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THERMAL CHARACTERIZATION OF MODIFIED PHYLLOSILICATES WITH AROMATIC HETEROCYCLIC AMINES

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Vermiculite with the general formula of $[Si_{6.85}Al_{1.15}][Mg_{4.68}Al_{0.51}Fe_{0.63}]O_{20}(OH)_4Ca_{0.128}Na_{0.032}K_{0.094}$ was made to react with heteroaromatic amines α-, β- and γ-picolines in aqueous solution. The products were characterized by elemental analysis, infrared spectroscopy, X-ray diffraction and thermogravimetry. The intercalated nanocompounds maintained the crystallinity which changed the original interlayer distance of 1422 to 1474, 1456 and 1474 pm, for the sequence of the guest picoline molecules. Thermogravimetry data suggested the intercalation reactions were governed by basicity of amines.

Keywords: *aromatic amines, phyllosilicate, thermal analysis*

Introduction

A relevant modifying route applied to change the physical and chemical properties of natural or synthesized materials has been devoted to the incorporation of organic moieties, whose pendant attached chains, either on the external part or internal surface, can improve the ability of the new multifunctional materials in this class of inorganic–organic hybrids, which are applied in a variety of academic or technological activities. In this context, intercalation has been a route for synthesis of inorganic–organic [1]. The present investigation deals with the exploitation of vermiculite as a support for reaction with organic derivatives. This mineral has a 2:1 lamellar arrangement whose disposed inorganic layers could technologically be of great practical importance. Thus, the natural exfoliated vermiculite is used as lightweight aggregate in concrete, plaster, and adsorbent [2]. In addition to these attractive features, vermiculite also exhibits a wide chemical surface that takes place at the layer edges, like in exchange reactions. The cation residing in the vermiculite interlayer space can be exchanged by numerous cations, whose new formed materials change the properties of the original clay [3–5]. On the other hand, vermiculite has been utilized for evaluating structural changes and adsorptive, catalytic and electrochemical properties [6–10]. Phyllosilicate-organic reactions have been extensively investigated, generating information on different types of interactive mechanisms like the multivariable reactions involving silicate layers, inorganic cations, water and organic molecules [11]. Therefore, many experimental routes have been proposed to explore solid/solid [12] and solid/liquid [13] interface reactions. In such direction, organic compounds of wide range of functionalities can interact with surface of clay minerals such as amides [14, 15], amino acids [16], dyes [17, 18], amines [19, 20] and mercapto compounds [21], due mainly to its swelling behavior among them montmorillonite is the best studied clay mineral.

An attempt was made in order to have more information on the vermiculite/heteroaromatic amine intercalation process. Three of them were chosen to investigate with respect to the synthesis and characterization of the vermiculite hybride derivatives.

Experimental

Chemicals

The vermiculite sample was supplied by União Brasileira de Mineração (Santa Rita, Paraiba, Brazil). Vermiculite was reacted with hydrogen peroxide to eliminate the organic impurities. Gravimetric determination of SiO_2 was carried out after mixing the mineral with sodium carbonate and potassium nitrate and successive treatments with hydrochloric acid [22]. Other elements were quantified by using a Perkin-Elmer 5100 Model AAS instrument with an air-acetylene flame after previous treatment of samples with HF and HNO_3. Its chemical composition, in mass%: SiO_2 (44.62), Al_2O_3 (9.18), Fe_2O_3 (5.46), CaO (0.78);

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MgO (20.44); Na_2O (0.11), K_2O (0.48), with a mass loss of 18.9% after heating to 1000°C. Considering the present data, the structural formula of the studied sample gave the following general composition: $Al_{1.66}Si_{6.85}Mg_{4.68}O_{20}(OH)_4Ca_{0.128}Na_{0.032}K_{0.094}Fe_{0.63}$ where Fe^{3+} corresponds to total iron content obtained from the chemical analysis. Picolines (Merck) were used without further purification.

Intercalation isotherms

The intercalation isomers and cation adsorption were obtained using the batchwise method where 50 mg of pristine vermiculite was suspended in 25.0 cm^3 of aqueous solutions, containing amine at several concentrations, varying from zero to 0.010 mol dm^{-3} at 298±1 K. The suspensions were mechanically stirred for 48 h previously established as optimal time. The solid was then filtered and in each sample the picoline content was determined by acid-base titration. The number of amine moles N_f in mass (m) of the solid was calculated using the following expression: $N_f=(N_i-N_s)m^{-1}$, where N_i and N_s are the initial and final amounts of the amine in the solution, respectively. The intercalated solids were characterized by infrared spectroscopy, X-ray diffraction and thermogravimetry.

Instruments

X-ray diffraction (XRD) patterns were obtained on a Shimadzu XD3A diffractometer equipped with monochromatic CuK_α, operating at 40 kV and 30 mA. The diffraction patterns were recorded from 1.4 to 70° at a scan rate of 0.67° s^{-1}.

FTIR spectra of the samples dispersed in KBr disks were recorded at room temperature using a Bomem MB spectrometer in the range of 4000 to 400 cm^{-1} with a resolution of 4 cm^{-1} and 30 scans for each run.

Thermogravimetric curves (TG) were recorded using a DuPont 1090 B model thermogravimetric apparatus coupled to a DuPont 951 thermobalance. The samples were heated up to 970°C at 10 K s^{-1} heating rate in a dry nitrogen. The sample masses varied between 15.0–30.0 mg.

Results and discussion

One of the most explored reactions on lamellar compounds is related to intercalation, not only because its easy way of detection the interlamellar expansion, but also for detecting the guest molecule inside the interlayer space. At first, the time required for the attainment of reaction equilibrium was evaluated by measuring the uptake rates of the three picoline isomers, whose kinetic studies were conducted with 0.010 mol dm^{-3} for each guest molecule. The effectiveness of the reactions was evaluated through nitrogen, using acid-base titration. The outlined isotherms clearly demonstrated that a low variation in the adsorption was observed after 48 h and this time was employed for all other operations. Therefore, when the three isomers of picolines reacted with vermiculite during 48 h, the intercalation isotherms (Fig. 1) were obtained.

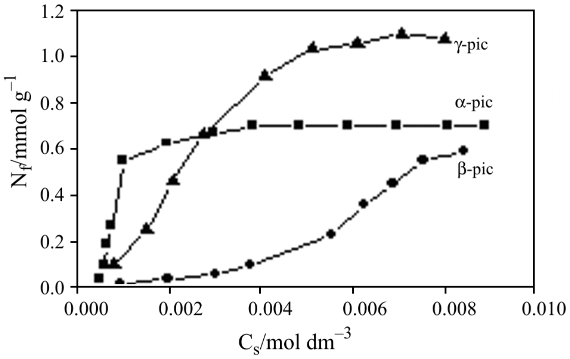

Fig. 1 Concentration effect of guest molecules in incorporation of picolines inside vermiculite at 298±1 K

The amount of reacted picolines depends on the position of methyl group attached to the organic ring, by presenting alpha and beta forms with a very close extension in intercalation. Thus, the highest value for γ-picoline can be associated with the favorable position of methyl group, which inductive effect induces the electron density on basic nitrogen atom, and facility chemisorption of amine molecules into the acid centers of the clay surface. On the contrary, the steric effect of the methyl groups on the other picoline molecules makes difficult the entrance of molecules in the interlayer nanospace decreasing their amount.

Typical thermogravimetric curve and its derivate are illustrated in Fig. 2 where the first decomposition step between 25 and 380°C associated to the loss of concomitant water and organic molecules, while the second decomposition between 672 and 927°C is due to condensation of hydroxyl structural groups.

Thermogravimetry data showed similar thermal degradation of modified vermiculites, as it is illustrated in Fig. 3. In the precursor compound an overall mass loss of 13.9% is observed, whereas after intercalation the mass loss is 15.8, 15.0 and 16.0% for hybrids V–α-pic, V–β-pic and V–γ-pic respectively, in a wide temperature range (from 25 to 970°C), causing 1.2–2.1% difference in the mass loss values. The results are in agreement with the data derived from the isotherms, which is therefore another indication of the incorporation of the organic moieties amine on solid.

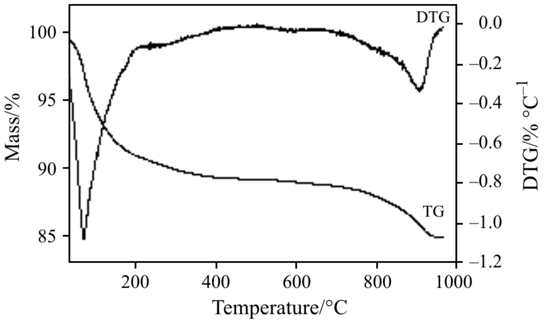

Fig. 2 TG/DTG curves of hybrid derived from vermiculite and α-picoline

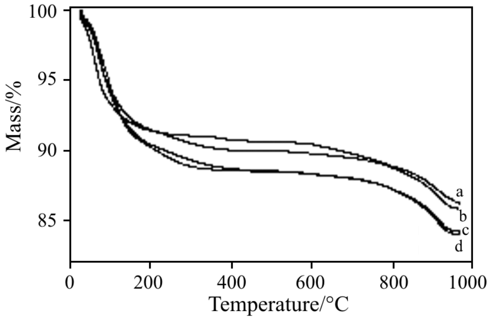

Fig. 3 Thermogravimetric curves of a – vermiculite precursor and its forms derived from interaction with b – β-, c – α- and d – γ-picoline

An interesting feature related to the reaction is the relation between pK_a values, which are 5.97, 5.68 and 6.02 for α-, β- and γ-picolines, respectively, and the total mass loss of the hybrids between 25 and 400°C (Fig. 4). This result suggests that the intercalation reaction is strongly influenced by the basicity of amines. Thus, the highest obtained value for γ-picoline suggested the more pronounced basic behavior. Therefore, the principal amine-interaction mechanism can be an intercalation of neutral amines and their incorporation at acidic sites on surface of the vermiculite.

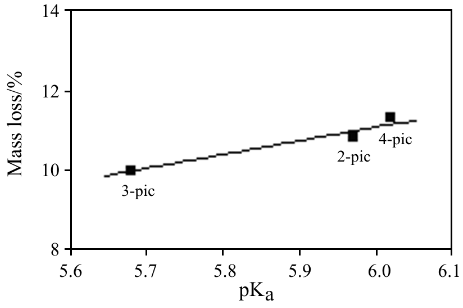

Fig. 4 Effect of pK_a of picolines on the mass loss of the obtained vermiculite hybrids

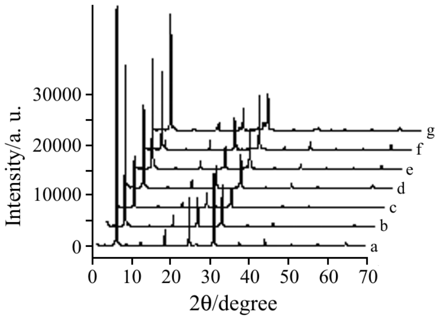

Fig. 5 X-ray diffraction patterns of a – vermiculite and α-picoline adsorbed, b – 0.04, c – 0.35, d – 0.63, e – 0.69, f – butyl 0.85 and g – 1.12 mmol g^{-1}

The diffraction patterns of pristine clay and the nanocompounds are very similar, suggesting the maintenance of the original crystallinity for the inorganic matrix, when reactions take place (Fig. 5). The basal spacing (*d*) values of 1422, 1474, 1456 and 1474 pm were detected for precursor and α-, β- and γ-picoline derivates, respectively. Substantially, the guest molecules can interact either to external surface or in the interlayer space of clay. In this latter condition the intercalation inside the interlayer nanospace of the phyllosilicates can change the basal spacing. Studies on the interaction of different kinds of organic guest molecules in clay minerals showed that the basal spacing of original hydrated clay can decrease, increase, or does not change, depending on the degree of hydration of the obtained clay and the size of the intercalated molecules [22]. In the present case, the small difference in the basal spacing is consistent with the incorporation of picolines on external surface.

The infrared spectrum of vermiculite showed the main bands at 3447 cm^{-1} which are attributed to the overlapping absorptions due to O–H stretching from water of hydration and silanol groups HO–Si bonded to the native matrix; and at 997 cm^{-1} due to stretching vibrations corresponding to Si–O–Si and Si–O–Al bonds [23]. The intercalated materials showed changes in intensities of these bands and the appearance of new ones at 2924 and 2849 cm^{-1}, due to asymmetric and symmetric C–H stretching bands, respectively [24]. The C–N stretching vibration was detected at 1456 cm^{-1} for all hybrids [25].

Conclusions

Native vermiculite was applied as host for aromatic amines showing the incorporation of 0.70, 0.60 and 1.10 mmol g^{-1} for α-, β- and γ-picolines, respectively. Thermogravimetry data were in agreement with pKa of picolines suggesting that the basicity of these molecules is a preponderant factor in this kind of reactions. The new solids showing neutral amine in gallery space or/and surface can interact with other species like heavy cations.

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