

Physical and catalytic characterization of smectites from Boa-Vista, Paraíba, Brazil (*Caracterização física e catalítica de esmectitas de Boa Vista, Paraíba, Brasil*)

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Abstract

The original crystalline structure of clay minerals can be altered in a controlled way, through acid or thermal treatments, resulting then in suitable products to be used as catalysts. This paper aims to characterize the red smectite clays of Boa-Vista, Paraíba (Brazil) in their natural form, and after chemical, thermal and acid treatments by X-ray fluorescence, differential thermal analysis, dynamic X-ray diffraction, classic X-ray diffraction analysis, scanning electron microscopy, nitrogen adsorption and model reaction. The results show that acid treatment partially altered the structure of the montmorillonite. An important increase in the surface area of the solid obtained was observed. The obtained reaction for the treated material showed that the clay was more acid than the natural one, yielding a better catalytic activity.

Keywords: catalyst, smectite, chemical treatment, thermal treatment.

Resumo

A estrutura cristalina original dos argilominerais pode ser alterada de um modo controlado através de tratamentos ácidos ou tratamentos químicos, resultando em produtos satisfatórios para serem usados como catalisadores. O objetivo deste trabalho é caracterizar a argila esmectítica vermelha de Boa-Vista, Paraíba (Brasil) na sua forma natural e após tratamentos químicos e térmicos. Os métodos usados foram fluorescência de raios X, análise térmica diferencial, difração de raios X, microscopia eletrônica de varredura, adsorção física de nitrogênio e reação modelo. Os resultados mostram que o tratamento ácido alterou parcialmente a estrutura da montmorilonita. Foi observado um importante aumento na área específica do sólido obtido. A reação obtida para o material tratado mostrou que a argila foi mais ácida que a natural conduzindo a uma melhor atividade catalítica.

Palavras-chave: catalisador, esmectita, tratamento químico, tratamento térmico

INTRODUCTION

Clays are in general constituted essentially by minerals that are hydrous silicates of aluminum and/or magnesium, with significant amounts of iron, nickel, chromium and other cations in the crystalline structure as an isomorphic substitution. The peculiar crystalline structure of some clay minerals generates a capacity of reversible exchange with organic or inorganic cations and metal-organic such as in this case of smectites. The exchange of specific cations can generate active centers in the clay minerals, making them catalysts, which can be then used for a large number of chemical reactions in industries. The clay minerals mostly used as catalysts are smectite, kaolinite, halloysite, palygorskite, attapulgite and sepiolite [1-3].

Clays are very versatile materials and hundreds of millions of tons currently find applications not only in ceramics and building materials, paper coatings and fillings, drillings muds, foundry moulds, pharmaceuticals, etc., but also as adsorbents, catalysts or catalyst supports, ion exchangers, etc., depending on their specific properties [4-8].

The smectite may possess up to about 33% of cation substitution in its structure. The neutrality of a crystalline

structure or structure unit of smectite is obtained by adsorption of exchangeable cations (either anhydrous or hydrated) in the interlayered space, generating its cation-exchange capacity (capacity of reversible exchange of cations). The usually reversible exchangeable cations are: Na⁺, K⁺, Ca²⁺, Mg²⁺; rarely Al³⁺, Fe³⁺ or Fe²⁺, and H₃O⁺ [1, 9].

The properties of clays, in particular smectite, that make them useful as catalysts are (a) the crystalline structure, especially the hexagonal arrangement of oxygen atoms on the surface of the tetrahedrons, (b) the alteration of the original crystalline structure in a controlled way, through acid treatment, (c) the anisometric morphology and small sizes of the particles (crystals) quite adapted for use in catalysis, and (d) the change of its basal spacing by acid treatment and subsequent activation modification [10-14].

The physico-chemical behavior of clay minerals has been studied because of its relation to the adsorbent and/or catalytic properties. This behaviour is governed by the extent and nature of their external surface, which can be modified by suitable acid and thermal treatments. Acid and thermal treatments increase the catalytic and adsorbent activity of certain clay minerals, but further and stronger treatments decrease this activity [11, 15-18].

Acid treatment of montmorillonite has been observed to

enhance mesoporosity making it an effective catalytic support. Thus, it is important to understand the textural as well as the surface acidity changes resulting from acid treatment of clays under different conditions [19-20].

All these characteristics, however, do not fully apply for the catalytic property that confirms the general application of those clays in all the heterogeneous catalytic processes [21-23]. Bentonite is mainly used as a fluid added to water for petroleum drilling operation, or for paint and rubber industries, and as a discoloration agent of oils. Clays from the city of Boa-Vista, Paraíba State, Brazil, have been used only for drilling mud. This is the largest deposit of clay in the country. Consequently, there is a great regional interest for increasing their industrial use.

The objective of this paper is to characterize chemically, physically and structurally (stability toward acid and thermal treatments) these clays to be used as a possible catalyst.

EXPERIMENTAL

A red-colored smectite clay was obtained from the mines of Boa-Vista region in Paraíba state, Brazil.

The acid activation was performed in a Pyrex glass reactor and mechanical agitation. The clay was treated with HCl (Merck) in a hydrous solution, for 30 min. at 70 °C.

Elemental analyses were carried out by X-ray Fluorescence (XRF) using a Philips PW2400 spectrometer. X-ray diffractograms were obtained using Siemens diffractometer with $\text{CuK}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$) for virgin as well acid-treated samples.

For differential thermal analysis, 200 mg of the sample were placed in an aluminum crucible under a static air atmosphere and analyzed (BP Engenharia Equipment, model RB 3000) up to 1000 °C at a rate of 10 °C/min.

The surface area (SA) was obtained by physical adsorption of nitrogen using system ASAP2000 (Micromeritics). Approximately 150 mg of sample were deposited in the sample holder. After degassing for 3 h at 90, 150, 200, 300, and 300 °C for the 100, 200, 300, 400, and 500 °C samples, respectively, nitrogen was injected. The SA was measured using the BET method.

For scanning electron microscopy, each observed sample was previously suspended in acetone and placed in an ultrasonic cleaner for 15 min in order to segregate it completely. Once the acetone had evaporated, the samples were sputtered with gold for 150 s at 40 mA under high vacuum until they were completely covered. The samples were then examined with the SEM (Philips Model XL 30 series with 20 kV of tension).

Methylcyclohexane (99% pure), supplied by Aldrich, was used for model reaction. The reaction transformation of methylcyclohexane was carried out in a fixed bed reactor at 723 K, $P_{\text{N}_2} = 0.9 \text{ bar}$, $P_{\text{m-xylene}} = 0.1 \text{ bar}$. The global conversion was analysed by gas chromatography with a 50 m fused silica capillary column Plot $\text{Al}_2\text{O}_3/\text{KCl}$.

RESULTS AND DISCUSSION

Chemical composition

In both, the natural and HCl treated clay, SiO_2 and Al_2O_3

belonging to the smectite structure were identified as well as Na, K, Ca, Mg, Fe and Ti expressed also as free oxides (Table I).

In its natural state the red smectite clay from Boa-Vista has a mass ratio $\text{SiO}_2:\text{Al}_2\text{O}_3 = 3.33$, which agrees with the theoretical formulation of montmorillonites (3.20). A high percentage of Fe_2O_3 (6.47%) was also observed. This component substitutes, in an isomorphic way, Al^{3+} in the tetrahedral sheet, and alters the catalyst activity, being favorable to the coke formation. The acid treatment induced a significant decrease of Fe_2O_3 content (from 6.47% to 3.58%). After acid treatment, CaO and MgO contents decreased whereas SiO_2 and Al_2O_3 contents remained constant, suggesting that leaching did not destroy these oxides.

The ion exchange capacity generally occurs because of the structural defects, broken bonds, or because of structural hydroxyl transfers that can occur by calcination or acid treatment. HCl did not promote the exchange of OH^- by Cl^- , but that of Na^+ , K^+ , Mg^{2+} and Fe^{3+} with H_3O^+ ions. These data show that acid treatment is favorable to ionic exchange and probably increases the number of acid sites and, consequently, the catalytic activity.

Table I - Chemical analysis of the red smectite clay from Boa-Vista, Paraíba, Brazil.

[Tabela 1 – Análise química da argila esmectítica vermelha de Boa-Vista, Paraíba, Brasil.]

Chemical composition (%)	Red Smectite clay	
	natural	activated
SiO_2	51.6	52.54
Al_2O_3	15.49	17.59
Fe_2O_3	6.47	3.58
TiO_2	0.89	0.88
CaO	0.63	0.18
MgO	1.61	1.04
Na_2O	0.39	0.42
K_2O	0.20	0.19
P.F.	20.60	23.55
	97.88	99.97

Structural modification

The X-ray diffractogram of the natural, untreated smectite is shown in Fig. 1. The $d_{(001)}$ at 15.25 Å is a smectite characteristic. Other reflections are observed at 7.18 Å and 3.35 Å, which correspond to kaolinite, cristobalite and quartz, respectively. The red smectite was then constituted of a mixture of montmorillonite and kaolinite minerals, in different proportions, and a low percentage of quartz and cristobalite. The latter is seldom identified in a smectite clay, but its presence is possible if of volcanic origin. The qualitative result by XRD of natural clay (without treatment) shows that the

smectite is the predominant phase.

After the acid treatment, a decrease in intensity of the characteristic peak of the montmorillonite ($d_{(001)} = 14-15 \text{ \AA}$) was observed (Fig. 2). It was also observed that the intensity of the reflections belonging to the other minerals remained. This suggests a partial destruction of the structure in the present phases. So, an alteration of the crystallization states of montmorillonite occurred when treated with acid.

Acid or thermal treatments have a fundamental role in the preparation of catalysts because they can change the number of acid sites, crystalline structure and particles size.

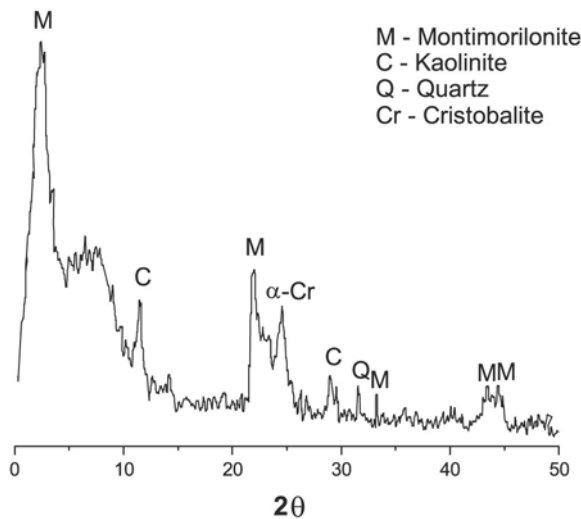


Figure 1: X-ray diffractogram of the natural untreated red smectite. [Figura 1: Difratoograma de raios X da argila esmectítica vermelha natural.]

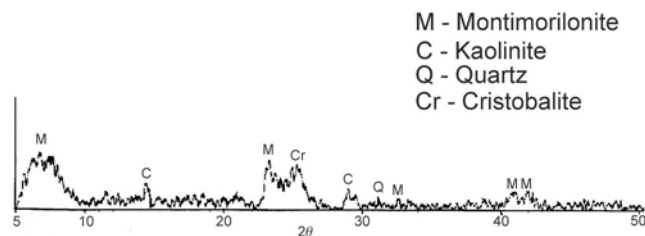


Figure 2: X-ray diffractogram of the smectite activated with HCl. [Figura 2: Difratoograma de raios X da argila esmectítica vermelha ativada com HCl.]

Structural modification after heating

The differential thermal analysis (DTA) of natural, untreated red smectite showed a characteristic and very well known curve profile for the montmorillonites group. Two intense endothermic peaks were observed with their respective maxima at 160 °C and 550 °C. The first peak was related to the loss of free water and of the adsorbed water on the external surface of clay mineral; the second correspond to the deshydroxylation process. This temperature for hydroxyl loss characterizes a sample rich

in iron, which is related to the chemical analysis mentioned above. The intense exothermic peak at 900 °C can be related to the mullite nucleation. The endothermic peak, generally observed before the mullite formation, is not identified, meaning that the formation of mullite occurred without structural destruction.

The structural changes affecting the clay minerals can be better observed through diffraction analyses of the heated materials.

In Fig. 4, the diffractogram was obtained during a *in situ* thermal cycle applied to natural clay with heating from 20 to 1000 °C, followed by a cooling to room temperature. However, it is possible to note that the peak for cristobalite became better established between 20 °C to 800 °C, suggesting that the sample becomes better crystallized after the loss of the adsorbed water and of hydroxyls. Between 800 °C and 900 °C, the profile of the diffractogram shows the disappearance of the (020) peak of montmorillonite, located near $2\theta = 20^\circ$, which existed until

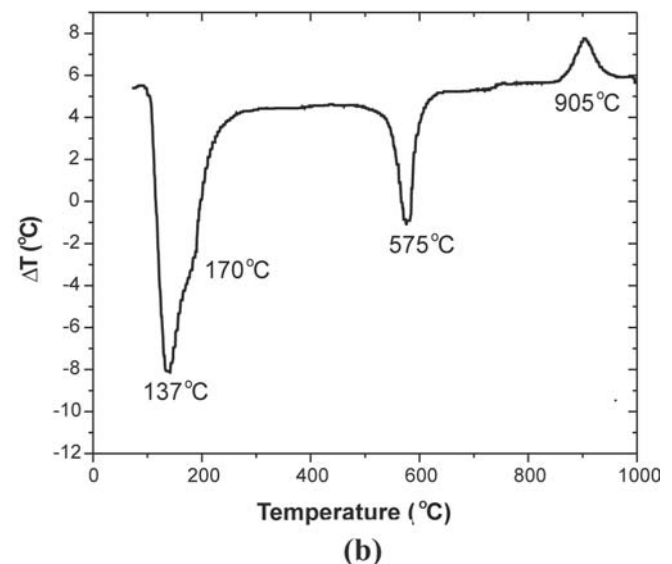
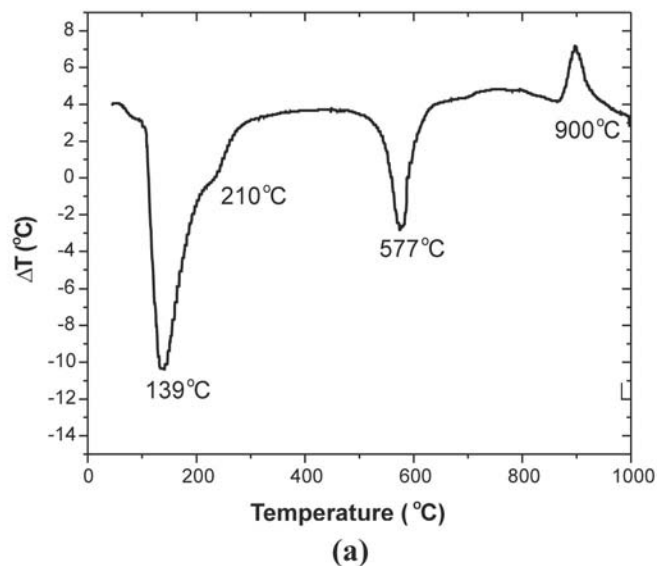


Figure 3: DTA curves of natural and activated red smectite. [Figura 3: Curvas ATD das esmectitas vermelhas natural e ativada.]

800 °C. This temperature coincides with the exothermal peak observed in the DTA curve (Fig. 3). The diffractogram for the 900 °C sample shows no more peaks for the clay mineral (montmorillonite and kaolinite). Changes in the diffractogram can be attributed to the formation of other phases. It is possible that one phase was mullite, but due to the small intensity of peaks, the confirmation of this hypothesis needs further detailed analysis, keeping the heat until 1000 °C, peaks became better defined for cristoballite and quartz, during the cooling, these minerals, remained unchanged. Particularly the peak at $2\theta = 21.7^\circ$, of cristoballite which was always present during the whole thermal cycle. The transformation of the α -quartz - β -quartz - α -quartz phases, near $2\theta = 25^\circ$ was also observed during the heating cycle.

For the acid treated clay, the diffractograms shown in the Fig. 4, correspond only to the results obtained during the heating within a restricted 2θ area because of a lack of adequate apparatus. When the sample was heated, a reaction was observed at about 900 °C, the observed results at this temperature show that despite the equipment gauge for small angles, the diffractogrammes of the heated samples exhibited some changes besides the unaffected cristoballite peak (Cr). Indeed the (020) peak of montmorillonite remained unaffected up to 500 °C before moving to 2θ after heating to 900 °C. This displacement is related to the collapse of the interlayered spaces, the heating at 500 °C producing a mica structure.

The weak peak at $12^\circ 2\theta$ (of kaolinite) disappeared before reaching 500 °C, a classic behavior of this mineral when heated up to this temperature.

The mullite reflection was not present and not present until 900 °C. The presence of a cristoballite phase, as with natural clay (without treatment), remains unaltered during the whole heating.

After the acid treatment the BET tests showed a significant increase of the specific area of the clay (Table II). After this treatment, the obtained specific area was $137 \text{ m}^2/\text{g}$, a value very similar to the ones found in synthetic catalysts.

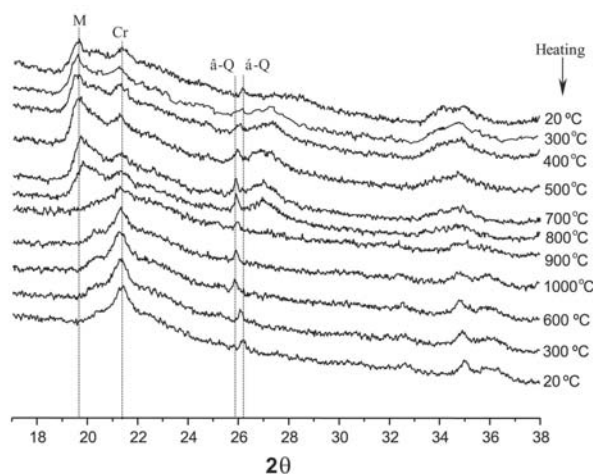


Figure 4: X-ray diffractogrammes obtained during the heating-cooling cycle (natural red smectite).

[Figura 4: Difratoqramas de raios X obtidos durante o ciclo de aquecimento-resfriamento (esmectita vermelha natural).]

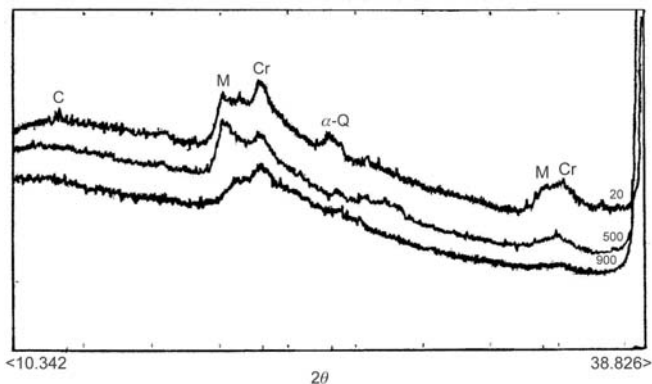


Figure 5: X-ray diffractogram obtained during heating of the activated smectite, with HCl.

[Figura 5: Difratoqramas de raios X obtido durante o aquecimento da esmectita ativada com HCl.]

Table II – Specific surface area (S) of samples of red smectite clay.

[Tabela II – Área específica nas amostras de argila esmectítica vermelha.]

Sample	$S_{\text{BET}} (\text{m}^2/\text{g})$
Natural smectite clay	103
Activated smectite clay	137

SEM micrographs show that (Fig. 6) the red smectite clay is composed of very irregular lamellae of different sizes, which are partly curled.

Study of the use of clay treated with acid as catalyst

With the help of the methyl-cycle-hexane transformation: model reaction, the acid function of the samples was observed. Fig. 7, which represent catalytic activity as a function of time-on-stream, clearly shows that the methyl-cycle-hexane is more rapidly transformed over activated red smectite than natural untreated red smectite (2 times). This increase can be related to its greater acidity.

CONCLUSIONS

Acid treatment partially altered the structure of the montmorillonite. Thermal treatment caused little alteration on the structure of clay minerals up to 500 °C. This behavior is very positive because the catalytic reactions to be studied will be within this temperature range, and besides, the structural stability is an important and fundamental requirement for the efficiency of the catalyst. An important increase of the surface area of the solid obtained was observed. Clays are considered as one of the important class of catalysts in the synthetic organic chemistry [24]. The most important feature of clays is their thermal stability, which makes them suitable catalysts for the high temperature reactions. Clays, being low-priced, are commercially attractive. The thermal stability and acidity of the

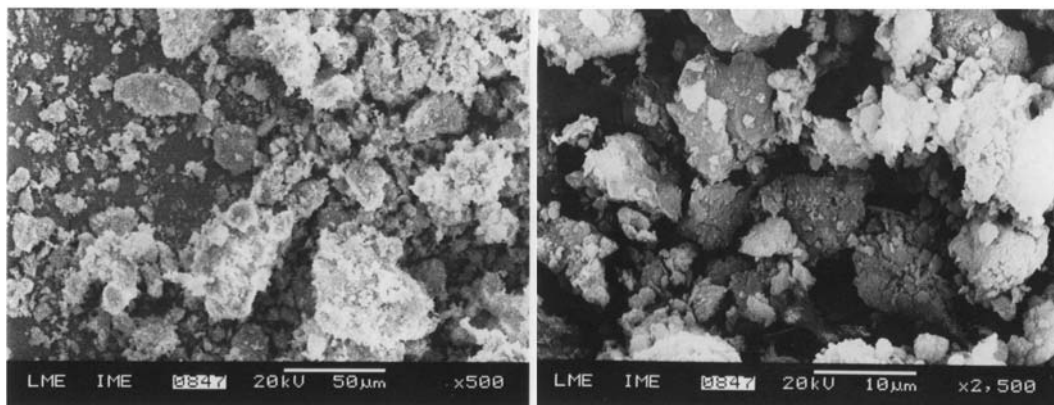


Figure 6: SEM micrographs of red smectite clay.

[Figura 6: Micrografias da argila esmectítica vermelha.]

clays can be substantially improved by acid treatment. The obtained reaction for the treated material showed that the clay is more acid than the natural one, yielding a better catalytic activity.

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Figure 7: Catalytic activity as a function of time-on-stream at 723 K in methyl-cycle-hexane transformation with natural and activated smectite. [Figura 7: Atividade catalítica em função do tempo de reação a 723 K na transformação do metilciclohexano com as esmectitas natural e ativada.]

