Journal of Thermal Analysis and Calorimetry, Vol. 87 (2007) 3, 783–787

TG AND DSC AS TOOLS FOR CONFIRMING HYBRID VERMICULITES DERIVED FROM INTERCALATION

Maria G. da Fonseca[*], *Albaneide F. Wanderley, Oberto G. da Silva, Luiza N. H. Arakaki and J. G. P. Espínola*

Departamento de Química, CCEN, Universidade Federal da Paraíba, 58059-900 João Pessoa, Paraíba, Brazil

Vermiculite was prepared to react with aliphatic diamines (ethylene-, trimethylene-, tetramethylene- and hexamethylene-) diamine. The products were characterized by elemental analysis, infrared spectroscopy and X-ray diffraction. The amounts of diamines adsorbed were 0.89, 0.86, 0.79 and 0.68 mmol g^{-1}, respectively for $NH_2(CH_2)\cdot nNH_2$ where n=2, 3, 4, 6. The basal spacings of the intercalated vermiculites varied between 1300 and 1470 pm. Thermogravimetry and DSC data confirmed intercalation of diamines in gallery space of vermiculite.

Keywords: *diamines, DSC, TG, vermiculite*

Introduction

Intercalation process involves a reversible insertion of mobile guest species such as molecules, atoms, or ions into a crystalline host lattice forming new materials with distinct optical, electrical, and catalytic properties from the precursor host [1, 2]. One example concerning the natural material is the expansible clay minerals whose lamellar structure behaves as a good support for intercalation reactions. This kind of clay lamellar material is normally classified in two groups of hydrous phyllosilicates having inorganic structural arrangement in 1:1 or 2:1 layers. The first natural layered structure consists of single tetrahedral coordinated $[Si_2O_5](OH)_2$ layer which is connected to an edge-shared octahedral $M(OH)_6$ sheet, where M is Mg^{2+} and Al^{3+} [3, 4]. The 2:1 layered material contains one octahedral sandwiched by two tetrahedral layers and in both cases the oxygen atoms are responsible to connect the sheets. However, the main inorganic layered structure can have the cation substituted in either the tetrahedral or octahedral sites for cations of comparable radii. e.g. one expected substitution such as Si^{4+}/Al^{3+} generates a negative charge in the layers. To compensate the excess of this layered charge, typical cations like Na^+ or Ca^{2+} are incorporated into the interlayer space. The materials of this general class are normally called to smectites such as montmorillonite and saponite. At this point, the attention focuses on vermiculite, which is an aluminum phyllosilicate having very similar structure to the montmorillonite with higher negative charge in the inorganic sheets [4]. Several works related to the modification of vermiculite have been reported, e.g. vermiculite-polymer nanocomposites for reinforcing purposes [5–7], vermiculite-alkylammonium for industrial applications [8] or pillared vermiculite as catalytic support [9, 10]. The present investigation deals with the synthesis and characterization of hybrids derived from reaction of aliphatic diamines and vermiculite using thermogravimetry (TG) and differential scanning calorimetry (DSC) to identify the mechanisms of the intercalation reactions.

Experimental

Chemicals

Vermiculite sample was obtained from ‘União Brasileira de Mineração’ company from the municipality of Santa Rita (Paraiba, Brazil). Chemical analyses of the sample were performed by AAS using a PerkinElmer 5100 model instrument with an air-acetylene flame. The samples were digested in a mixture of HF–HCl. The cation exchange capacity (CEC) was measured by using ammonium acetate buffered at pH 7.0 [11]. The nitrogen content was measured in a PerkinElmer model 2400 analyzer. Ethylenediamine, trimethylenediamine, tetramethylenediamine and hexamethylenediamine (Aldrich) were used as received.

Reactions with diamines

50.0 mg s of vermiculite samples (V) were dispersed in 25.0 cm^3 of aqueous solutions, containing diamines

---

[*] Author for correspondence: mgardennia@quimica.ufpb.br

1388–6150/$20.00

Akadémiai Kiadó, Budapest, Hungary
Springer, Dordrecht, The Netherlands

with several concentrations, varying from zero to 0.010 mol dm^{-3}. The solutions were stirred for 48 h. This equilibrium time was previously estimated at 298±1 K. The solid was separated by filtration. The diamine concentrations were measured by acid-basic titration with HCl standard solution. The number of N_f amine moles adsorbed per mass (*m*) of the solid was calculated from the $N_f=(N_i-N_s)m^{-1}$ expression, where N_i and N_s are the initial and final amount of the diamine in solution, respectively. The intercalated vermiculites were characterized by infrared spectroscopy, X-ray diffraction, CHN elemental analysis, TG and DSC.

Methods

Carbon, hydrogen and nitrogen contents were measured using a PerkinElmer model 2400 analyzer. At least two parallel measurements were performed for each sample.

X-ray diffraction patterns were obtained by a nickel-filtered CuK_α radiation on a Shimadzu model XD3A diffractometric apparatus in the 2θ=1.5 to 70° range and at a scan rate of 0.67° s^{-1}. Infrared spectra between 4000 and 400 cm^{-1} were recorded in a Bomem MB-Series spectrophotometer using KBr pellets with 4 cm^{-1} of resolution and 35 accumulations.

Thermal behavior of the samples was followed by TG and DSC. TG curves were obtained in a DuPont 1090 B model thermogravimetric apparatus coupled to a DuPont 951 thermobalance. The samples were heated up to 1273 K at 0.17 K s^{-1} heating rate in a dry nitrogen. The sample masses were between 15.0–30.0 mg. DSC curves have been recorded on a Shimadzu model DSC-50 unit. About 15 mg of sample was placed to an aluminium pan and heated from room temperature to 773 K at 0.17 K s^{-1} in a dry nitrogen. The reference was an empty aluminium pan.

Results and discussion

The chemical composition of vermiculite in mass% was: SiO_2 (44.62), Al_2O_3 (9.18), Fe_2O_3 (5.46), CaO (0.78), MgO (20.44), Na_2O (0.11), K_2O (0.48) with 18.93% mass loss after heating at 1273 K. Based on these data, the structural formulae of the studied sample (calculated on the basis of $O_{20}(OH)_4$ per formula unit) was $Mg_{4.68}Ca_{0.128}Na_{0.032}K_{0.094}Fe_{0.63}Al_{1.66}Si_{6.85}$, where Fe^{3+} is equal to the total Fe on the basis of wet chemical analysis. The CEC was 135 meq/100 g.

The reactions of (ethylene-, trimethylene-, tetramethylene- and hexamethylene-) diamine with vermiculite were followed by an acid-basic titration. The isotherms are shown in Fig. 1.

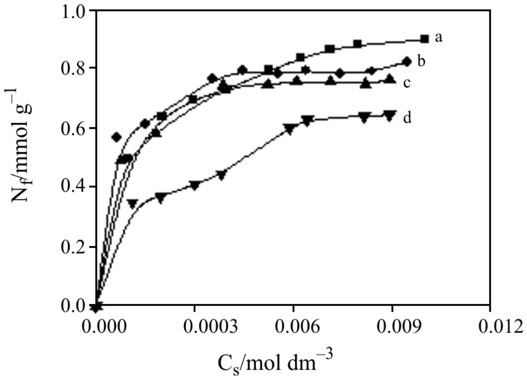

Fig. 1 Interaction isotherms of vermiculite with a – ethylene-, b – trimethylene-, c – tetramethylene- and d – hexamethylene-diamine at 298±1 K

The intercalation decreased from the ethylene-> trimethylene->tetramethylene->hexamethylene-diamine order, whose N_f values were 0.89, 0.82, 0.76 and 0.64 mmol g^{-1}, respectively. The maximum amount of each diamine intercalated was also estimated by CHN analysis (Table 1). The carbon:nitrogen ratio for diamine before and after reaction with vermiculite was established. Therefore, based on the nitrogen content of the samples, the maximum numbers of adsorbed diamine moles were 0.90, 0.86, 0.78 and 0.68 mmol g^{-1} for ethylenediamine, trimethylenediamine, tetramethylenediamine and hexamethylenediamine, respectively. These values are in agreement with the N_f values obtained from the isotherm 0.89, 0.82, 0.76 and 0.64 mmol g^{-1} for the same sequence of diamines. The C:N molar ratio calculated from the C and N content was very close to the predicted values.

Table 1 Carbon (C), hydrogen (H) and nitrogen (N) content and carbon:nitrogen molar ratio (calculated value in parenthesis) for the reaction of alkylenediamines in vermiculite (V) at the saturation condition

Sample	C/%	H/%	N/%	C/N (cal)
V–ethylenediamine	2.04	1.58	1.79	1.14 (1.0)
V–trimethylenediamine	2.53	1.62	1.72	1.40 (1.5)
V–tetramethylenediamine	2.82	1.51	1.57	1.80 (2.0)
V–hexamethylenediamine	4.03	1.96	1.36	2.90 (3.0)

The infrared spectrum (Fig. 2) of vermiculite showed a band at 1002 cm^{-1} associated to asymmetric stretching vibrations of Si–O–Si and Si–O–Al [12, 13].

The bending vibration of Al–OH appeared at 814 cm^{-1}; the OH stretching vibration was observed at 3416 cm^{-1} related to OH hydroxyl groups of inter-

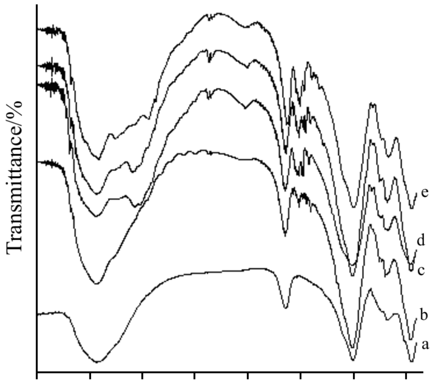

Fig. 2 Infrared spectra of a – vermiculite and vermiculite intercalated with b – ethylenediamine, c – trimethylenediamine, d – tetramethylenediamine and e – hexamethylenediamine

lamellar water and the silanol groups. Absorption at 1640 cm^{-1} was attributed to the characteristic bend deformation of the O–H group of the water. After diamine adsorption, a drastic change in spectra occurred.

For the V–ethylenediamine the absorption bands at 2936 and 3013 cm^{-1} were attributed to the CH_2 stretching modes. Hydrogen bonds between OH and NH_2 groups were confirmed by the band at 1509 cm^{-1} corresponding to characteristic bending deformation of the NH_3^+ group [14, 15].

For V–trimethylenediamine, the spectrum showed bands are due to asymmetric and symmetric NH_3^+ stretching modes at 3062 and 3008 cm^{-1}, respectively. Asymmetric and symmetric NH_3^+ deformations were detected at 1513 and 1463 cm^{-1}, respectively. The absorption at 2896 cm^{-1} was related to the C–H stretching mode [14, 15].

V–tetramethylenediamine showed also the bands for the asymmetric and symmetric NH_3^+ stretching vibration at 3091 and 3013 cm^{-1}, respectively. Asymmetric and symmetric C–H stretching bands were observed at 2942 and 2877 cm^{-1}, while the asymmetric and symmetric C–H bending deformation bands were detected at 1450 and 1413 cm^{-1}, respectively [14, 15].

For V–hexamethylenediamine, the bands associated to asymmetric and symmetric were observed at 2944 and 2874 cm^{-1}. The presence of protonated amine was indicated by bands at 3243 cm^{-1} related to the NH_3^+ stretching mode and at 1512 and 1467 cm^{-1} due to asymmetric and symmetric NH_3^+ deformations, respectively [14, 15].

The absorption band corresponding to symmetric deformation vibration of the NH_3^+ group in all hybrid samples appeared near 1500 cm^{-1} in agreement with formation of weak hydrogen bonds.

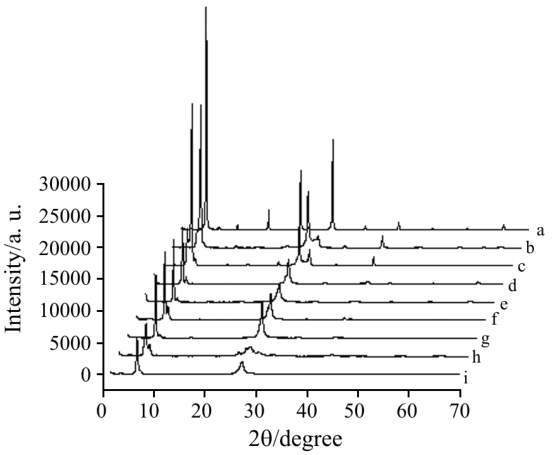

Fig. 3 X-ray diffraction patterns of a – vermiculite and diamine adsorbed (mmol g^{-1}) ethylene- b – 0.69, c – 0.73; trimethylene- d – 0.763, e – 0.788; tetramethylene- f – 0.742, g – 0.759; hexamethylene- h – 0.367, i – 0.409

The X-ray diffraction patterns for vermiculite and the intercalated forms are summarized in Fig. 3.

The native vermiculite showed a peak at 2θ=6.03° angle indexed to the 002 plan, corresponding to interlayer distance (*d*°), of 1465.0 pm [4]. The other peaks detected characterize the vermiculite inorganic matrix [4]. The diffraction patterns observed for the native and the intercalated samples suggest the maintenance of the original crystallinity inorganic matrix as the intercalation process takes place. The diffraction patterns of the diamine derivatives indicated basal spacings around 1280–1300 pm. Comparing with clays, as the same contraction process occurred, the interpretation takes into account the adopted difference in diamine structural conformations when simultaneously the host matrix dehydration occurred with the entrance of the guest molecules. The influence of the humidity in vermiculite matrix was previously demonstrated by considering magnesium saturated vermiculite in equilibrium with humid atmosphere. In such conditions the basal space gave 1436 pm with two slightly incomplete interlayer planes of water molecules as hydration shell around the exchangeable cations [4]. The immersion in water causes an increase in the basal spacing to 1481 pm, which could affect the system to complete the two interlayer planes of water molecules. On the other hand, by dehydrating on heating the original 1436 pm phase gives an interlayer distance of 1382 pm, which could be more associated to a structure containing two slightly incomplete planes of water in different arrangement than the original phase [4]. Continuing the dehydration process a 1159 pm phase was detected with a single plane of water molecules; and a final 902 pm talc-like phase resulted with no interlayer water [4]. In the present case, the interlayer cation and the water content should be the responsible agents for generating differences in stages of intercalation by changing the interlayer distance. During the progress of intercalation it could be expected that the diamine conformations change from parallel to inclined positions inside the interlayer space with a different degree of hydration compared to the native vermiculite. This possibility was investigated by using DSC and TG.

The TG curve of vermiculite (Fig. 4) showed a single mass loss of 9.1%, which was related to the release of surface and coordination water of interlayer space [16].

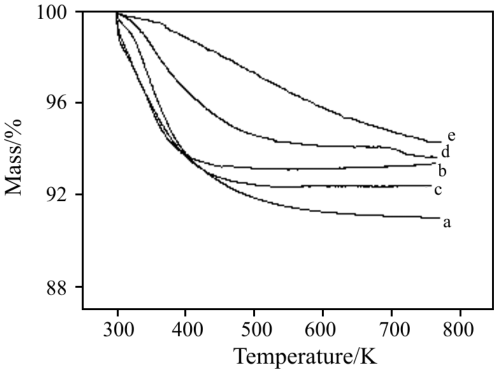

Fig. 4 TG curves of a – vermiculite, b – V–ethylenediamine, c – V–trimethylenediamine, d – V–tetramethylenediamine and e – V–hexamethylenediamine

The V–ethylenediamine, V–trimethylenediamine, V–tetramethylenediamine and V–hexamethylenediamine hybrids generated 6.7, 7.3, 5.82 and 5.60% mass losses, respectively.

In the DSC curves (Fig. 5) two endothermic peaks at 396 and 448 K were detected for vermiculite and attributed to surface and coordination water of interlayer space removal. And with respect to hybrids, two endothermic peaks dislocated to lower temperature and new exothermic ones were revealed as it is illustrated in Table 2.

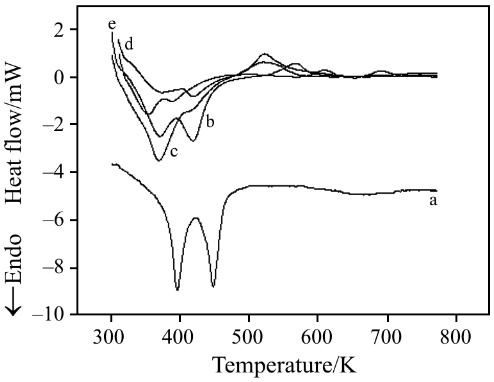

Fig. 5 DSC curves of a – vermiculite, b – V–ethylenediamine, c – V–trimethylenediamine, d – V–tetramethylenediamine and e – V–hexamethylenediamine

The first peaks of V–ethylenediamine (Fig. 5b) correspond to a lower area when compared to precursor vermiculite, being then attributed to the rearrangement of matrix resulting from entrance of organic molecules. The exothermic peak at 568 K might be due to the diamine conformation change in the interlayer space of solid. The same behavior was observed for V–trimethylenediamine and V–hexamethylenediamine hybrids. For all hybrid system the area of the endothermic peak which is attributed to the dehydration of matrix is smaller than the precursor vermiculite, as indicated by ΔH values obtained from DSC data. In the V–tetramethylenediamine hybrid just one endothermic event was detected corresponding to ΔH=122.6 J g^{-1}, as is shown in Table 2. In this latter case, the evaporation of adsorbed and coordination water and the organic decomposition occurred in a single stage. New exothermic peaks were detected for all hybrids in the range of 520–650 K, which according to the TG curves were not accompanied by mass losses. Thus, these events in DSC were attributed to the diamine conformation change in interlayer space of solid, resulting a more stable arrangement of organic chains. This set of data is an indication of the dehydration of solid with the entrance of diamine in gallery space.

Table 2 Temperature ranges, maximum peak temperature and associated enthalpies originating from the DSC curves of vermiculite and hybrids

Solid	T_{range}/ K	T_{max}/ K	ΔH_1/ J g^{-1}	T_{range}/ K	T_{max}/ K	ΔH_2/ J g^{-1}	T_{range}/ K	T_{max}/ K	ΔH_3/ J g^{-1}
V	381–412	396	+81.2	433–463	448	+59.8	–	–	–
V–ethylenediamine	334–391	371	+43.3	398–441	419	+36.8	532–591	567	–19.1
V–trimethylenediamine	338–403	373	+22.7	405–447	419	+12.5	492–566	523	–55.3
V–tetramethylenediamine	333–402	369	+122.6	–	–	–	477–570	521	–40.4
V–hexamethylenediamine	318–373	355	+33.4	378–413	389	+5.3	585–632	610	–7.5

Conclusions

The synthesis of hybrids resulted from interaction of vermiculites with aliphatic diamines as it was confirmed by X-ray diffraction, infrared spectroscopy studies and elemental analyses. In one hand, TG and DSC results supported the dehydration of solid with the concomitant entrance of organic moieties in interlayer space and, in the other hand confirmed the hypothesis of intercalation and replacement of water molecules by diamines.

Acknowledgements

The authors thank to CNPq and CAPES for financial support and fellowships.

References

1 F. Franco and M. D. R. Cruz, J. Therm. Anal. Cal., 85 (2006) 369.
2 I. A. Pastre, I. N. Oliveira, A. B. S. Moitinho, G. R. Souza, E. Y. Ionashiro and F. L. Fertonani, J. Therm. Anal. Cal., 75 (2004) 661.
3 G. W. Brindely and G. Brown, Crystal Structures of Clay Minerals and their X-ray Identification, 1st Ed., Mineralogical Society, London 1980.
4 L. A. Pérez Maqueda, M. C. Jiménez de Haro, J. Poyato and J. L. Pérez-Rodríguez, J. Therm. Anal. Cal., 71 (2003) 803.
5 S. D. Burnside, H.-C. Wang and E. P. Giannelis, Chem. Mater., 11 (1999) 1055.
6 S. C. Tjong, Y. Z. Meng and A. S. Hay, Chem. Mater., 14 (2002) 44.
7 J. Xu, Y. Z. Meng, R. K. Y. Li, Y. Xu and A. V. Rajulu, J. Polym. Sci. B, 41 (2003) 749.
8 V. Ramírez-Valle, M. C. Jiménez de Haro, M. A. Avilés, L. A. Pérez-Maqueda, A. Durán, J. Pascual and J. L. Pérez-Rodríguez, J. Therm. Anal. Cal., 84 (2006) 147.
9 F. J. Rey-Perez-Caballero and G. Poncelet, Microporous Mesoporous Mater., 37 (2000) 313.
10 M. Nakatsuji, R. Ishii, Z.-M. Wang and K. Ooi, J. Colloid Interf. Sci., 272 (2004) 158.
11 B. W. Bache, J. Sci. Food. Agric., 27 (1976) 273.
12 V. C. Farmer and J. C. Russel, Spectrochim. Acta, 20 (1964) 1149.
13 P. J. Launer, Am. Mineral., 51 (1967) 764.
14 R. M. Silverstein, G. C. Basser and T. C. Morrill, Spectrometric Identification of Organic Compounds, John Wiley & Sons Inc., 2nd Ed., New York 1991.
15 D. L. Pavia, G. M. Lampman and G. S. Kriz, Introduction to Spectroscopy, Saunders College Publishing, 2nd Ed., New York 1996.
16 L. A. Pérez-Maqueda, V. Balek, J. Poyato, J. L. Pérez-Rodríguez, J. Šubrt, I. M. Bountsewa, I. N. Beckman and J. Málek, J. Therm. Anal. Cal., 71 (2003) 715.

DOI: 10.1007/s10973-006-7860-3