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Influence of the acid activation of pillared smectites from Amazon (Brazil) in adsorption process with butylamine

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Abstract

Smectite-bearing clay samples from Para state, Amazon region, Brazil, were used for pillaring process in the present study. The natural and pillared/activated matrices were characterized using XRD, FTIR, ^{27}Al, ^{29}Si MAS NMR, TGA-DTG and textural analysis using nitrogen adsorption–desorption isotherms. The aluminum pillaring solutions (Al_{13}) were analyzed by ^{27}Al MAS NMR. The ion of intercalation (Keggin's ion) was obtained through chemical reaction of $AlCl_3 \cdot 6H_2O$ and NaOH solutions with an approximate OH/Al 2.0 molar ratio and $Al(NO_3)_3$ and NaOH solutions with an OH/Al = 1.5. The nontronite intercalation was carried out using two methods: (1) with sodium hydroxide solution that was incorporated drop by drop in the aluminum chloride solution; and (2) using aluminum nitrate, which was maintained under vigorous stirring at 25 °C, during 3 h and calcined at 450 °C (adequate temperature for calcination) and 600 °C. The pillared clays were treated with HCl (0.10, 0.30 and 0.60 mol dm^{-3}). The resulting materials were submitted to adsorption process with butylamine. The results showed that the pillarization process increases the basal spacing of the natural clay from 15.60 to 18.97 Å and the superficial area from 44 to 197 m^2/g. The thermal stability of the natural clay was improved by the pillaring procedure.

Keywords: Pillared clay; Al_{13}; Smectite

1. Introduction

Pillared interlayered clays (PILCs) are considered to be a new generation of microporous materials, where large two-dimensional pores allow large molecules to react, although maintaining some shape selectivity catalysts for large molecule reaction [1]. These materials are prepared through charge-compensating cations after exchanging the original cation in the interlayer space of the swelling clays with different cations polymers (Al [2–4], Fe [5,6,4], Zr [5–7], Cr [5,6,8], Ti [9] and Ga [10], among others). On calcining, the inserted cations polymers yield rigid, thermally stable oxide species, named pillars, which maintain the clay layers and prevent their collapse in high temperatures.

The main objective in pillaring clays is to achieve a basal spacing as large as possible, the operation of which contributes to the development of large surface area and porous volume [11–14].

The PILCs are generally prepared from smectites clays that are formed by 2:1 layer phillosilicates, where one octahedral sheet containing Al^{3+} in an octahedral coordination lies between two tetrahedral sheets and when isomorphic substitutions take place resulting in the inorganic layer. This negative charge is balanced by Na^+, Ca^{2+}, $K^+$and Mg^{2+} adsorption in interlayer position, the cations of which are easily exchangeable [11,13,15,16].

Several intercalation studies have been reported in the literature. Brindley and Sempel [17] intercalated smectite with the same types of polymers described above. Basal spacing

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(d_{001}) of about 18 Å and specific area of 200–300 m^2/g were reported by Pinnavaia [18] and Vaughan et al. [19]. These studies proposed that the intercalated species that give rise to this stable basal spacing is the so-called Keggin,s ion ($Al_{13}O_4(OH)_{24}(H_2O)_{12}{}^{7+}$), which has been characterized by angle X-ray scattering technique and by ^{27}Al nuclear magnetic resonance (^{27}Al NMR) data.

The chemical, surface, and structural properties of PILCs determine and can limit the potential applications which fall mainly into two categories: catalytic and adsorption processes. Presently, those materials can be used in a wide range of catalysis reactions, such as cracking, cycle hexane conversion, toluene with methanol alkylation, and propylene oligomerization. They are also commonly employed in the petroleum industry for long-chain hydrocarbons filtering and azeotropic cracking [20–30].

The aim of the present investigation is to study the structural and physical–chemical characteristics of two different types of smectites, such as natural and pillared clays, which were developed with $Al_{13}O_4(OH)_{24}(H_2O)_{12}{}^{7+}$ intercalation. This study investigated various parameters (chemical composition of the matrices, temperature of calcination, method of synthesis of the PILCs and effect of the acid activation) and their application into adsorption process with butylamine. Their adsorptive capacity was examined through adsorption isotherms, and the influence of the variation of parameters on PILCs texture was analyzed by different techniques.

2. Experimental

2.1. Raw material

Clay samples used in this investigation were obtained from the "Serra do Maicuru" area Para state, north of Brazil. Two different samples were used in this paper as starting materials and are named as A_1 and A_2. The particles that were lesser than 2 μm fraction of the sample were separated by sedimentation. The cation-exchange capacity (CEC) was ensured in order to evaluate the potential use of those clays for intercalation, following the ammonium acetate method by using a concentration of 2 mol dm^{-3} at pH 8. The results obtained were 9.2 mmol g^{-1} (A_1) and 10.5 mmol g^{-1} (A_2) on an air-dried basis and pointed for the continuation of the study. Mineralogical and chemical characterizations were carried out using the analytical techniques that will be described further.

2.2. Sample preparation and preliminary characterization

The samples were dried at 60 °C up to humidity between 12% and 15%. They were ground and passed in USS sieve No. 200 (74 mm) and examined through powder X-ray diffraction to confirm the presence of smectite clays by conventional sample preparation procedures, such as air-dried oriented mounts, ethylene glycol solvated and heated at 300 and 500 °C.

2.3. Synthesis of the pillaring solution and pillaring processes

Two distinct methods were used in the preparation of PILC materials:

(A) Method 1: The samples were saturated with Na_2CO_3 by adding the solution to dry materials at room temperature. This treatment was carried out using saturated solution of Na_2CO_3 (0.20 g cm^{-3}) in proportion of 1.00 mmol g^{-1} of sample. The mixture was homogenized and left standing for 12 h. The intercalating solution was obtained by slow addition of NaOH (0.2 mol dm^{-3}) in a $AlCl_3 \cdot 6H_2O$ (0.2 mol dm^{-3}) solution, with a basicity relationship OH/Al = 2. The sodium hydroxide solution was incorporated drop by drop in the aluminum chloride solution, which was maintained under vigorous stirring at 60 °C. The resultant solution was aged under reflux during 24 h. The polymeric solution was incorporated drop by drop in a suspension composed by 5% of Na-montmorillonite in a mixture of deionized water and ethanol. The amount of oligocation incorporated exhibited 20 mmol of Al per gram of natural clay. The resultant solution (polymeric solution and Na-montmorillonite) was filtrated and washed with deionized water. The sample was calcinated at 450 and 600 °C for 2 h. The resultant material was called Al-$PILC_1$.

(B) Method 2: The aluminum oligocation was prepared by using a solution of the following commercial product: Locron® $Al(NO_3)_3$ (0.2 mol dm^{-3}). The intercalating solution was obtained by slowly adding NaOH (0.2 mol dm^{-3}) into a $Al(NO_3)_3$ (0.2 mol dm^{-3}) solution, which was incorporated drop by drop into a suspension made with 50% of natural clay into a mixture of water, ethylene glycol and glycerin. The basicity ratio was 2 and quality of Al (0.2 M) was 20 mmol per gram of natural clay. The final solution containing clay, aluminum nitrate and sodium hydroxide was continuously stirred for 4 h and allowed to stand for 5 days. Finally, the material was washed with deionized water and calcinated at 450 and 600 °C. The resulting material was called Al-$PILC_1$ (450 °C) and Al-$PILC_1$ (600 °C), for sample A1 and Al-$PILC_2$ (450 °C) and Al-$PILC_2$ (600 °C), for sample A2.

2.4. Acid treatment

The pillared clays were activated with HCl in concentrations of 0.6 mol dm^{-3} by slowly adding the solutions to dry materials at room temperature, with continuous stirring for 2 h. The resultant solutions obtained (HCl and pillared clays) were filtrated and the resultant materials were washed with deionized water and dried at 60 °C. The resulting materials were called Al-PILC.

2.5. Adsorption process with butylamine

The adsorption process was carried out by suspending about 0.60 mg of the pillared clay in aqueous solution of each butylamine at room temperature. The isotherms of