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MONTMORILLONITE INCORPORATED WITH MAGNESIUM OXIDE
Preparation, characterization and adsorption of organic compounds

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MgO was incorporated into montmorillonite (MMT) though the controlled formation of $Mg(OH)_2$ followed by calcination. The evidence for Mg^{2+} in MMT before calcination was concluded from TG curves where two different temperature ranges for $Mg(OH)_2$ dehydroxylation suggested that the location of Mg^{2+} at its internal and external surfaces. FTIR by diffuse reflectance technique of calcined sample showed a typical MgO band. XRD indicated a decrease in structural order and no collapse of clay structure. The organic compounds adsorption to MMT modified with MgO as suggested by increased degradation temperatures occurred at internal and external clay surfaces besides in an area formed probably by MgO and MMT layers.

Keywords: *infrared analysis, magnesium oxide, montmorillonite, organic compound adsorption, thermogravimetry, XRD*

Introduction

Clay minerals have long been used as catalysts for organic synthesis. Among them montmorillonite (MMT) is one of the most important smectite for this application. It is a phyllosilicate with 2 tetrahedral and one octahedral sheets. Montmorillonite shows a positive charge deficiency due to an isomorphous substitution of magnesium by iron(III) or aluminium in the octahedral sheet during its formation. This charge is equilibrated by cations (typically Ca^{2+}, Na^+ or K^+) located in the space between layers, denominated 'interlamellar space'. These interlamellar cations can be exchanged by others (Al or Fe) or organic molecules (e.g. quaternary ammonium salts, polar polymers and dyes) resulting in clays with special properties [1–4]. This modification allied to a high cation-exchange capacity (CEC) and good swelling properties of MMT result in a wide variety of catalytically active forms of montmorillonite [5]. One of these forms are the pillared clays consisting of clay platelets linked by pillars of Al, Zr and Fe oxides without clay exfoliation, in which high temperatures can be used without collapse of the structure [6–8]. The literature does not discuss the formation of Mg-based clays nor the incorporation of MgO to MMT.

The condensation of aldehydes to form esters known as Tishchenko reaction is catalysed by alkaline-earth oxides such as MgO. Although MgO can provide the basic and acid sites needed to this reaction [9, 10], a low yield [11] was obtained in the preparation of benzyl benzoate from benzaldeyde. This kind of reaction could benefit from a catalyst prepared from MMT and an alkaline-earth oxide as MMT would provide more acid sites.

In this work three methods were described for the incorporation of MgO into montmorillonite. Thermal analysis (TG), X-ray diffraction (XRD) and infrared spectroscopy (FTIR) were used to characterize the modified clays. A preliminary study on their capacity to adsorb organic molecules was also conducted, by using benzyl benzoate and trimethyl octadecyl ammonium chloride as probes.

Experimental

Materials

A montmorillonite from Mineração Campos Novos, Campina Grande, Brazil, was employed. Its chemical analysis, published elsewhere [12] presented SiO_2 (51.1%), Al_2O_3 (18%), Fe_2O_3 (9.8%), CaO (1.5%), TiO_2 (0.9%), K_2O (0.5%), NaO (0.6%), MgO (3.12%) while the CEC was 119 meq/100 g. It was purified by sedimentation in distilled water following a method described by Sequio [13]. Trimethyl octadecyl ammonium chloride was supplied by Herga S.A., Brazil; benzyl benzoate (95%) and magnesium chloride hexahydrated were from VETEC S.A., Brazil.

Incorporation of MgO into montmorillonite (MMT)

Three methods (A, B and C) were used to incorporate MgO to MMT. In method A, 1 g of MMT was agitated in 100 mL of a 0.5 M water solution of $MgCl_2{\cdot}6H_2O$ at 50°C for 24 h. After this time, the so-

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lution was filtered and the clay was washed with enough water to eliminate chloride ions and dried at 70°C for 72 h. The presence of residual chloride was monitored by the addition of drops of 0.1 M $AgNO_3$ to the water fractions. It was calcined at 600°C for 3 h (MMT-A). In method B, 5 g of MMT were agitated with 250 mL of a 0.1 M aqueous solution of NH_4Cl at room temperature for 48 h to promote an exchange of interlamellar cation for NH_4^+. The solution was filtered and the clay was washed with water to eliminate chloride ions and dried at 50°C. After that, the clay was agitated with a 100 mL of a 0.1 M aqueous solution of $MgCl_2{\cdot}6H_2O$ at 50°C, for 2 h, followed by filtration, washings with water, drying and calcination in the same conditions (MMT-B). The procedure for method C was adapted from Xeidakis [14, 15]: 12 meq g of Mg^{2+} ($MgCl_2{\cdot}6H_2O$) per gram of clay were added to 100 mL distilled water, followed by the slow addition of 0.5 M aq. NaOH to attain an OH/Mg proportion equal to 1.5 (MMT-C). The same procedure was followed to isolate, dry and calcine the clay, as already described.

Incorporation of ammonium salt and benzyl benzoate into MMT

The clay modified by method C (MMT-C) and calcined was either agitated with an aqueous solution of 0.1 M tri-methyl octadecyl ammonium chloride, for 1 h at 70°C, or agitated with 10 mL of a hexane solution of 20% (*m*/*v*) of benzyl benzoate, for 2 h at 40°C. These suspensions were filtered, and either washed with distilled water to eliminate chloride ions or with hexane to eliminate excess of ester. The solids were dried at 70°C for 48 h.

Control preparations

MgO sample used as reference was prepared by heating $MgCl_2{\cdot}6H_2O$ at 120°C. Calcined MMT sample, also used as reference was prepared by heating the parent MMT at 600°C for 3 h.

Characterization of modified clays

Thermogravimetric analysis of the materials, before and after being calcined, were conducted on a TGA 51 Shimadzu thermobalance, heating from 30 up to 800°C at 10°C min^{-1}, under nitrogen. Infrared spectra were obtained on a Nicolet Magna 750 with Fourier transformed by transmittance or reflectance. X-ray diffraction studies were conducted in an equipment Rigaku Miniflex (radiation CuK$_\alpha$: 1.5418 $0<\theta<30$). Samples were analyzed by the powder technique and oriented plates.

Results and discussion

The TG curve of the parent MMT (Fig. 1a) showed two regions of mass loss. The first loss of 5%, between 30 and 200°C is due to losses of physically adsorbed water and water of hydration of interlayered cations. The second loss is proper of silanol dehydroxylation in MMT. The TG curve of the material prepared by method A before calcination (MMT-A) (Fig. 1b) showed 25% mass loss up to 800°C without defined maxima. This curve pattern is not typical of MgO formation from $MgCl_2$ hexahydrated or from the dehydroxylation of $Mg(OH)_2$, for these are well known reactions that occur at 120 and 300°C, respectively [15, 16]. Although a shift of the degradation temperatures could be expected in the presence of MMT, the actual behavior is explained as having been due to water loss, water being bounded in different ways. It was not possible to infer from this curve that MgO could be formed upon calcination.

The FTIR spectra of MMT-A (before and after calcination) were similar to that of the parent MMT as shown in Fig. 2. The typical absorption bands of montmorillonite are: the O–H stretching vibration band from silanol group at 3628 cm^{-1}, water absorption bands at 3470 and 1630 cm^{-1}, the band of Si–O bond on tetrahedral sheet at 1040 and 1042 cm^{-1}, the absorption band at 526 cm^{-1} due to Si–O–Fe bond (iron inside the octahedral sheet) and the band at

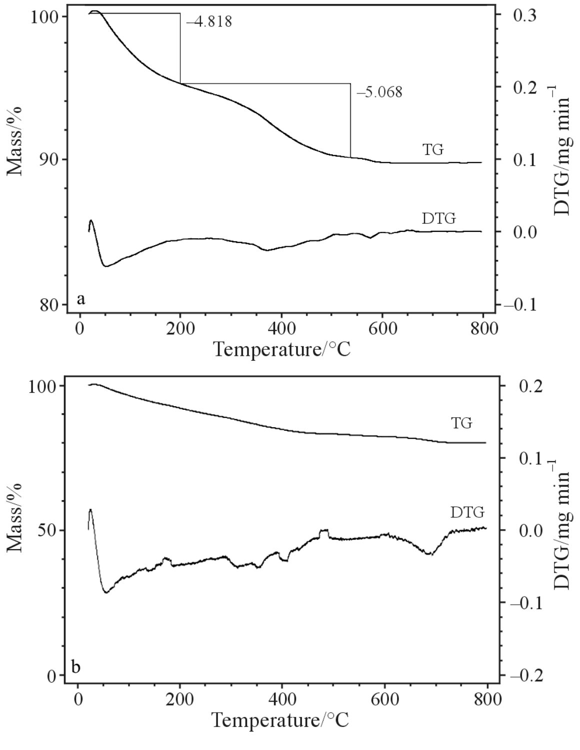

Fig. 1 TG and DTG curves of a – MMT and b – MMT-A before calcination

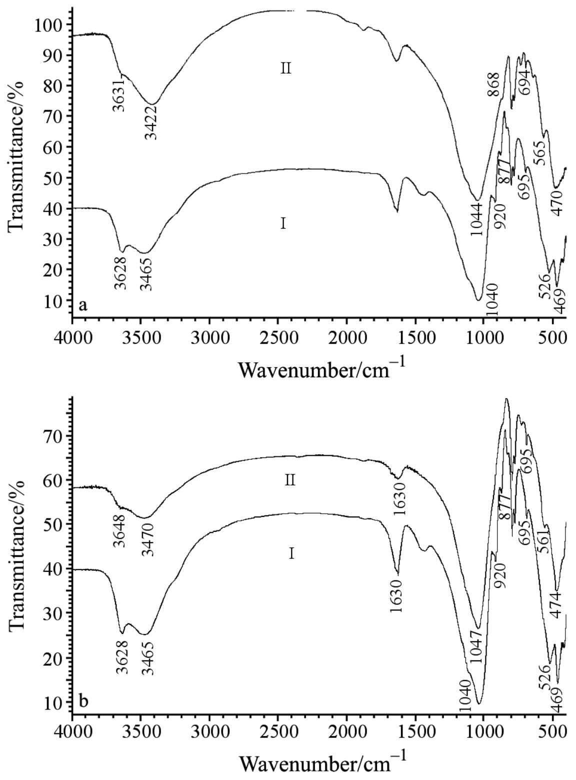

Fig. 2 FTIR spectra of MMT a – I – before and a – II – after calcination and that of MMT-A b – I – before and b – II – after calcination

468–470 cm^{-1} due to the vibration mode of Si–O–Si bond [17]. After MMT calcination, its FTIR spectrum presented two major differences compared to the non-calcined sample: the absorption bands at 1040 and 526 cm^{-1} were shifted to 1044 and 561 cm^{-1}. The same modifications were observed in the spectrum of MMT-A after calcination. Madejova [17] attributed these band shifts to higher frequencies to the penetration of interlayer cations into hexagonal hole causing a distortion of tetrahedral silicate.

Sample MMT-A submitted to XRD (Fig. 3) before calcination presented a basal space of 14.1 Å (2*t*=6.24), while parent MMT showed the value of 12.8 Å (2θ=6.8). These results suggest that a partial intercalation of Mg^{2+} occurred. After calcination, the basal space of both MMT-A and parent MMT were 9.3 Å (2θ=9.45). This change indicates a collapse of the clay structure after calcination, which can be understood by recalling the possible penetration of small cations into hexagonal cavities of the clay as indicated by FTIR [17].

The TG of the material prepared by method B (MMT-B) before calcination (Fig. 4a) showed 6.5% of water loss below 200°C and two peaks of mass loss at 323 and 481°C. The first loss (2%) was associated with the dehydroxylation of $Mg(OH)_2$ and the second (3%) with the dehydroxylation of silanol groups of the natural clay [16]. The infrared spectrum of MMT-B, besides presenting all the bands of the parent MMT, presented a band at 1410 cm^{-1} assigned to NH_4^+ bending vibration that disappeared after calcination. According to the XRD of MMT-B that showed a basal space of 10 Å this material also collapsed after calcination.

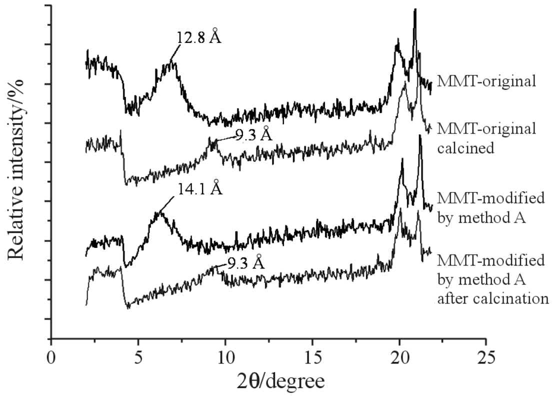

Fig. 3 XRD of parent MMT and MMT-A before and after calcination

These results obtained by using methods A and B indicated that some magnesium ion had been incorporated by both procedure but, in such a small amount that it did not prevent the collapse of the clay structure.

The third method for the incorporation of MgO to MMT (MMT-C) involved the previous formation of $Mg(OH)_2$. The TG of MMT-C before calcination (Fig. 5a) showed two mass losses in the 200–600°C range (14%), besides the water loss below 200°C. The first event (peak at 360°C) corresponded to the tem-

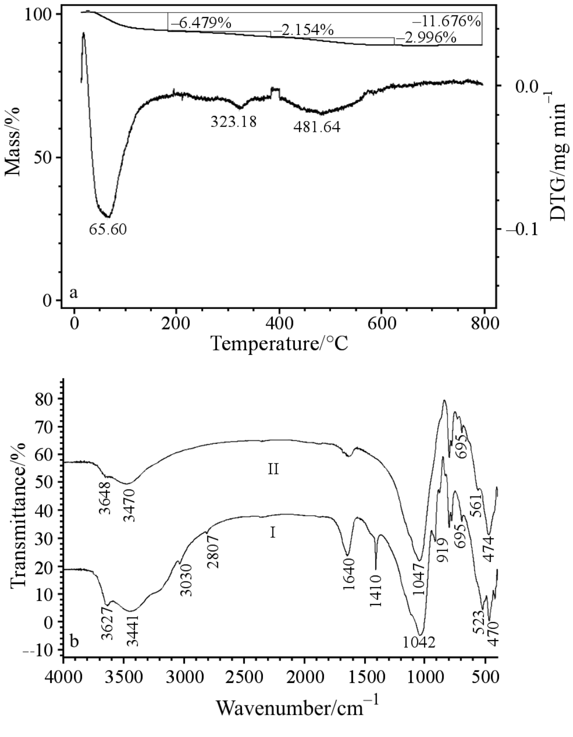

Fig. 4 a – TG and DTG curves of MMT-B; b – FTIR spectra of MMT-BL; b – I – before and b – II – after calcination

perature for the dehydroxylation of $Mg(OH)_2$, and the second (at 434°C) was attributed to the dehydroxylation of $Mg(OH)_2$ located in the interlayer space following Xeidakis [16]. In this case the $Mg(OH)_2$ accounted for 14% of mass loss while, in clays prepared by methods A and B, the mass losses, at the same regions were below 5%.

The FTIR spectrum by diffuse reflectance of MMT-C after calcination (Fig. 5b) showed several absorption bands that are common to the spectrum of calcined MMT except for the band at 1455 cm^{-1}. This band is present in the MgO spectrum (Fig. 5b–III). In spite of this evidence it is not possible to say that MgO is located either in or out the interlayer space.

A comparative analysis of FTIR transmittance spectra of MMT-C before and after calcination (Fig. 6a) revealed a major alteration: the shift of Si–O–Si absorption band to 1024 cm^{-1}.

The basal space due to the reflection $d(001)$ was not observed in the XRD of MMT-C (Fig. 6b), but the absence of the diffraction peak at 9.3 Å indicated that the clay structure had not collapsed. It can be suggested that a non-crystalline material resulted from the MgO incorporation on a semi-crystalline MMT.

The MMT-C sample after calcination was used to perform the adsorption experiments with the organic compounds: trimethyl octadecyl ammonium chloride and benzyl benzoate. The TG of MMT-C adsorbed with trimethyl octadecyl ammonium chloride (Fig. 7a) presented three main mass losses at 257, 370 and 543°C. In a previous work [13] it was shown that the two mass losses (at 257 and 357°C) were due to the decomposition of the ammonium salt adsorbed at the MMT external surfaces and to the ammonium salt incorporated in the interlayer space of the clay. The same explanations are in agreement with the observations made in the present work. The third loss at the highest temperature (543°C) could be associated with the degradation of ammonium salt that would be interacting with MgO particles at the interlayers. The MMT-C after calcination showed no mass loss (Fig. 7b).

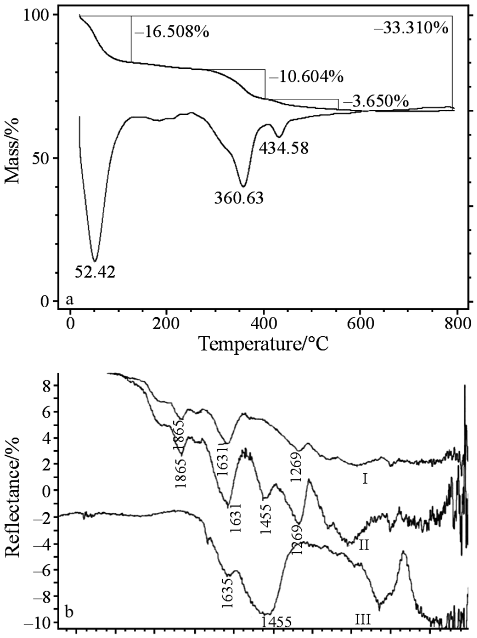

Fig. 5 a – TG and DTG curves of MMT-C; b – FTIR by diffuse reflectance of MMT-C; b – I – before calcination MMT-C; b – II – after calcination and b – III – MgO

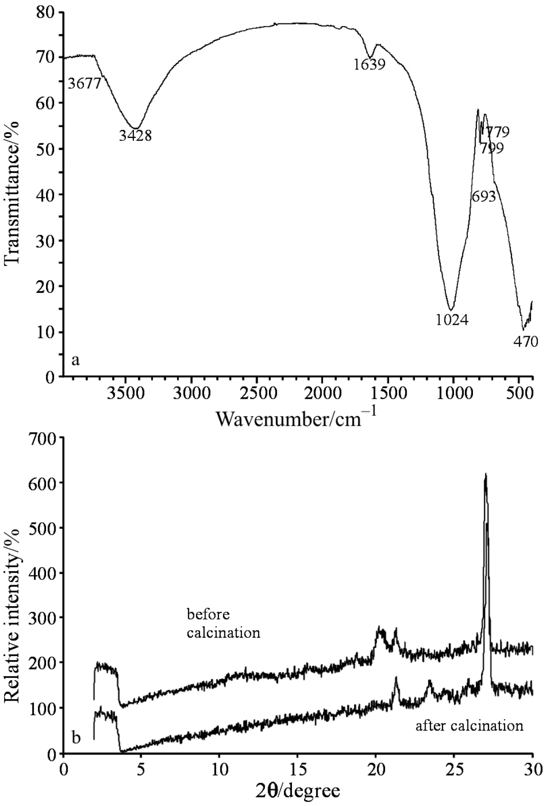

Fig. 6 a – FTIR by transmittance of MMT-C after calcination; b – XRD of MMT-C before and after calcination

The TG curve of MMT-C incorporated with benzyl benzoate followed the same pattern showing three main regions of mass loss (Fig. 8a). This curve was compared to that from the parent MMT not treated with Mg^{2+} but incorporated with benzyl benzoate (Fig. 8b). The mass loss at the first region, seen in both curves, is due to the degradation of benzyl benzoate adsorbed to the external surface of MMT. The second regions are rather different: while the curve of MMT not treated with Mg^{2+} (Fig. 8b) shows about 480°C the dehydroxylation of silanol groups, the MMT-C curve (Fig. 8a) presents a 4% of mass loss with a maximum at 358°C probably due to the degradation of benzyl benzoate located at an interlayer space. In the third region in curve of Fig. 8a a degradation is observed as for the ammonium salt added to MMT-C, which can be associated with the degradation of benzyl benzoate interacting with MgO.

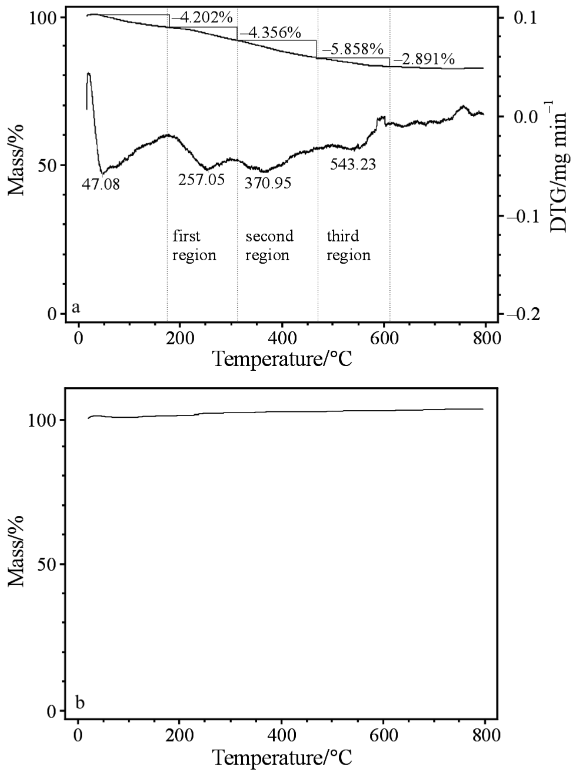

Fig. 7 TG and DTG curves of a – MMT-C after calcination and adsorption of ammonium salt and b – TG curve of MMT-C calcined

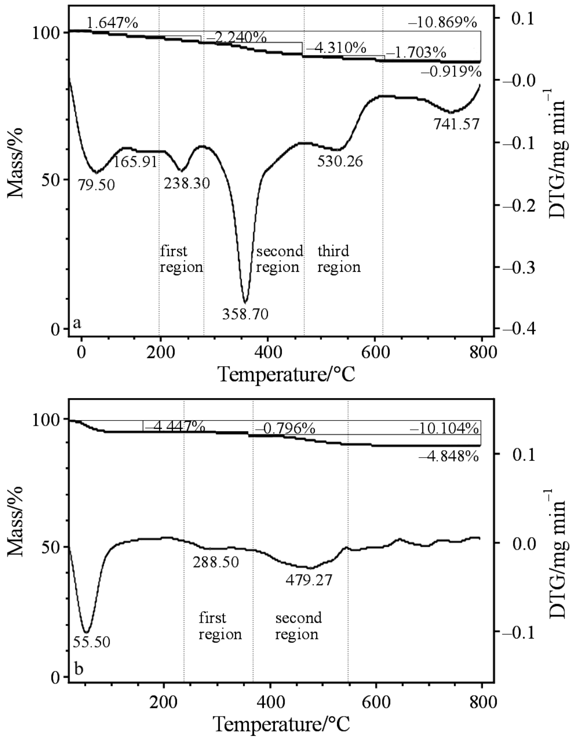

Fig. 8 TG and DTG curves of a – MMT-C calcined and adsorbed with benzyl benzoate; b – parent MMT adsorbed with benzyl benzoate

Conclusions

The most efficient method for the incorporation of MgO into montmorillonite without the collapse of the clay structure was through the controlled formation of $Mg(OH)_2$. The FTIR analysis by transmittance and diffuse reflectance and thermogravimetric analysis proved the formation of MgO. The two first regions of degradations detected by TG analysis of MMT-MgO incorporated with organic molecules are evidences that the organic compounds were adsorbed to internal and external surfaces of MMT. A third region at a higher temperature, not present in the TG curves of parent MMT indicate that these organic compounds are also interacting with MgO particles present in the interlayers of MMT. Thermogravimetry was the unique technique that distinguished interlayer and external formation of MgO.

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