Journal of Colloid and Interface Science 335 (2009) 210–215

Contents lists available at ScienceDirect

Journal of Colloid and Interface Science

www.elsevier.com/locate/jcis

Hybrid materials prepared by interlayer functionalization of kaolinite with pyridine-carboxylic acids

Emerson H. de Faria [a,*], Omar J. Lima [a], Katia J. Ciuffi [a], Eduardo J. Nassar [a], Miguel A. Vicente [b], Raquel Trujillano [b], Paulo S. Calefi [a,*]

[a] Universidade de Franca, Av. Dr. Armando Salles Oliveira, Parque Universitário, 201, 14404-600 Franca, SP, Brazil
[b] Departamento de Química Inorgánica, Facultad de Ciencias Químicas, Universidad de Salamanca, Plaza de la Merced, S/N, 37008 Salamanca, Spain

ARTICLE INFO

Article history:
Received 15 December 2008
Accepted 7 March 2009
Available online 7 April 2009

Keywords:
Kaolinite
Functionalization
Pyridine-carboxylic acids

ABSTRACT

This paper presents the results of the functionalization of Brazilian São Simão kaolinite with pyridine-2-carboxylic and pyridine-2,6-dicarboxylic acids. The functionalization involved refluxing of the pyridine-carboxylic acid in the presence of kaolinite previously intercalated with dimethyl sulfoxide; both acids effectively displaced dimethyl sulfoxide from the clay interlayer. The resulting materials were characterized by X-ray diffraction, thermal analysis, infrared absorption spectroscopy, and C and N elemental analysis. The X-ray diffractograms revealed the incorporation of the acid molecules into the interlayer space of kaolinite. The thermogravimetric curves of the kaolinite samples functionalized with the pyridine-carboxylic acids indicated that the materials were thermally stable up to 300 °C. The displacements of the bands due to interlayer hydroxyls in the infrared absorption spectra also confirmed the functionalization of the kaolinite with the pyridine-carboxylic acids.

1. Introduction

Hybrid organic–inorganic materials are the result of the interaction between organic substances and inorganic matrices at the atomic-molecular level. These materials are multifunctional and have attracted great interest in various areas of science and technology because they combine the chemical and thermal resistance of their inorganic matrices (zeolites [1,2], clays [3–5], silica [6,7], etc.) with the elasticity and reactivity of organic compounds. This combination of constituents gives the materials singular properties that allow them to have adjustable applications. Such materials include those obtained by the intercalation or functionalization of clay minerals, whose morphological characteristics permit superficial and interplanar chemical modifications that lead to the effective immobilization of complexes, metalloporphyrins, organic pigments, polymers, and alkoxides [8–12].

Kaolinite, with theoretical formula $Al_2Si_2O_5(OH)_4$ and basal interlayer space of 7.1 Å, is a 1:1 or TO type clay mineral, since it is formed by combining sheets of SiO_4 tetrahedra (T) and $Al(OH)_6$ octahedra (O), in 1:1 proportion. Each lamella remains attached to each other because they share common oxygen atoms, giving rise to the structure of the clay mineral [13,14]. The different nature of both layers favors the preparation of intercalated and/or functionalized compounds [15]. According to Cruz et al., the interlayer bonds in kaolinite are produced by van der Waals forces between the hydrogen atoms of the hydroxyls in the octahedral sheet and the oxygen atoms in the tetrahedral sheet of the other lamella, as well as by electrostatic attraction [16]. This strong interaction prevents the insertion of substances into the interlamellar space, so expansion of kaolinite occurs through the intercalation of small and highly polar molecules. This increase in the basal space allows for the insertion of larger and functional molecules. The most commonly employed substances for expansion of the interplanar space of 1:1 clays are *N*-methylformamide (NMF) and dimethyl sulfoxide (DMSO). DMSO-intercalated kaolinite presents an interplanar space of 11.2 Å and is widely used as a precursor for the synthesis, via molecular displacement, of materials that cannot be directly intercalated. Thus, functionalization of kaolinite is based on the substitution of previously intercalated molecules by others of greater interest, followed by formation of covalent bonds. This method has proved to be a highly feasible route for the preparation of hybrid materials, since it promotes the insertion of very interesting molecules into the basal space of kaolinite without causing exfoliation or delamination [5,8,17–21].

Functionalization usually occurs by condensation of the interplanar or superficial aluminol (Al—OH) groups of kaolinite with OH groups of the intercalating molecule, leading to the formation of covalent Al—O—C bonds. In recent studies, Detellier and coworkers obtained various hybrid organic–inorganic materials by functionalizing the interplanar space of kaolinite with different

* Corresponding authors. Fax: +55 16 3711 8878.
E-mail addresses: eh.defaria@gmail.com (E.H. de Faria), pscalefi@unifran.br (P.S. Calefi).

0021-9797/$ - see front matter © 2009 Elsevier Inc. All rights reserved.
doi:10.1016/j.jcis.2009.03.067

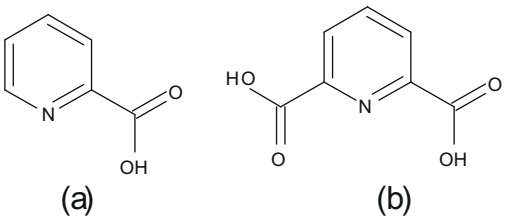

Fig. 1. Structures of (a) pyridine-2-carboxylic acid (pa), and (b) pyridine-2,6-dicarboxylic acid (dpa).

alcohols and amino alcohols [5,8,9,22]. In these studies, formation of covalent bonds between the clay mineral and the organic substances increased the thermal stability of the materials.

Picolinic acid (pyridine-2-carboxylic acid, abbreviated "pa") and dipicolinic acid (pyridine-2,6-dicarboxylic acid, abbreviated "dpa"), whose structure is depicted in Fig. 1, are, together with nicotinic and quinolinic ones, carboxylic acid derivatives of pyridine. All of them are widely used as ligands in the formation of coordination compounds. pa and dpa are commonly used as ligands in luminescent complexes when coordinated with lanthanide ions [23–26], as well as in compounds with high catalytic activity when they form complexes with transition metal ions such as Fe^{3+} [27–29]. A factor that limits the use of these complexes in luminescent devices is their low thermal stability; thermally more stable luminescent complexes may be obtained by their immobilization in inorganic matrices.

With these precedents, in this paper we have carried out the functionalization of kaolinite from São Simão, Brazil, with pyridine-carboxylic acids by displacement of DMSO molecules from the previously formed kaolinite–DMSO complex. The materials resulting from the reaction between the acids and the kaolinite–DMSO solids were characterized by thermal analysis, elemental analysis, X-ray diffraction, and infrared absorption spectroscopy.

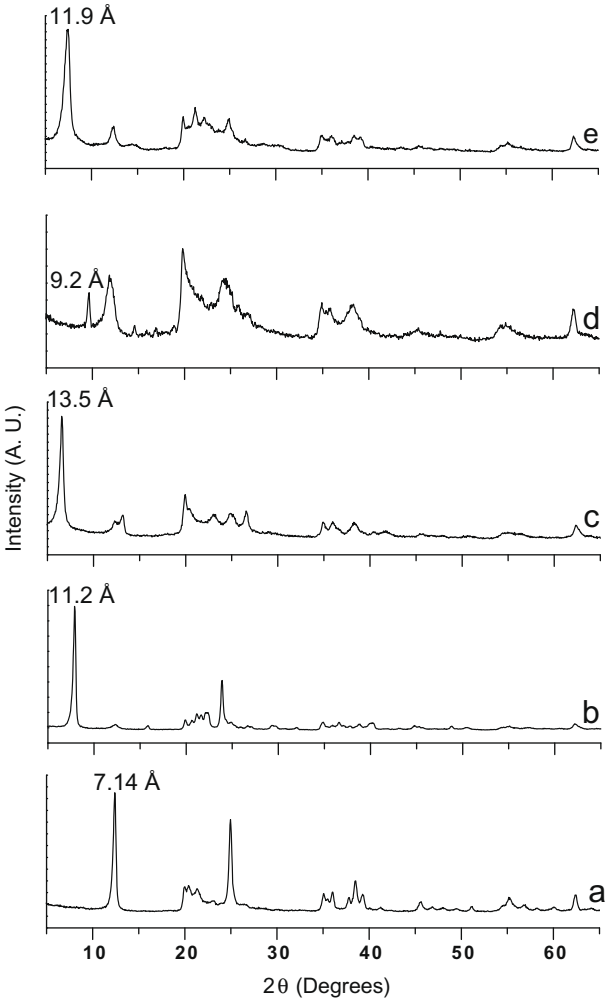

Fig. 2. X-ray powder diffraction patterns ($2\theta = 2$—65°) of (a) purified kaolinite, and the compounds formed with DMSO (b), and with picolinic (c), dipicolinic (250 °C) (d) and dipicolinic (190 °C) (e) acids.

2. Experimental

2.1. Purification of kaolin

The kaolin employed in this work came from the municipality of São Simão in the State of São Paulo, Brazil, and was kindly supplied by the mining company Darcy R. O. Silva & Cia. It is classified as the ball-clay type, characterized by fine granulometry and for being rich in hexagonal kaolinite. This is a rare occurrence; in fact, São Simão deposit actually is the only occurrence of this type of material in Brazil [30]. The diffractogram of the natural sample (Fig. S1, Supplementary material) showed that it is very rich in kaolinite, but also showed the presence of quartz and mica as mineral impurities; thus, it was purified by the dispersion–decantation method [31–33], which allowed obtaining very pure kaolinite (Fig. 2), used for further intercalation experiments. In the formulation of the intercalated compounds, purified kaolinite is abbreviated as Ka.

2.2. Synthesis of kaolinite intercalated with DMSO

To obtain the precursor intercalated with dimethyl sulfoxide (Ka-DMSO), the methodology described by Detellier and co-workers was employed [8,9]. Twenty grams of the purified kaolinite was suspended in a mixture of 180 mL of DMSO and 20 mL of H_2O, which was maintained at 60 °C under agitation for 10 days. The material was centrifuged at 2000 rpm, washed with ethanol, and oven-dried at 60 °C.

2.3. Synthesis of the picolinic acid–kaolinite hybrid materials

The hybrid organic–inorganic materials were obtained by keeping a mass of the precursor (Ka-DMSO) in the presence of the melted pyridine-carboxylic acids for 40 h. The molar ratio carboxylic acid/kaolinite was, in both cases, 5/1. In the case of pa, the reaction was carried out at 150 °C, using a thermostatic bath containing silicone oil, while the temperature was 250 °C in the case of dpa, for which the mixture was deposited in a crucible and kept in a furnace at this temperature for 4 h. This sample showed bad structural properties, and the synthesis was repeated in the thermostatic bath at 190 °C. The resulting materials were washed with ethanol and oven-dried at 80 °C. They were designated as Ka-pa and Ka-dpa, when derived from picolinic and dipicolinic acids, respectively.

2.4. Characterization techniques

The X-ray diffractograms of the solids were taken in a Siemens D-500 diffractometer operating at 40 kV and 30 mA (1200 W), using filtered Cu$K\alpha$ radiation and varying the angle from 2° to 65° 2θ. All the analyses were processed at a scan speed of 2° per minute.

The elemental analysis of the natural kaolinite was performed at Activation Laboratories Ltd., in Ancaster, Ontario, Canada, using

Table 1
Chemical composition of the purified clay, expressed in water-free form.

Oxide	SiO_2	Al_2O_3	Fe_2O_3	MnO	MgO	CaO	Na_2O	K_2O	TiO_2
Content (%)	52.99	43.98	1.05	0.005	0.23	0.04	0.02	0.43	1.24

inductively coupled plasma-atomic emission spectroscopy (ICP-AES). The C and N elemental analysis of the functionalized materials was conducted in a Perkin-Elmer CHN 2400 analyzer.

Thermal analyses (TG/DTA) were carried out in a TA Instruments SDT Q600 Simultaneous DTA-TGA thermal analyzer, in the temperature range 25–1100 °C, at a heating rate of 20 °C/min and with an air flow of 100 mL/min.

Infrared absorption spectra were obtained with a Perkin-Elmer 1739 spectrophotometer with Fourier transform, using the KBr pellet technique.

3. Results and discussion

The chemical analysis of natural kaolinite is given in Table 1, these results being normalized to water-free sample, that is, without considering the amount of water. From them, the following chemical formula is deduced: $Si_{2.0}Al_{1.96}Fe_{0.03}Mg_{0.01}K_{0.02}Ti_{0.03}O_{7.06}$. This formula is very close to the theoretical one of kaolinite, $Si_2Al_2O_7$, also usually reported as $Si_2Al_2O_5(OH)_4$, most of the differences being due to the small amounts of impurities in the solid. Thus, Fe^{3+} can be located in octahedral positions of the clay, but the presence of Mg^{2+} and K^+ can be associated with the presence of other clays, as mica. This observation is expected from the initial mineralogical composition of kaolin, although X-ray diffraction shows an excellent purification of the raw clay, and in fact no mineral admixtures are detected by this technique in the purified solid. In the case of titanium, although it can be a component of the octahedral sheet of clays, its presence is more probably due to an impurity as rutile or ilmenite, also not detected by XRD. In any case, as indicated before, the structural formula confirms the excellent quality of the 2-μm fraction of kaolinite.

The X-ray diffractograms of the intercalated solids derived from kaolinite, compared to that of the original clay, can be seen in Fig. 2. The treatment with the organic molecules produces, in all cases, an increase in the basal distance, clearly showing the insertion of these molecules into the interlayer region. On the other hand, the rest of the diffraction effects, those not depending on the stacking of the layers in the *c*-dimension, do not change, indicating that intercalation does not alter the structure of each layer.

The original kaolinite has a basal spacing of 7.14 Å, which increases in the sample treated with DMSO up to 11.20 Å. Thus, the expansion of the interlayer space produced by the incorporation of DMSO molecules is 4.06 Å, which agrees with literature data [36]. However, a small fraction of kaolinite layers is not intercalated, as proved by the maintenance of the small peak at 7.14 Å. The materials obtained after treatment of the Ka-DMSO complex with the picolinic acids at the melting point of the acids were 13.50 and 9.20 Å, when mono- and di-carboxylic acids, respectively, were used (Fig. 2, diffractograms c and d). However, it is evident that the intercalation of the sample treated with dipicolinic acid is not correct. The peak at 9.20 Å is slightly intense, while the peak corresponding to nonintercalated kaolinite is more intense. This is probably due to the high synthesis temperature, conditioned by the high melting point of dipicolinic acid. For this reason the synthesis was repeated under the melting point of the organic compound, choosing the temperature of 190 °C and carrying out the synthesis in the silicone-oil thermostatic bath. The new sample was well intercalated, having a basal spacing of 11.90 Å (Fig. 2, diffractogram e), being considered for further characterization. Comparing the basal spacings of the intercalated samples to that of kaolinite, the heights occupied by the molecules of the acids in the interlayer space are 6.36 and 4.76 Å, respectively (Table 2). This difference could be related to the fixation of different amounts of each picolinic acid or to a different orientation of both molecules, which is discussed later. In both cases, together with the apparition of the new peaks, it is observed that the peak at 11.2 Å completely disappears, which suggests the complete substitution of DMSO by the picolinic acids, thus effectively functionalizing the kaolinite with these compounds, to be demonstrated later by other techniques. However, the small peak at 7.14 Å, characteristic of natural kaolinite, continues to appear, which nicely illustrates the unavailability of the direct synthesis; that is, the layers that had not been previously intercalated by DMSO cannot be intercalated by the picolinic acids.

Table 2
Basal interplanar space, d_{001}, and variation of the interplanar space (Δd) of the hybrid materials in relation to purified kaolinite.

Sample	d_{001} (Å)	Δd(Å)
Ka	7.14	–
Ka-DMSO	11.20	4.06
Ka-pa	13.50	6.36
Ka-dpa	11.90	4.76

Table 3
C and N chemical analysis of picolinic acid-containing solids, and structural formulas of the resulting complexes.

Sample	C content (%)	N content (%)	Acid:Ka[a]	Acid:Ka[b]
Ka-pa	25.0	5.18	1.59	1.56
Ka-dpa	11.5	1.67	0.374	0.387

[a] Calculated from chemical analysis.
[b] Calculated from thermogravimetric curves.

Table 3 shows the results of C and N elemental analysis of the samples functionalized with the picolinic acids. First, it may be observed that the ratios C/N in the functionalized solids are very close to those in the pure molecules. Thus, while the C/N weight ratio is 5.14 in pure picolinic acid, it is 4.83 in the Ka-pa sample, while this ratio is 6.00 in pure dipicolinic acid and 6.89 in Ka-dpa solid. The small discrepancies found may be due to the difficulty of analysis of these elements, mainly in the case of nitrogen, present in the samples in low amounts. These results clearly suggest that the organic molecules do not suffer significant alteration when incorporated into the solids; it may be considered that they can be protonated, not observable by chemical analysis, but other changes do not seem to occur. The total amount of organic matter in the samples was calculated from their content in N. Although N is present in a low amount, an thus its determination having higher relative error, it was chosen because the content in C may be affected by traces from DMSO or solvents, which could remain in the solids after the treatment with the picolinic acids. This was verified by carrying out a specific chemical analysis of sulfur, and finding low amounts of this elements in the samples. The results obtained are also reported in Table 3, reaching values as high as 45.5% and 20.0% of organic matter for picolinic- and dipicolinic-treated solids, respectively. This is somehow surprising, and as the molecular weight of pa is lower than that of dpa, it is deduced

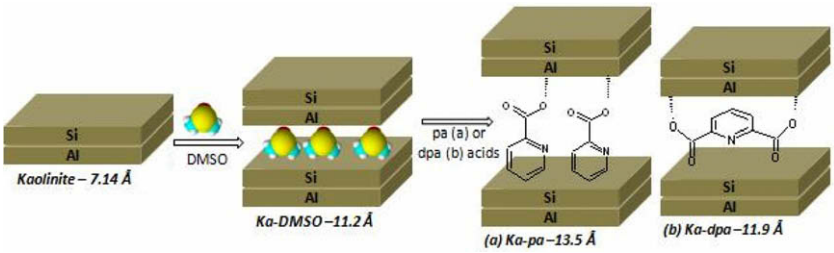

Fig. 3. Schematic representation of the functionalization of natural kaolinite with pyridine-carboxylic acids.

that the number of acid molecules fixed by the solid is much higher in the first case. This may be related to the basal spacing of the solids, higher in the first case. If the number of carboxylic groups per gram of kaolinite is calculated, it is found that it is double in the first case (5.9 mmol of acid groups per gram of clay in the case of Ka-pa and 3.0 mmol/g in the case of Ka-dpa), which suggests that the interaction with the carboxylic groups has a large importance in the interaction.

Another way to express the amount of each acid fixed by the clay is to calculate an elemental formula for each intercalation compound, considering the "molecular weight" of kaolinite (that of the structural formula above reported) and of each picolinic acid. Again, N content was used for calculating the number of moles of each acid. The formulas obtained were Ka-$(pa)_{1.59}$ and Ka-$(dpa)_{0.37}$, respectively. In other words, the samples contain 1.59 and 0.74 carboxylic groups, respectively, per kaolinite unit cell. This allows aluminol groups of each unitary formula of kaolinite to form covalent bonding with the carboxylic groups, and may also explain the different basal spacing of the solids, which may be related to different arrangements of both molecules. In the case of dpa, one acid molecule may be bonded with the aluminol groups of two neighboring cells of kaolinite. The acid molecule must be parallel to the clay layers. The distance between their two carboxylic groups and the size of kaolinite unit cell make possible this disposition and the two suggested bonds. However, for pa, as each molecule has a single carboxylic group, molecules must be stacked more compact and in a vertical or at least bowed disposition; the aromatic ring may not be parallel to the host layers, thus explaining the higher basal spacing of Ka-pa solid. The procedure followed to obtain the picolinic acid-functionalized kaolinite and the structure suggested for the final complexes is schematically represented in Fig. 3.

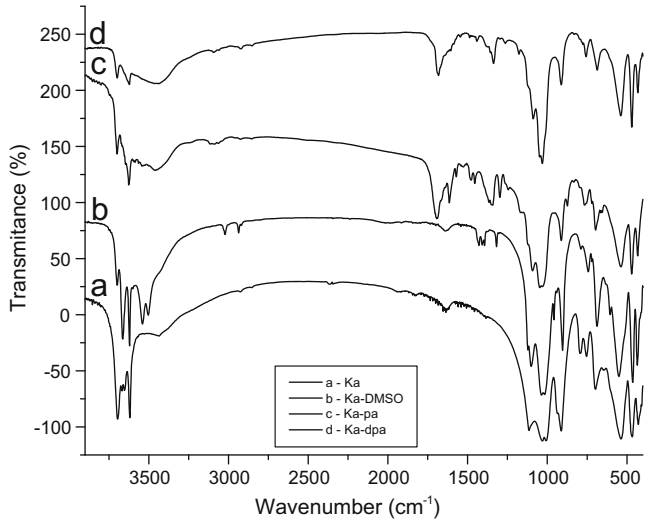

Fig. 4. Infrared absorption spectra of purified kaolinite (a) and of the compounds formed with DMSO (b) and with the picolinic (c) and dipicolinic (d) acids.

Fig. 4 shows the infrared absorption spectra of the Ka, Ka-DMSO, Ka-pa, and Ka-dpa samples. The bands at 3693, 3667, and 3650 cm^{-1} in the spectrum of purified kaolinite correspond to interlamellar hydroxyls, Al—OH, while the band at 3620 cm^{-1} corresponds to the intralamellar hydroxyl. After intercalation with DMSO, the hydroxyl bands are strongly affected, two of them shifting to 3540 and 3497 cm^{-1}. Several authors have assigned this displacement to the intercalation of DMSO molecules through hydrogen bonding to the interlamellar hydroxyls of the clay mineral (S=O—HO) [34–36]. This interaction is confirmed by the displacement of the characteristic band of the interlamellar Al—OH groups, which appears at 938 cm^{-1} in the purified kaolinite spectrum, while it shifts to 957 cm^{-1} in the spectrum of the kaolinite intercalated with DMSO. Bands at 2937 and 3022 cm^{-1} were also observed, which correspond to the vibrations of the C—H bonds in DMSO [34–36].

Kaolinite functionalized with pyridine-2-carboxylic acid displayed bands at 3698 and 3620 cm^{-1}, characteristic of inter- and intralamellar hydroxyls, respectively. The other bands for intralamellar hydroxyls (at 3667 and 3650 cm^{-1}) were not observed. Bands characteristic of asymmetric and symmetric stretching of the anhydride acid group were also observed at 1684, 1566, and 1456 cm^{-1} [37]. However, the typical band for the interlamellar aluminol group at 938 cm^{-1} was absent, thus confirming the participation of this group in a bond with the carboxylic acid molecules. Similar results were obtained for the Ka-dpa sample. The band assignments are summarized in Table 4. The displacement of the bands corresponding to interlamellar hydroxyls and the appearance of new bands in regions related to the pyridine-carboxylic groups give evidence of the entrance of picolinic acid molecules into the interlamellar space of kaolinite.

The thermal analysis of purified kaolinite is shown in Fig. 5. Adsorbed water is removed by an endothermal effect at low temperature, centered at 60 °C. Then, the structural water of kaolinite, that derived from its hydroxyl groups, is removed as an endothermic effect centered at 516 °C; in this step kaolinite suffers dehydroxylation leading to the formation of metakaolinite. The mass loss in this stage, 14.0%, is very close to the theoretical value in kaolinite, 13.7%, deduced by adding two water molecules, derived from four hydroxyl groups, to the structural formula reported above. In the high temperature region, another exothermic process was observed at 1000 °C, which was attributed to structural reorganization of the material, with nucleation of mullite, which can be considered a mixture of Al_2O_3 and SiO_2. This process was observed in the thermal analyses of all the materials; thus the residue at 1100 °C was mullite in all cases [5,8,9,21].

In the TG/DTG and DTA curves (Fig. 6) of the precursor material kaolinite intercalated with DMSO (Ka-DMSO), the endothermic peak at 180 °C (12.6%) corresponds to elimination of DMSO intercalated with kaolinite, while the peak at 516 °C is the result of the kaolinite dehydroxylation process [5,8,9,21]. Considering the

Table 4
Assignments of infrared absorption bands of kaolinite and its derivatives Ka-DMSO, Ka-pa, and Ka-dpa.

	Ka (cm^{-1})	Ka–DMSO (cm^{-1})	Ka-pa (cm^{-1})	Ka-dpa (cm^{-1})
$\nu(OH)_{intra}$	3620	3620	3620	3620
$\nu(OH)_{intra}$	3650, 3667, 3693	3668, 3674, 3646, 3654	3698	3698
δ H—O—H	1635	1635	–	–
Si—O	1006, 1030, 1114	1015, 1036, 1101	1025, 1046, 1091	1029, 1050, 1088
ν Al—OH_{intra}	912	903	912	912
ν Al—OH_{inter}	938	957	–	–
SiO_2 or quartz	795	795	–	–
δ Si—O—Al	754	743	760	755
δ Si—O—$Si_{out\ of\ plane}$	698	687	698	685
δ Si—O—Al_{oct}	536	551	536	536
δ Si—O—$Si_{in\ plane}$	467	462	467	467
Si—O	426	432	432	432
S=O—HO	–	3497, 3540	–	–
ν_{ass} COO^-	–	–	1689, 1566, 1456	1684, 1545, 1487
ν_{sym} COO^-	–	–	1350	1334
ν $C=C_{(aro)}$	–	–	1614	1435
Ω C—H	–	3022, 2937	–	–
β C—H	–	–	1295, 1161, 1117, 1090,	1264, 1176 1083, 1048,

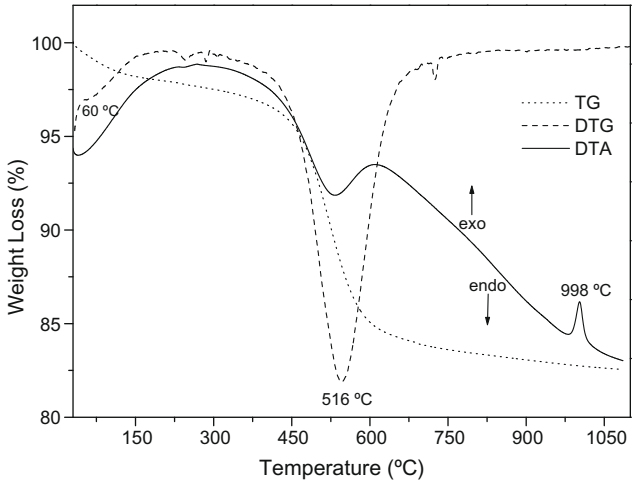

Fig. 5. TG, DTG, and DTA curves of purified kaolinite performed in O_2 atmosphere.

weight loss between 100 and 220 °C, the amount of DMSO fixed by the solid was calculated, this leading to a stoichiometry of Ka-$(DMSO)_{0.448}$.

TG/DTG and DTA curves of the Ka-pa sample (Fig. 7) reveal one main mass loss process, and up to three small mass loss stages, in addition to the mullite nucleation process. The first mass loss stage at 75 °C, with an endothermic peak, was attributed to the elimination of solvent adsorbed in the clay mineral. The second step confirmed the functionalization of kaolinite. This exothermic step, occurring at a maximum mass loss temperature of 370 °C, was attributed to the decomposition of pyridine-2-carboxylic acid inserted into the basal interlayer space. The step centered at a maximum mass loss temperatures of 470 °C was attributed to kaolinite dehydroxylation [5,8,9,21]. The mass loss at 670 °C can be ascribed to the elimination of residual carbon trapped in the interlayer space of kaolinite after decomposition of pa [9].

Similar results were obtained for the Ka-dpa sample (Fig. 8). In both hybrid materials, the dehydroxylation of kaolinite is observed at 470 °C, a temperature slightly lower than characteristic of pure kaolinite, 516 °C [38].

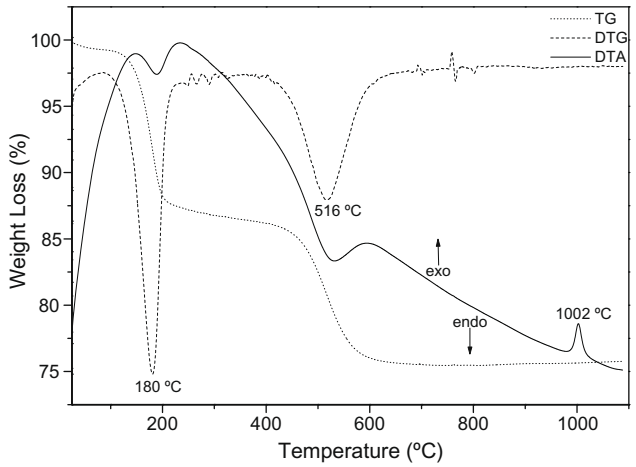

Fig. 6. TG, DTG, and DTA curves of Ka-DMSO performed in O_2 atmosphere.

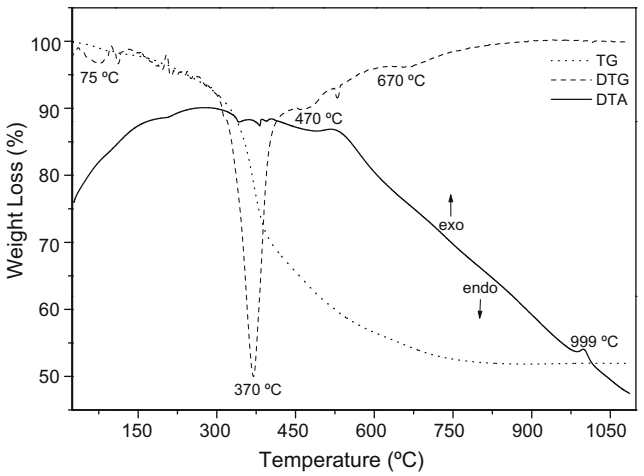

Fig. 7. TG, DTG, and DTA curves of Ka-pa performed in O_2 atmosphere.

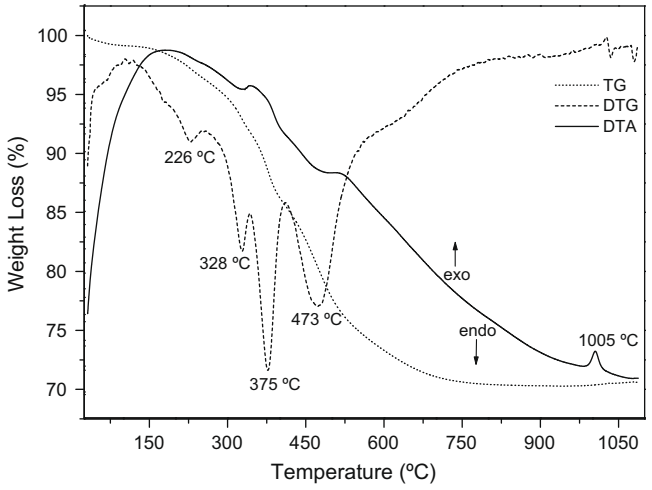

Fig. 8. TG, DTG, and DTA curves of Ka-dpa performed in O_2 atmosphere.

The samples functionalized with the pyridine-carboxylic acids show the complete substitution of DMSO molecules by pa and dpa acids, respectively. The high thermal stability (300 °C), the decrease in the temperature of dehydroxylation, and the presence of residual carbon trapped in the basal space of kaolinite in ka-pa and ka-dpa samples are evidences of the functionalization of kaolinite by pyridine-carboxylic acids. These results are similar to materials containing other organic molecules, such as methanol, ethylene glycol, diols, and recently polyols, amino alcohols, and alkoxides covalently grafted in the aluminol surface of kaolinite [5,8,9,20,22,34,37]. Data from TG curves were used for calculating the number of moles of each acid per unit cell of kaolinite, finding results very close to those obtained from chemical analysis of C and N (Table 3).

4. Conclusions

It has been demonstrated that it is possible to obtain hybrid organic–inorganic materials by functionalizing the interlamellar space of kaolinite with pyridine-carboxylic acids. These substances are covalently bound to the inorganic matrix by condensation between their carboxylic —COOH groups and the aluminol Al—OH groups of the clay, giving rise to covalent Al—O—R type bonds, as confirmed by infrared absorption spectroscopy. The condensation reaction occurred after substitution of DMSO in the interlamellar space, as confirmed by the XRD diffractograms. C and N elemental analysis of these new hybrid materials indicated that the molecular proportion of acid/unit kaolinite formula is defined by the quantity of carboxylic groups in the molecules of the acids. Thermal analysis indicated that the materials were thermally stable up to 300 °C. The hybrids produced here are potentially applicable as luminescent materials when complexed with photoluminescent lanthanide ions such as Eu^{3+} and Tb^{3+}. They can also be potentially employed as catalysts for hydrocarbon oxidation reactions when complexed with d-block ions such as Fe^{3+}.

Acknowledgments

This work has been carried out in the frame of an Interuniversity Cooperation Project between Spanish and Brazilian Ministries of Education (references PHB2005-0077-PC and CAPES 110/06). The Spanish authors thank financial support from Junta de Castilla y León (reference SA101A07). R.T. acknowledges the financial support from MEC through the Ramon-y-Cajal program. The Brazilian group thanks support from FAPESP and CNPq.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jcis.2009.03.067.

References

[1] O. Vassylyev, J. Chen, G.S. Hall, J.G. Khinast, Micropor. Mesopor. Mater. 92 (2006) 101.
[2] G. Calzaferri, D. Brühwiler, C. R. Chim. 8 (2005) 391.
[3] S. Gopinath, S. Sugunan, Appl. Clay Sci. 35 (2007) 67.
[4] R.L. Frost, J. Kristof, E. Horvat, J.T. Kloprogge, Spectrochim. Acta A 56 (2000) 1191.
[5] J.J. Tunney, C. Detellier, Can. J. Chem. 75 (1997) 1766.
[6] A. Walcarius, S. Sayen, C. Gérardin, F. Hamdoune, L. Rodehüser, Colloids Surf. A 234 (2004) 145.
[7] N.M. José, L.A.S. de A. Prado, Quim. Nova. 28 (2005) 281.
[8] J.J. Tunney, C. Detellier, Chem. Mater. 5 (1993) 747.
[9] K.B. Brandt, T.A. Elbokl, C. Detellier, J. Mater. Chem. 13 (2003) 2566.
[10] J.L. Guimarães, P. Peralta-Zamora, F. Wypych, J. Colloid Interface Sci. 206 (1998) 281.
[11] J.E. Gardolinski, L.P. Ramos, G.P. de Souza, F. Wypych, J. Colloid Interface Sci. 221 (2000) 284.
[12] F. Annabi-Bergaya, Micropor. Mesopor. Mater. 107 (2008) 141.
[13] J.E. Gardolinsky, G. Lagaly, Clay Miner. 40 (2005) 547.
[14] J. Murakami, T. Itagaki, K. Kuroda, Solid State Ionics 172 (2004) 279.
[15] K.C. Lombardi, J.L. Guimarães, A.S. Mangrich, N. Mattoso, M. Abbate, W.H. Schreiner, F. Wypych, J. Braz. Chem. Soc. 13 (2002) 270.
[16] M. Cruz, H. Jacobs, J.J. Fripiat, in: J.M Serratosa, A. Sánchez (Eds.), Proceedings of the International Clay Conference 1972, Madrid, 1973, pp. 25–46.
[17] T.A. Elbokl, C. Detellier, J. Colloid Interface Sci. 323 (2008) 338.
[18] S. Letaief, I.K. Tonle, T. Diaco, C. Detellier, Appl. Clay Sci. 42 (2008) 95.
[19] T. Itagaki, K. Kuroda, J. Mater. Chem. 13 (2003) 1064.
[20] J.J. Tunney, C. Detellier, Clays Clay Miner. 42 (1994) 552.
[21] J.E. Gardolinski, P. Peralta-Zamora, F. Wypych, J. Colloid Interface Sci. 211 (1999) 137.
[22] S. Letaief, C. Detellier, J. Mater. Chem. 15 (2005) 4734.
[23] P.P. Lima, O.L. Malta, S. Alves Júnior, Quim. Nova. 28 (2005) 805.
[24] P.S. Calefi, A.O. Ribeiro, A.M. Pires, O.A. Serra, J. Alloys Compd. 374 (2004) 151.
[25] V.F. Zolin, J. Alloys Compd. 380 (2004) 101.
[26] C. Reinhard, H.U. Gudel, Inorg. Chem. 41 (2002) 1048.
[27] K. Kalinowska, M. Borawska, R. Swislocka, J. Piekut, W. Lewandowski, J. Mol. Struct. 834–836 (2007) 419.
[28] L.S. Pinheiro, M.L.A. Temperini, Surf. Sci. 601 (2007) 1836.
[29] P. Lainé, A. Gourdon, J.P. Launay, Inorg. Chem. 34 (1995) 5129.
[30] J.A. de Senna, C.R. de Souza Filho, R.S. Angélica, Appl. Clay Sci. 41 (2008) 85.
[31] A. Pérez-Santano, R. Trujillano, C. Belver, A. Gil, M.A. Vicente, J. Colloid Interface Sci. 284 (2005) 239.
[32] C. Belver, M.A. Bañares-Muñoz, M.A. Vicente, Chem. Mater. 14 (2002) 2033.
[33] L.R.D. da Silva, L.C. Garla, Quim. Nova. 22 (1998) 169.
[34] R.L. Frost, J. Kristof, G.N. Paroz, J.T. Kloprogge, J. Phys. Chem. B 102 (1998) 8519.
[35] J.E. Gardolinsky, L.C.M. Carreira, M.P. Cantão, F. Wypych, J. Mater. Sci. 35 (2000) 3113.
[36] I.K. Tonlé, T. Diaco, E. Ngmeni, C. Detellier, Chem. Mater. 26 (2007) 6629.
[37] G.S. Heo, B. Moon, Tetrahedron Lett. 49 (2008) 5540.
[38] S. Letaief, C. Detellier, Chem. Commun. (2007) 2613.