Materials Research Bulletin 44 (2009) 485–491

Contents lists available at ScienceDirect

Materials Research Bulletin

journal homepage: www.elsevier.com/locate/matresbu

Adsorption of mercury cation on chemically modified clay

Denis L. Guerra [a,*], Rúbia Ribeiro Viana [b], Claudio Airoldi [a]

[a] *Chemistry Institute, State University of Campinas, P.O. Box 6154, 13084-971 Campinas, São Paulo, Brazil*
[b] *Universidade Federal de Matogrosso, UFMT, Centro de Recursos Minerais, Cuiabá, Matogrosso 68060 900, Brazil*

ARTICLE INFO

Article history:
Received 24 July 2007
Received in revised form 1 July 2008
Accepted 5 August 2008
Available online 12 August 2008

Keywords:
A. Inorganic compounds
B. Intercalation reaction
C. X-ray diffraction
D. Surface properties

ABSTRACT

A montmorillonite clay (M) sample from the Amazon region, Brazil, was intercalated with pyridine (Py), dimethyl sulfoxide (DS) and 3-aminopropyltriethoxysilane (APS). The chemically modified montmorillonite ($M_{P/APS}$) sample showed modification of its physical–chemical properties including: specific area 41.39 $m^2\,g^{-1}$ (M) to 198.45 $m^2\,g^{-1}$ ($M_{P/APS}$). Solid-state ^{29}Si CPMAS/NMR of the silylated montmorillonite samples showed Q^2 and Q^3 signals as well as T^2 and T^3 signals. The appearance of T^2 and T^3 signals can be attributed to the grafting of APS to the interlayer surface silanol groups. The natural and modified clays were used for mercury cation adsorption from aqueous solutions at room temperature and pH 3.0. The energetic effects ($\Delta_{int}H^\circ$, $\Delta_{int}G^\circ$ and $\Delta_{int}S^\circ$) caused by mercury cation adsorption were determined through calorimetric titrations.

1. Introduction

Industrial activities generate a wide diversity of wastewaters, often containing agents that cause pollution, which can cause dangerous consequences for human beings by affecting the ecosystems. To minimize these unfavorable conditions, adsorption methodologies have been proposed as an alternative process for resolving such problems. In this context, many materials have been proposed and some of them are useful candidates, such as natural and functionalized clay surfaces [1–7].

Montmorillonite clay is generated from soils and sedimentary deposits through weathering, diagenesis and hydrothermal effects. This process involves degradation and transformation of precursor phyllosilicates, including precipitation from solution. Thus, clays are derived from various abundant minerals in soils, influenced by conditions that contain basic igneous rocks and also soil clay fractions from arid climates, originating from granitic pediments [8]. Some smectite samples can be found naturally in the Amazon region. However, this smectite occurrence is rare due to the fact that the Amazon climate is normally warm-humid, causing acidic lixiviation in soils, conditions that are unfavorable for smectite formation [9].

The use of chemically modified clays for removal of divalent copper, cobalt, nickel and zinc cations has been intensively investigated in recent years. Chemically modified clay minerals have also been investigated for remediation of polluted wastes and gas adsorption with excellent performance [10–13].

The aim of the present investigation was to study the performance of montmorillonite, obtained from Amazon region, in natural and chemically modified forms. The chemical modification process was developed with intercalation of pyridine/3-aminopropyltriethoxysilane (APS) and dimethyl sulfoxide/3-aminopropyltri-ethoxysilane. After chemical modification the resulting materials were used for mercury cation adsorption from aqueous solutions.

2. Experimental

The clay was sampled in the Amazon region, in northern Brazil. Size fractions of less than 2 μm were separated by sedimentation. The cation-exchange capacity (CEC) was measured in order to evaluate the potential use of clays for intercalation, following the ammonium acetate method with concentrations of 2.0 mol dm^{-3} at pH 8.0. The result obtained was 80.0 mequiv./100.0 g of clay (M) on an air-dried basis. Chemical characterization was also carried out, using analytical techniques that will be described below.

For intercalation with dimethyl sulfoxide, 5.0 g of natural clay sample was mixed in 100.0 cm^3 of dimethyl sulfoxide (DS) (1.5 mol dm^{-3}) in water at room temperature under vigorous stirring for 50 h. The suspension was centrifuged (4000 rpm, for 60 min). The liquid portion was decanted to prevent the finer particles from re-entering suspension. This solid sample called M_{DS} was dried at 323 K for 17 h.

---

[*] Corresponding author. Tel.: +55 19 33429407; fax: +55 19 32323775.
E-mail address: dlguerra@iqm.unicamp.br (D.L. Guerra).

0025-5408/$ – see front matter © 2008 Published by Elsevier Ltd.
doi:10.1016/j.materresbull.2008.08.002

For intercalation with pyridine (Py), 5.0 g of natural clay was mixed in 100.0 cm^3 of pyridine in water in room temperature under vigorous stirring for 100 h. The result suspension was centrifuged (4000 rpm, for 60 min). The liquid portion was decanted and the sample was dried at 323 ± 1 K for 17 h. The resulting sample was called M_P.

The silane coupling agent was APS [3-aminopropyltriethoxysilane: $H_2N–C_3H_6Si(OC_2H_5)_3$] (Aldrich). The ASP solution was prepared to be 0.10 mol dm^{-3} in methanol (95%). The samples M_{DS} and M_P (5.0 g) were dispersed in 15.0 cm^3 of this solution (ultrasound for 30 min) at 298 ± 1 K. The dispersion was evaporated to dryness for 48 h at 333 K, to result in samples called $M_{P/APS}$ and $M_{DS/APS}$, respectively.

The natural clay sample was analyzed by induced coupled plasma-optical emission spectrometry (ICP-OES), using an ARL 34000 instrument. X-ray powder diffraction (XDR) patterns were recorded with a Philips PW 1050 diffractometer using Cu Kα (0.154 nm) radiation in the region between 2 and 65° (2θ) at a speed of 2°/min and a step of 0.050°.

The samples were dried at 333 K to reach a humidity between 12.0 and 15.0%. X-ray powder diffractometry confirmed the presence of montmorillonite clay by conventional sample preparation procedures. Preliminary analyses were made with natural samples from three conventional investigations: air-dried (1.32 nm), ethylene glycol (1.8 nm) solvated and heated at 573 and 773 K (1.0 nm). Thermogravimetric and the derivative curves were carried out in a Stanton Redcroft 1000/1500 coupled to a DC and temperature controller, with a heating rate of 0.33 K s^{-1} between 313 and 1173 K, under CO_2 atmosphere.

BET (Brunauer–Emmett–Taller) surface areas and porosity measurements of the montmorillonite samples were determined using a Quantachome/Nova Surface Area-Pore Volume Analyzer, model 1200/5.01. The mesopore size distribution was obtained by applying the BJH (Barret–Joyner–Halenda) method to the adsorption branch of the isotherm.

The nuclear magnetic resonance spectra of solid materials were obtained on an AC 300/P Bruker spectrometer at 298 ± 1 K at 59.6 MHz for silicon. A pulse repetition time of 3 s and contact time of 3 ms were used for $^{29}Si\{^1H\}$ CPMAS experiments.

The thermal effects from mercury cation interacting on natural and modified montmorillonite samples were followed in an isothermal LKB 2277 microcalorimetric system. Portions of approximated 10 mg of natural or modified montmorillonite were used in calorimetric titration. After calorimetric baseline stabilization, the 20.0 cm^{-3} of mercury cations from a $HgNO_3H_2O$ (Aldrich) solution having a concentration of 0.050 mol dm^{-3}, were individually added to the vessel by means of a microsyringe coupled to a Teflon cannula. In each individual titration, the thermal effect caused by the reaction was recorded after each addition of the titrand.

Samples of about 10 mg of natural or modified montmorillonite were suspended in an aqueous solution containing mercury cation at 298 ± 1 K and pH 3.0 to carry out the adsorption process. The pH was maintained with addition of 0.10 mol dm^{-3} of nitric acid or 0.10 mol dm^{-3} sodium hydroxide. Isotherms of concentration versus time were obtained through the batch method [7–11]. The number of moles adsorbed per gram (N_f) is calculated by the difference between the initial (N_i) and the number of moles of metals remaining in the supernatant (N_s) divided by the mass (m) of the compound used, $N_f = (N_i - N_s)/m$. The number of moles of cation adsorbed (N_f) increased with time (t) as a function of the concentration in the supernatant (C_s), until a plateau related to total saturation of the acid centers in the layered structure was obtained [9,14,15].

The most commonly used isotherms are those related to Langmuir, which was originally derived for gas adsorption on planar surfaces such as glass, mica and platinum. For this adsorption model a quantity q_i of an adsorbate, which is related to the equilibrium solution concentration of the adsorbate c_i, is adjusted to K_L and b parameters. The plateau of the isotherm enables K_L determination by measuring the adsorbate on the surface. The value of b is the upper limit for q_i and represents the maximum adsorption of i determined by the number of reactive surface sites by converting Eq. (1) into its linear form [16]:

$$\frac{C_s}{N_f} = \frac{1}{K_L b} + \frac{C_s}{b} \qquad (1)$$

Then, $c_i/q_i = C_s/N_f$ and the so-called distribution coefficient K_L, can be plotted against q_i. If the Langmuir equation can be applied, the measured data should fall on a straight line with slope giving K_L and the intercept $K_L b$ values, $1/K_L b$ being the angular and $1/b$ the linear coefficients [16].

3. Results and discussion

3.1. ICP-OES data

Elemental analyses from the ICP-OES technique for the original clay sample gave the results listed in Table 1. These values are consistent with montmorillonite as the principal clay mineral with kaolinite and quartz clay mineral presences. Aluminum is the major component contained in clay sample structure.

3.2. X-ray powder diffraction

X-ray powder diffraction of M, $M_{DS/APS}$ and $M_{P/APS}$ showed significant changes. In Fig. 1 and Table 2 an increase in the interlayer distances is observed after the intercalation process, by changing $d_{0\,0\,1}$ from 1.32 to 1.91 nm ($M_{DS/APS}$) and 2.25 nm ($M_{P/APS}$) for the modified clays. This is attributed to the presence of APS molecules that were intercalated in the clay structure and the interaction of the intercalated species (DS and pyridine) with reactive centers anchored in the interlayer spacing of natural clay, such as the silanol groups. The interlayer spacing is characteristic of montmorillonite group mineral 2:1 [17]. The great influence of the number of pyridine and ASP ions on the interlayer spacing and on the constitution and distribution of the ions has been previously reported [14,15]. The mass fraction of intercalation material can be estimated as the relative intensities of the reflection originating from the 'unchanged' and the 'expanded' layers. In the intercalated sample, the degree of reaction could be estimated as 71.05%. This indicates that the APS molecules arrange in monolayers between the aluminosilicate layers [14].

3.3. ^{29}Si CP/NMR

The ^{29}Si CPMAS/NMR spectra of the natural and modified montmorillonite samples are shown in Fig. 2. The natural

Table 1
Elemental analyses of the natural montmorillonite sample from ICP-OES

Sample	M
%SiO_2	60.30
%Al_2O_3	17.89
%Fe_2O_3	7.32
%CaO	4.78
%Na_2O	2.20
%K_2O	3.80
%TiO_2	1.90
%MgO	1.01
%P_2O_5	0.80