Materials Letters 189 (2017) 225–228

Contents lists available at ScienceDirect

Materials Letters

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

Structural analysis of mesoporous vermiculite modified with lanthanum

Marcus Venicio da Silva Fernandes [a,*], Lindomar Roberto Damasceno da Silva [b]

[a] *Instituto de Formação de Educadores, IFE, Universidade Federal do Cariri, UFCA, Campus de Brejo Santo, CEP: 63260-000 Ceará, Brazil*
[b] *Laboratório de Pesquisa, Desenvolvimento e Inovação em Minerais Não-Metálicos, Universidade Federal do Ceará, UFC, Campus do Pici, CEP: 60440-970 Fortaleza, Ceará, Brazil*

ARTICLE INFO

Article history:
Received 9 April 2016
Received in revised form
20 November 2016
Accepted 3 December 2016
Available online 15 December 2016

Keywords:
Structural analysis
Mesoporous vermiculite
Lanthanum
^{27}Al MAS NMR

ABSTRACT

Clays have demonstrated an important role in many industrial processes and its modification have been a promising line of research, such as its intercalation and pillaring. The synthesis of vermiculite modified with aluminum and aluminum-lanthanum has great relevance, since the materials obtained can be used in separation processes by adsorption and catalysis. For characterization of the crystallographic phases of the synthesized materials were obtained diffraction patterns (XRD) that confirmed the effectiveness of the methodology used, and to evaluate the morphology were carried out nitrogen adsorption analysis (BET), where the results confirmed the mesoporosity of the synthesized materials. ^{27}Al MAS NMR spectrometry was applied to distinguish between tetrahedrally coordinated aluminum and octahedrally coordinated.

1. Introduction

Vermiculite has been exploited widely over the past 60 years as a valuable insulating, coating, lightweight, high thermal resistivity and filler material among its other uses [1]. Is a layered micaceous mineral formed by the hydrothermal alteration of mica [2].

Vermiculites are a significant group of phyllosilicates 2:1 clay minerals composed of one octahedral sheet between two tetrahedral sheets [3]. Vermiculite possesses a net negative structural charge (due to Al^{3+} substitution for Si^{4+} in the tetrahedral layers and Al^{3+} and/or Fe^{2+} substitutions for Mg^{2+} in the octahedral layers), which is balanced by the presence of inorganic exchangeable cations in its interlayer space [4]. The interlayer space of vermiculite, characterized by ion exchange, adsorption etc., provides a good place for chemical reactions [5,6]. The name vermiculite is derived from the *latin vermiculus "little worm"* and this mineral expands greatly upon heating, during which the particles move in a similar way to the worms [7].

In the preparation of mesoporous materials, the most used method is called "pillaring" in which the pillared clays have been intercalated through the introduction of large polymeric metal cations $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$ and then hydrothermally treated to form stable metal oxides, which act as pillars, preventing the collapse of the expanded interlayers and thus generating high-surface area materials [8,9].

Textural and catalytic properties of the mesoporous clays are related to its intrinsic characteristics due great exposure of active sites by the presence of metal oxides or pillars in the interlayer spacing, thereby increasing the surface area and creating porosity in the material [10].

This research work aims to obtain mesoporous adsorbent materials synthesized from precursor vermiculite and characterized by X-ray diffraction, nitrogen adsorption isotherms (BET) and ^{27}Al MAS NMR.

2. Experimental procedure

2.1. Sample preparation

Chemical modification of natural vermiculite (V_{NAT}) to obtain mesoporous vermiculite (Al_{13}PILV, $LaAl_{12}$PILV e La_2Al_{11}PILV) was based on previous studies [11]. The samples were pretreated and intercalated with aluminum-lanthanum oligomeric solution obtained from NaOH 0.2 mol L^{-1}, $AlCl_3 \cdot 6H_2O$ 0.2 mol L^{-1} and $LaCl_3 \cdot 7H_2O$ 0.2 mol L^{-1}, mixed in the ratio: $[OH^-]/[Al^{3+}]=2.4$ and La_xAl_{13-x} (where x=0, 1 or 2), and then calcined at 823 K for 3 h.

2.2. Sample characterization

X-ray diffraction measurements were performed on a powder diffractometer, model DMAXB – Rigaku. Copper radiation (Cu-Kα,

---

* Corresponding author.
E-mail address: marcus.fernandes@ufca.edu.br (M.V. da Silva Fernandes).

http://dx.doi.org/10.1016/j.matlet.2016.12.003
0167-577X/© 2016 Elsevier B.V. All rights reserved.

$\lambda = 1.54056$ Å) was used with a tube operating at 40 kV and 25 mA.

Analyses for textural characterization of the samples were obtained with a mass of 200 mg and degassing at 300 °C for 12 h on a Micromeritics ASAP equipment Model 2020 Research Laboratory, Development and Innovation in Non-metallic Minerals, Department of Organic and Inorganic Chemistry of the Federal University of Ceará (UFC).

The ^{27}Al MAS NMR spectra were recorded at 300.13 MHz on a Bruker DRX-300 spectrometer (7.05 T), operating at 78.2 MHz using a pulse sequence, a 10 kHz sampling frequency wiring, all measurements were made at room temperature; at Analyses were conducted using a pulse $\pi/6$ short (0.5 s), 6000 accumulations and chemical shifts they were measured against the standard $AlCl_3 \cdot 6H_2O$.

Table 1.
Evaluation of textural characteristics by nitrogen adsorption, XRD e ^{27}Al MAS NMR of different samples.

Sample	Textural characteristics			XRD	^{27}Al MAS NMR (δ, ppm)
	S_{BET} ($m^2\,g^{-1}$)	$S_{LANGMUIR}$ ($m^2\,g^{-1}$)	$D_{P\ (BJH)}$ (nm)	d_{001} (nm)	
V_{NAT}	7.1	9.1	3.48	1.23	9.6 (Al^{VI}) e 54.2 (Al^{IV})
Al_{13}PILV	230.1	291.7	2.19	1.78	4.4 (Al^{VI}) e 55.4 (Al^{IV})
$LaAl_{12}$PILV	190.9	242.3	4.57	1.83	3.7 (Al^{VI}) e 56.0 (Al^{IV})
La_2Al_{11}PILV	91.1	121.2	5.38	1.87	5.3 (Al^{VI}) e 57.9 (Al^{IV})

3. Results and discussion

3.1. X-ray diffraction (XRD)

It is observed in Fig. 1a XRD patterns peak at 7.21° 2θ characteristic of natural precursor vermiculite. The XRD patterns 1b, 1c and 1d (Fig. 1) show an increase in basal interplanar distance (Table 1) between samples modified with Al_{13}, $LaAl_{12}$ and La_2Al_{11} oligomers, where the latter showed a greater basal interplanar distance, possibly due to its higher ionic radius ($La^{3+} = 0.116$ mm [12]) in relation to aluminum ($Al^{3+} = 0.068$ nm [13]), thus forming polycations with higher steric characteristics. Al_{13}PILV (Fig. 1b) showed a higher crystallinity for samples doped with lanthanum, which according to Ouhadi et al. [14] the intensity of any reflection *hkl* diffracted from any crystalline material can be related to its composition, matrix and textural characteristics. $LaAl_{12}$PILV, and La2Al11PILV (diffractograms 1c and 1d) show behavior similar to the samples Al_{13}PILV relative to pillarization, differentiated only by low crystallinity.

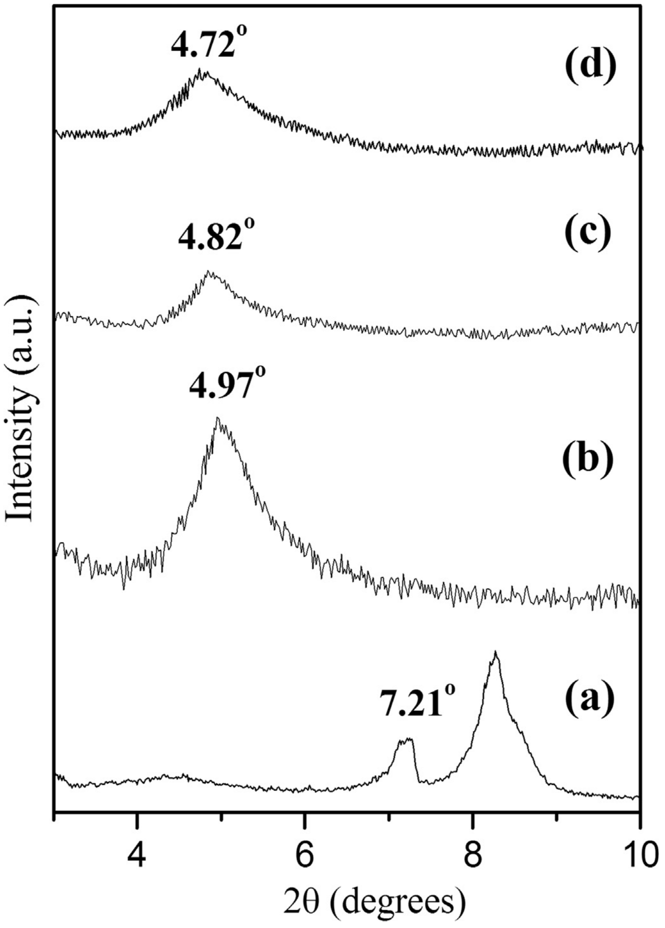

Fig. 1. XRD (d_{001}) patterns of samples: (a) V_{NAT}, (b) Al_{13}PILV, (c) $LaAl_{12}$PILV and (d) La_2Al_{11}PILV.

3.2. Textural characterization by BET

The sample of natural vermiculite (Fig. 2a) represents an isotherm of type III, which according Porpino [15] this type relates to the very weak interactions in systems containing macro and mesopores. The adsorption curve resembles the desorption curve (Fig. 2a), were not observed the hysteresis phenomenon. As the hysteresis due to capillary condensation of materials especially mesoporous, the sample V_{NAT} before the treatments had specific surface area, total micropore and considerably lower pore diameters.

According to Sing et al. [16] the N_2 isotherm (Fig. 2b) is classified as type IV demonstrating hysteresis, which is related to capillary condensation in mesopores. The top of the Type IV isotherm is assigned to the monolayer-multilayer adsorption, it follows the same trend as the corresponding part of a Type II isotherm. Type IV isotherms are observed in many industrial mesoporous adsorbents, and $LaAl_{12}$PILV and La_2Al_{11}PILV samples (Fig. 2c and d) have roughly the type IV isotherm with type doping probably related distortion lanthanum. The isotherm La_2Al_{11}PILV sample (Fig. 2d) virtually no hysteresis.

It is observed in Table 1 that the surface area values of the samples are shown gradually narrowed and the pore diameter increasing as doping with lanthanum increases, which can be taken as evidence of the actual existence of Lanthanum on the pillars of this sample as this has cation ionic radius significantly larger than the aluminum, resulting in increased pore diameter.

Despite the evidence of existence of lanthanum in the pillar structure, due to the small difference does not seem to have occurred the formation of an oligomeric precursor structure pillar having Lanthanum as a central element, since in Keggin type structures, the central element has tetrahedral symmetry in coordination with oxygen and hydroxyl ions.

The pore diameter values obtained for the modified sample only with aluminum salt, has a relationship with the value obtained from the doped lanthanum, which clearly reflects the different symmetries between aluminum hydroxide and lanthanum hydroxide. There is evidence that due to the considerably larger ionic radii and the tendency to form more content and coordination structures, lanthanum assume central atom position of the oligomer in octahedral symmetry and not tetrahedral, as has been reported for aluminum.