occurred at temperatures near 1000ºC, as in the starting kaolinite (Figure 4). The number of moles of organic material loaded in the nanohybrids was obtained from TGA analysis (n_{TGA}), and from elemental analysis (n_{EA}). Table 2 gives the number of moles of pyrrolidinium salt per structural unit of kaolinite, $Al_2Si_2O_5(OH)_4$. The number of organic molecules loaded in the interlamellar spaces is smaller for larger salts, borne out by observations of the space occupied by the organic cation along the *a* and *b* axes.

Figure 5 shows IR spectra for kaolinite (K), the starting material (DMSO-K), and the intercalated materials (Pyr-*n*-K, *n* = 1−3). The kaolinite and

Table 3. ^{13}C NMR chemical shifts (ppm).

	δ_{CH_3}	$\delta_{C\alpha}$	$\delta_{C\beta}$	$\delta_{C\alpha'}$	$\delta_{C\beta'}$	δ_{CAr}[c]
Pyr-*n*[a]						
n = 1	23.6	69.3	50.7	66.3	−	135.3−130.9
n = 2	22.5	64.2	48.4	62.3	46.0	−
n = 3	21.2	65.0	48.5	55.9	65.3	−
Pyr-*n*-K[b]						
n = 1	22.1	65.9	52.7; 47.3	62.3	−	134−130
n = 2	21.8	66.2	52.4; 47.3	62.8	46.0	−
n = 3	21.7	62.4	50; 47.8	56.8	65.9	−

a: pyrrolidinium salts in solution (D_2O)
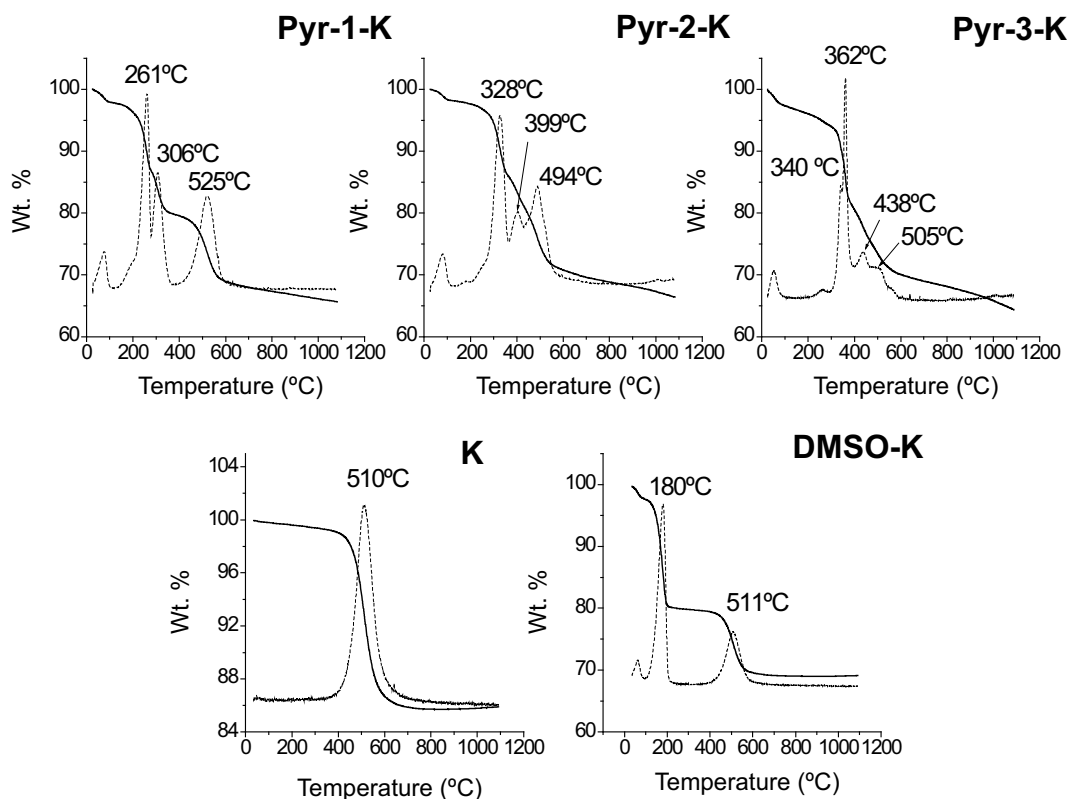b: intercalates (solid state)
c: aromatic ring

Figure 3. TGA and DTG patterns of kaolinite (K), kaolinite intercalated with DMSO (DMSO-K), and kaolinite intercalated with pyrrolidinium salts (Pyr-*n*-K, *n* =1−3).

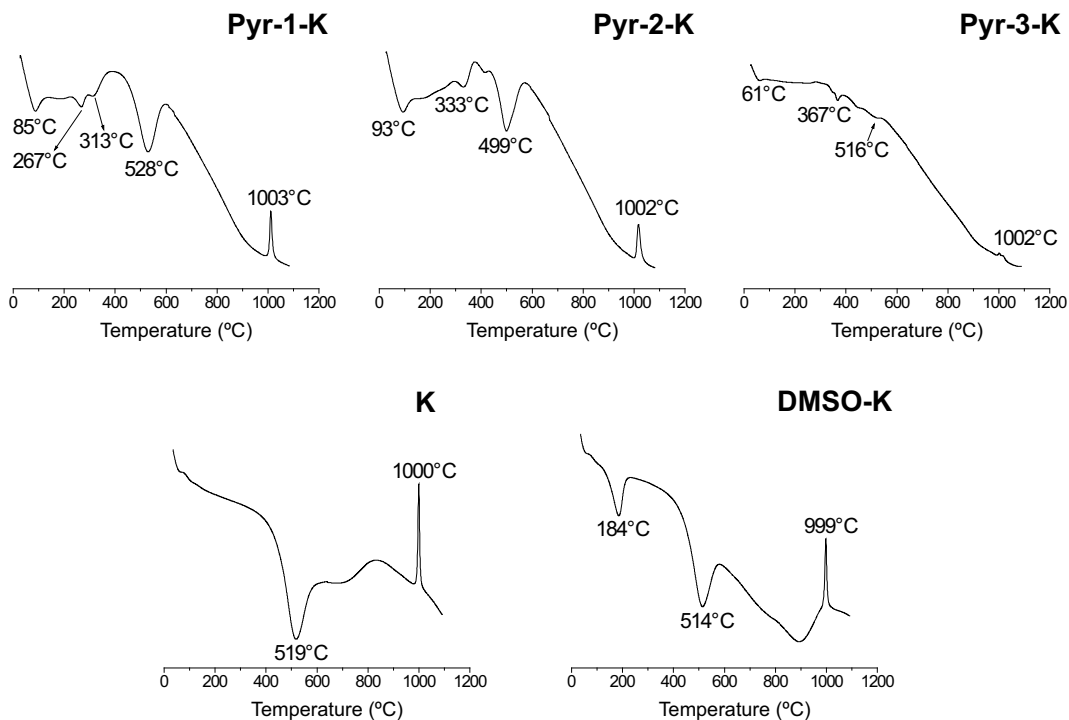Figure 4. DTA patterns of kaolinite (K), kaolinite intercalated with DMSO (DMSO-K), and kaolinite intercalated with pyrrolidinium salts (Pyr-*n*-K, *n* =1−3).
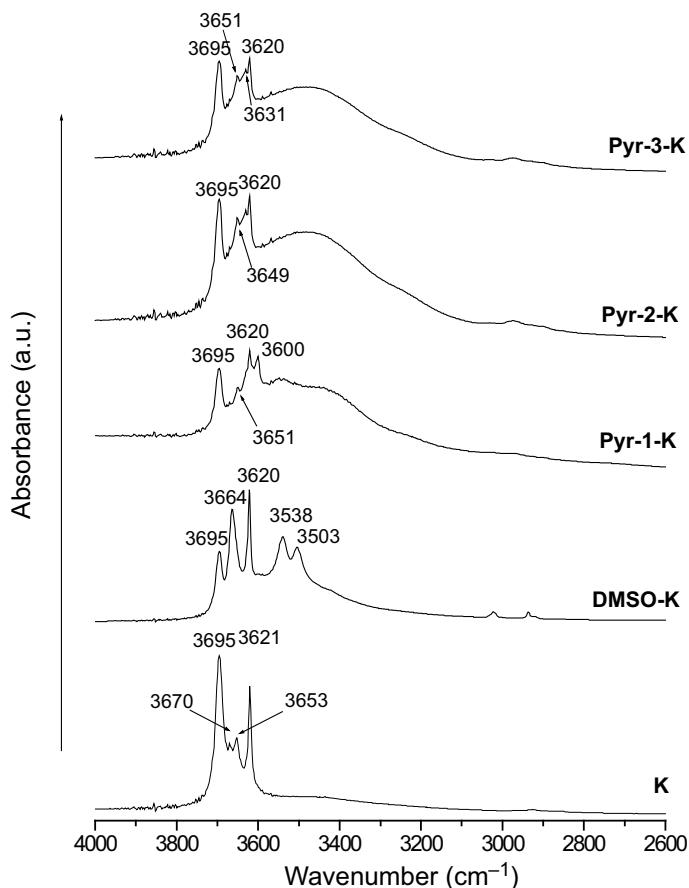
Figure 5. FTIR spectra of of kaolinite (K), kaolinite intercalated with DMSO (DMSO-K), and kaolinite intercalated with pyrrolidinium salts (Im-*n*-K; *n* = 1−3).

DMSO-K spectra have been described previously (Martens *et al.*, 2002; Letaief and Detellier, 2005). The IR spectrum of pure kaolinite presents four bands at 3695, 3670, 3653, and 3621 cm^{-1}. Upon intercalation of DMSO, only the bands at 3695, 3670, and 3653 cm^{-1}, assigned to inner-surface hydroxyls, are perturbed by the guest molecules, whereas the band at 3621 cm^{-1}, assigned to the inner-sheet hydroxyl bands, is not affected. Comparing the spectra of Pyr-*n*-K, *n* = 1−3, with those of kaolinite, and of DMSO-K, one should note two points in particular: the relatively sharp band observed at 3621 cm^{-1} is still observed when the pyrrolidinium salts have replaced DMSO. This band is attributed to the stretching vibrations of the internal hydroxyl groups. Its invariance confirms that the intercalation of pyrrolidinium salts does not modify the 1:1 layer structure of kaolinite. The bands attributed to the stretching of the interlamellar hydroxyl groups are modified. The band at 3695 cm^{-1} in kaolinite and DMSO-K persists almost unchanged, from one spectrum to the next, in agreement with the attribution of this band to the stretching of the interlayer hydroxyl group, titled with respect to the *c* direction (Neder *et al.*, 1999; Benco

et al., 2001). As such, it is not directly involved in the H-bonding with intercalates. In contrast, the other bands are strongly modified by the intercalation of DMSO and of the pyrrolidinium salts. The IR spectrum of the Pyr-*n*-K (*n* = 1−3) materials indicates the presence of hydrogen bonding between the hydroxyls of the lattice and the guest molecule loaded within the interlamellar space of kaolinite. The new band which appears in the case of Pyr-3-K, at ~3600 cm^{-1}, is similar to the patterns observed previously in the case of ethylpyridinium chloride (Letaief and Detellier, 2005; Letaief *et al.*, 2006), or polyol (Brandt *et al.*, 2003; Elbokl and Detellier, 2005) intercalates. The broad band below 3600 cm^{-1} is tentatively attributed to the stretching of the network of interlamellar H-bonded hydroxyl groups.

The ^{29}Si CP/MAS NMR spectra of kaolinite, DMSO-K, and Pyr-*n*-K (*n* = 1−3), at 99.35 MHz, are shown in Figure 6. In the case of kaolinite, two well separated signals of equal intensity are observed as expected, at −91.5 and −90.9 ppm (Sanz and Serratosa, 1984). In the case of DMSO-K, where the expansion of the basal spacing is 0.40 nm, the signal is shifted to lower frequencies, at −92.7 ppm, accounting for the
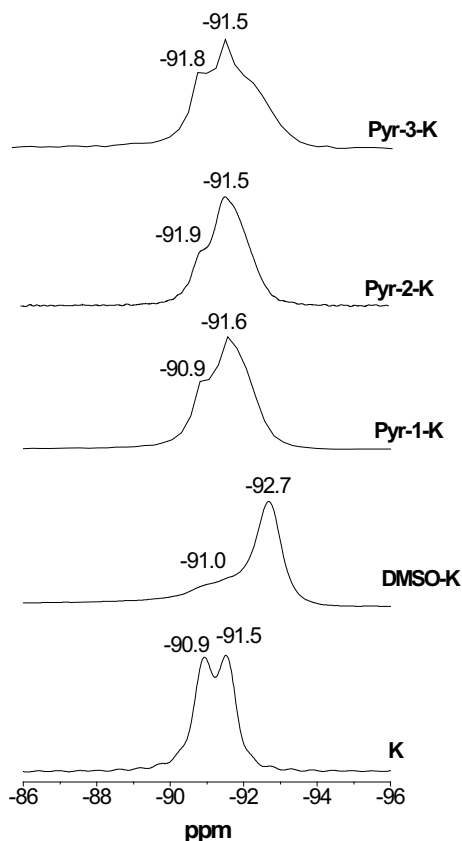
Figure 6. ^{29}Si CP/MAS NMR spectra for kaolinite (K), the starting material (DMSO-K), and the nanohybrid materials (Pyr-*n*-K, *n* = 1−3).

keying of one of the DMSO methyl groups in the siloxane rings of the tetrahedral sheets (Johnston *et al.*, 1984). In contrast, the ^{29}Si NMR spectra of the Pyr-*n*-K compounds display a relatively broad envelope around −91.5 ppm, with, in some cases, finer structures. A similar spectrum was observed in the case of the ethylpyridinium chloride intercalate (Letaief and Detellier, 2005; Letaief *et al.*, 2006). This is an indication that the silicate layer is less affected by the presence of the pyrrolidinium moiety than it is by the strong interactions with DMSO, in which case a methyl group is keyed in the siloxane ring (Johnston *et al.*, 1984; Hayashi, 1997). The local environments of the ^{29}Si nuclei are similar in Pyr-*n*-K and kaolinite, since the structural stress imposed by the keyed DMSO methyl group disappears when DMSO is replaced by the pyrrolidinium salts.

CONCLUSIONS

The possible modification of the interlamellar space in kaolinite, by intercalation of pyrrolidinium salts, was explored in this study. It was demonstrated that pyrrolidinium salts are compatible with kaolinite. The intercalation procedure is simple and could be achieved under soft conditions. The intercalation results in well ordered, layered nanohybrids, characterized by interlayer spaces of ~1.30−1.40 nm. The organic loading in the nanohybrid materials obtained was calculated from TGA analysis (n_{TGA}) and from elemental analysis (n_{EA}). Depending on their size, the organic salts occupy a space corresponding to two or three structural units of kaolinite. Both techniques are in excellent agreement to give the calculated occupancy ratio, which is also in agreement with the results obtained in our previous work on the intercalation of pyridinium and imidazolium salts (Letaief and Detellier, 2005; Letaief *et al.*, 2006; Letaief and Detellier, 2007). On that basis, all the results point to a structural model of alternating cationic and anionic species, closely packed in one layer in the kaolinite interlamellar spaces.

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