

Preparation and characterization of lanthanum palygorskite clays as acid catalysts

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Abstract

Palygorskite clays containing 2, 4, 6 or 10% lanthanum (w/w) were prepared by ion-exchange from acid-leached natural clays. Samples were characterized by chemical and thermogravimetric analysis, X-ray diffraction, infrared spectroscopy, and N_2 adsorption. Isopropyl alcohol was transformed in order to improve the acid behavior of the material. The introduction of La^{3+} did not change the structure of the palygorskite. Surface areas as high as $177.6 \text{ m}^2 \text{ g}^{-1}$ were measured for catalysts containing 2% lanthanum. This material also showed a very good activity for alcohol dehydration.

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Keywords: Palygorskite; Mineral clays; Characterization; Lanthanum

1. Introduction

Mineral clays, either pillared or not, have been used as catalysts to crack heavy fractions of oil, support for some metals or oxide phases, selective adsorbents, and in ion-exchange [1,2].

Palygorskite clays are potential candidates for a number of processes in heterogeneous catalysis [3–5]. These clays are characterized by porous crystalline structures containing tetrahedral layers alloyed together by longitudinal sideline chains [1]. These minerals consist of a typical unit cell with Mg and Al cations that can be easily exchanged [6,7]. Mg preferentially occupies the octahedral sites of the $(Mg,Al)_5Si_8O_{20}(OH)_2(OH_2)_4 \cdot 4H_2O$ unit cell [6,7]. This material exhibits large specific surface area, considerable porosity, and thermal stability [8]. The acidity of this material is associated to the presence of structural hydroxyl groups in its layers (Bronsted sites), as well as to interlayer species such as cations (Lewis sites) [9–11]. The outer OH groups of the molecule act as Bronsted acid sites whereas the Lewis sites are either the exposed or the three-coordinated Al^{3+} ions, substituting for Si^{4+} ions in the tetrahedral sheets [7].

Rare earth cations can promote both activity and stability of different materials, such as zeolites [11], mineral clays [1–5], and alumina [12] leading to efficient acid

catalysts. Conversion of 2-propanol has been used by various researchers as a probe reaction for acidic catalysis. Whereas acid sites essentially lead to propene as dehydration product, dehydrogenation of 2-propanol on basic or redox sites usually results in acetone [12].

The aim of the present research work was to verify the effect of the contents of La^{3+} on the physical–chemical and acid catalytic properties of palygorskite clays using the transformation of isopropyl alcohol as a test reaction.

2. Experimental procedure

The palygorskite clay used in this work originated from the Brazilian State of Piauí, located in the northeastern region of the country. It was calcined at 773 K to eliminate organic compounds (sample labeled S1). Sample S1 was leached with 6 N HCl solution at ambient temperature for 5 h in a rotavapour at 1800 rpm to improve proton acidity. This material was rinsed with deionized water to full chloride elimination and calcined under a flow of N_2/O_2 at 523 K (sample labeled S2). La^{3+} cations were then introduced into the palygorskite by ion-exchange carried out in a water suspension containing 10% solids and lanthanum nitrate— $La(NO_3)_3 \cdot 6H_2O$ —with concentrations of 2, 4, 6 or 10% w/w La^{3+} /palygorskite. The mixtures were stirred at 353 K for 48 h in a rotavapour. The products were filtered, dried out, and calcined at 523 K for

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2 h under a N_2 flow of 50 ml min^{-1} , resulting in samples labeled S3, S4, S5, and S6, respectively.

The main physico-chemical properties of the resulting samples were investigated by atomic absorption spectroscopy (AAS) using a Varian spectrometer, X-ray fluorescence using a Shimadzu EDX-800 system, X-ray diffraction (XDR) using a Shimadzu XD3-A set-up, infrared spectroscopy with adsorbed *n*-butylamine in a FTIR Perkin-Elmer 16PC system, N_2 adsorption using a Micromeritics ASAP-2000 BET equipment, and thermogravimetric analysis in a TGA-7 Perkin-Elmer model system. Particle size distributions in the $0.04\text{--}500 \mu\text{m}$ range were obtained in a CILAS 1064 laser analyzer.

The conversion reaction of 2-propanol was performed in a tubular glass flow microreactor of 1.5 mm internal diameter. The catalysts were activated in situ at the reaction temperature under a N_2 flow of 80 ml min^{-1} . The space velocity was set to 9.6 h^{-1} and the reaction test temperature was 473 K. The products were analyzed online using a gas chromatograph unit equipped with a Poropak-Q packed column and a Varian FID–GC flame ionization detector.

3. Results and discussion

The results obtained from atomic absorption and X-ray fluorescence analyses indicated that the lanthanum cations were introduced in the octahedral sites of the palygorskite structure replacing magnesium cations. The resulting structural formulas are summarized in Table 1.

Fig. 1 shows the XRD patterns of the original palygorskite (S1), acid palygorskite (S2), 2% La-palygorskite (S3) and 4% La-palygorskite. Natural palygorskite (sample S1) revealed a high degree of crystallinity. The interlayer distance of the peak observed at $2\theta=8.6^\circ$ (1.04 nm) was attributed to the basal space of the palygorskite framework [13]. The peaks at $2\theta=13.9$, 16.5 , and 20.9° represented the Si–O–Si crystalline layers of the clay [13]. The peak at $2\theta=12.4^\circ$ corresponded to a hydrated oxide containing sodium and magnesium cations presented between layers. Quartz impurities were also found as shown by its most intense peak situated at $2\theta=26.7^\circ$ ($d_{(001)}=0.334 \text{ nm}$). Acid leaching did not produce any significant loss in the crystallinity of the material. Moreover, the impurities could not be removed by this method (Fig. 1).

Table 1

Sample identification and structural formulas of natural and La-palygorskites

Sample label	Structural formula
Natural palygorskite (S1)	$(Al_{2.74}Fe_{0.58}Mg_{1.69}La_0)(Al_0Si_{8.7})O_{28}(OH)_2(OH_2)_4 \cdot 4H_2O$
Acid palygorskite (S2)	$(Al_{1.83}Fe_{0.53}Mg_{1.42}La_0)(Al_{0.27}Si_{7.97})O_{20}(OH)_2(OH_2)_4 \cdot 4H_2O$
Palygorskite 2% lanthanum (S3)	$(Al_{1.82}Fe_{0.56}Mg_{1.31}La_{0.052})(Al_{0.23}Si_{7.97})O_{20}(OH)_2(OH_2)_4 \cdot 4H_2O$
Palygorskite 4% lanthanum (S4)	$(Al_{1.83}Fe_{0.56}Mg_{1.37}La_{0.095})(Al_{0.33}Si_{7.96})O_{20}(OH)_2(OH_2)_4 \cdot 4H_2O$
Palygorskite 6% lanthanum (S5)	$(Al_{1.77}Fe_{0.56}Mg_{1.33}La_{0.152})(Al_{0.45}Si_{7.95})O_{20}(OH)_2(OH_2)_4 \cdot 4H_2O$
Palygorskite 10% lanthanum (S6)	$(Al_{1.68}Fe_{0.56}Mg_{1.33}La_{0.265})(Al_{0.522}Si_{7.94})O_{20}(OH)_2(OH_2)_4 \cdot 4H_2O$

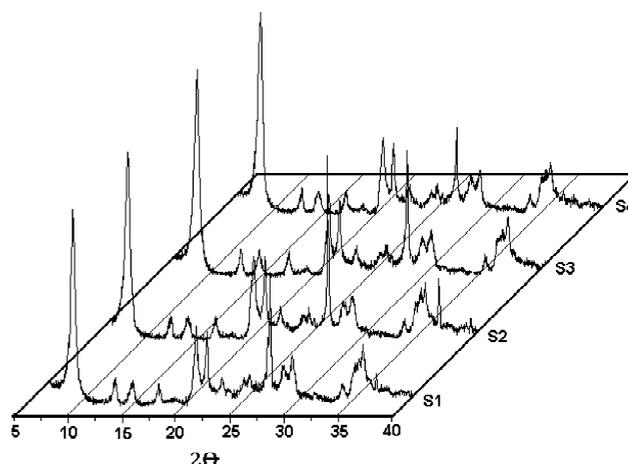


Fig. 1. XRD patterns of natural palygorskite (S1), acid palygorskite (S2), 2% La-palygorskite (S3), 4% La-palygorskite (S4).

Table 2

BET surface area of natural palygorskite S1, acid palygorskite S2, and La-palygorskites labeled S3, S4, S5 and S6, and containing 2.0, 4.0, 6.0 and 10.0% La, respectively

Sample	S_{BET} ($\text{m}^2 \text{g}^{-1}$)
S1	168.3
S2	150.1
S3	177.6
S4	155.8
S5	150.2
S6	108.0

Fig. 1 also shows the XRD patterns obtained from samples S3 and S4 calcined at 523 K. No considerable differences could be observed comparing those patterns with that of the natural palygorskite other than the low intensity of the peak corresponding to quartz impurities ($2\theta=26.7^\circ$) observed for the 2 and 4% La-palygorskite. The peaks corresponding to the palygorskite framework ($2\theta=8.7$, 19.9 , and 20.9°) were present and showed similar intensities compared to the natural palygorskite. No peak corresponding to lanthanum oxide was observed. The exchange of magnesium by lanthanum occupying octahedral sites could be inferred by the $d_{110}=1.03 \text{ nm}$ basal distance represented by the peak located at $2\theta=8.7^\circ$.

The average particle size of the analyzed samples was $14 \mu\text{m}$. The surface area of the material was evaluated by N_2 adsorption. The palygorskite containing 2% lanthanum presented the highest surface area values (Table 2).

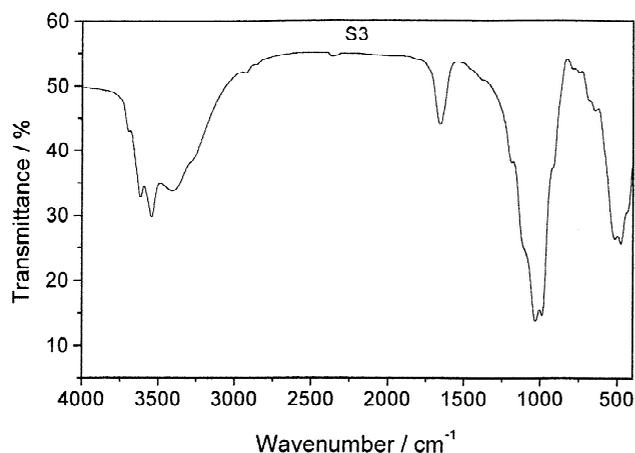


Fig. 2. Infrared pattern of 2% La-palygorskite (S3).

Combining the results from BET and chemical analysis it could be observed that the surface area of the catalyst decreased as the content of magnesium replacing lanthanum increased. This trend is shown in Table 2. Lanthanum contents in excess of 2% may cause deleterious effects on the applicability of the material.

Fig. 2 shows the 4000–400 cm^{-1} range of the infrared spectra for sample S3. The bands at 1083 and 465 cm^{-1} were attributed to in-layered Si–O–Si bonds [7,8]. The band near 800 cm^{-1} may correspond to the Al–O–Si bond [7,8]. Fig. 3 shows the FTIR patterns of natural palygorskite (S1), acid palygorskite adsorbed with *n*-butylamine

(S2A), and 2% La-palygorskite with *n*-butylamine (S3A). The Lewis and Bronsted acid sites were situated at 1630 and 1500 cm^{-1} , respectively, as identified by the adsorption of *n*-butylamine probe molecules [14,15]. This indicated that the lanthanum cations were responsible for these types of active sites, although the acid palygorskite also contains such sites, as suggested from Fig. 3. The results of the thermogravimetric analyses (Table 3) indicated that the S3A catalyst had the largest number of acid sites obtained by the adsorption–desorption of *n*-butylamine. Furthermore, the thermal desorption of *n*-butylamine indicated that the number of acid sites was maximum upon the addition of 2% lanthanum (Table 3). This behavior was later confirmed by infrared analysis which detected the presence of both Lewis and Brönsted acid sites in the samples which adsorbed *n*-butylamine (Fig. 3). The transformation of 2-propanol was carried out for samples S1, S2, S3, S4, S5, and S6. It can be seen from Table 4 that the initial conversion took place at 473 K, with $\text{WHSV}=9.6 \text{ h}^{-1}$ and $m=0.03 \text{ mg}$. Although propene was the main product of the dehydration of S3, S4, S5, and S6, 2-propanol was also observed. No acetone was observed, indicating that no basic sites were present. The best 2-propanol initial conversion was obtained from the palygorskite containing 2% lanthanum (Fig. 4) which was in good agreement with the results obtained from total acidity and surface area analyses. As thermal stability varies with temperature, initial conversion and conversion factor are not essentially identical.

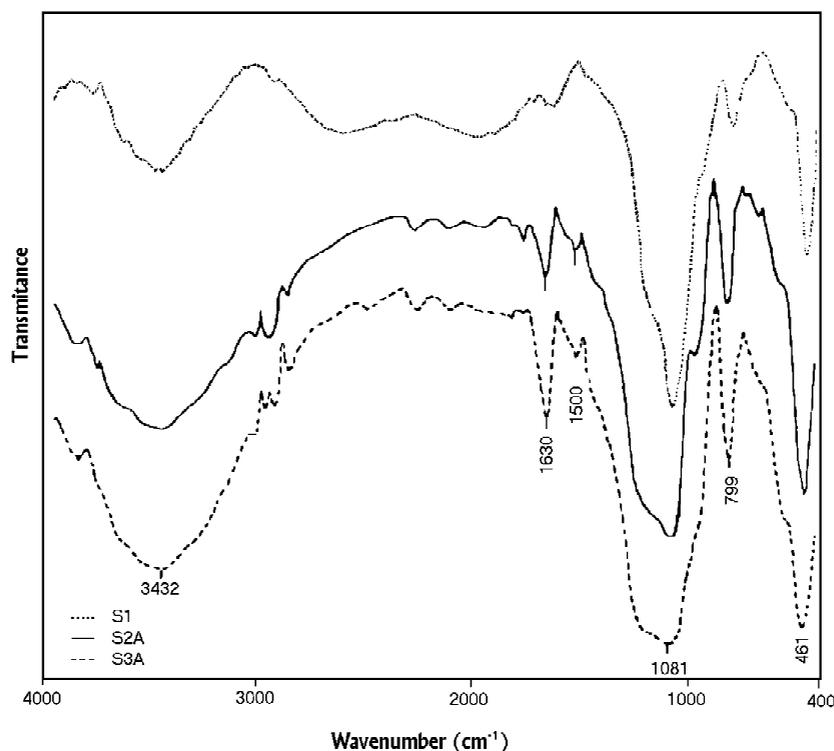


Fig. 3. Infrared pattern of natural palygorskite (S1) Lewis and Bronsted acid sites in *n*-butylamine adsorbed acid-palygorskite (S2A) and 2% La-palygorskite (S3A).

Table 3
Total number of acid sites for samples S1–S6

Adsorption site type and ΔT (°C)	Samples (mmol g ⁻¹)					
	S1	S2	S3	S4	S5	S6
Physisorption 50–110	0.116	0.166	0.152	0.174	0.186	0.3695
Low chemisorption 110–210	0.156	0.231	0.571	0.226	0.254	0.269
Medium chemisorption 210–330	0.1497	0.226	0.386	0.214	0.243	0.253
High chemisorption 330–720	0.1699	0.2699	0.617	0.422	0.542	0.454
Total number of sites	0.4756	0.7669	1.574	0.862	0.939	0.976

Table 4
Initial conversion at $T=200$ °C (WHSV=9.6 h⁻¹ and $m=0.03$ g)

	Sample					
	S1	S2	S3	S4	S5	S6
% of initial conversion ($t \rightarrow 0$)	3.97	76.75	88.09	71.05	58.28	43.13

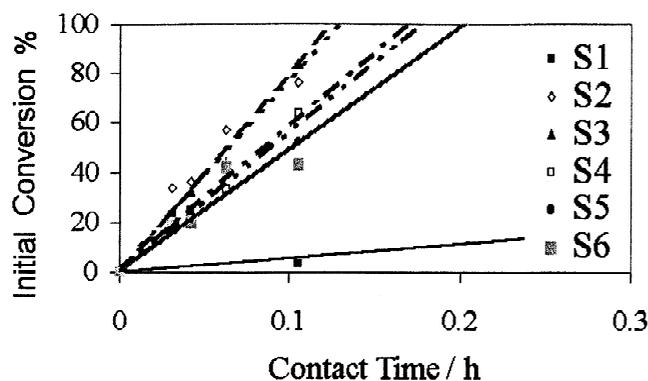


Fig. 4. Catalytic activity of S1 to S6 samples.

Acknowledgements

The authors would like to acknowledge CNPq (National Research Council of Brazil) for its financial support granted to this work. The authors also express their gratitude to Professor Elson Longo (LIEC-UFSCar) for carrying out the surface area analyses. J.A.C. Ruiz also acknowledges CAPES for his MSc scholarship.

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