

Study of the Effects of Lanthanum and the Iron Ion on the Acidic Properties of Al-pillared Vermiculite

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Received: September 9, 2012; Revised: May 20, 2013

The synthesis of porous materials has attracted interest for decades due to their applications in catalysis and gas adsorption. Clay obtained by insertion of mesoporous oligomer $[\text{La}_x\text{Al}_{13-x}\text{O}_4(\text{OH})_{24}(\text{H}_2\text{O})_{12}]^7+$ (where x equals the molar amount of lanthanum), followed by calcination, may cause variation in the acidic properties. The analyzes showed that increasing the amount of La on oligomer results in a higher acidity shown in the spectrum a characteristic band in the region of 1445 and 1545 cm^{-1} to Lewis and Brönsted respectively, predominantly of the last one. The Mössbauer spectroscopy results showed a relationship between increased symmetry of the octahedral site of iron (Fe^{3+}) and increased lanthanum doping, and consequently a sharp increase in acidity.

Keywords: acidity, mesoporous clay, lanthanum

1. Introduction

The first reports about obtaining clays mesoporous metal oxide occurred at the beginning of the 1970s. Since then the issue has been addressed in many studies¹⁻⁵. Ions such as Keggin, also called an polycationic oligomer $\text{Al}_{13}^{6,7}$, which has the empirical formula $[\text{Al}_{13}\text{O}_4(\text{OH})_{24}(\text{H}_2\text{O})_{12}]^{7+}$, are interspersed in the clay lamellae such as smectites and vermiculites by ion exchange⁸, which will subsequently calcined to obtain crystalline oxides structures like pillars in the clays internal structures^{9,10}.

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. Acidity study in pillared clays is of great importance due may help in understanding the catalytic selectivity, depending on the acid sites distribution^{11,12}.

Clay minerals from smectite group possess layered structure formed by tetrahedral and octahedral sheets. The tetrahedral contain mainly Si(IV) as the central atom, while the octahedral sites are occupied by Al(III), Fe(III) or Mg(II). Two types of octahedral sheets occur in clay minerals: the dioctahedral type, where two-thirds of the octahedral sites are occupied mainly by Al(III), Fe(III) or Mg(II) and the trioctahedral type, with most of the sites occupied by Mg(II) or Li(I)¹³⁻¹⁵. Iron is another important characteristic of the clay, which is a chemical species naturally occurring clay minerals from the vermiculites group^{16,17}.

Generally, the pillared clays properties depends on the modifying agent position. This behavior can be well evaluated by different methods, such as IR, Mössbauer spectroscopy, NMR, and others¹⁸. Related processes due iron

presence in the clay is best understood using the Mössbauer spectroscopy.

This work aims to obtain mesoporous material by intercalation aluminum oligomer ($[\text{OH}^-]/[\text{Al}^{3+}] = 2.4$) in vermiculite previously modified, followed by pillaring by calcination at 773K, and acidity increasing studies by aluminum doping (Al_{13}) in lanthanum (12Al : 1La and 11Al : 2La) and iron possible effects related.

2. Material and Methods

Precursor clay samples (vermiculite) are from the Paraiba State, Brazil. All of them were dried at 373K, crushed and sieved to 200 mesh to obtain a material with homogeneous particle size. Vermiculite treated with HNO_3 at 0.8 mol.L^{-1} 353K, calcined at 873K for 2 hours, was treated with oxalic acid 0.12 mol L^{-1} to 353K at reflux exchangeable for iron removal, next, was added NaCl 3 mol.L^{-1} to obtain the sodium form (VNa) (Table 1). Aluminum oligomer (Al_{13}) was prepared by addition of NaOH 0.2 mol.L^{-1} in $\text{AlCl}_3.6\text{H}_2\text{O}$ 0.2 mol.L^{-1} at reflux. Aluminum oligomer doped lanthanum ($\text{La}_x\text{Al}_{13-x}$), were obtained from solutions of NaOH 0.2 mol.L^{-1} , $\text{AlCl}_3.6\text{H}_2\text{O}$ 0.2 mol.L^{-1} and $\text{LaCl}_3.6\text{H}_2\text{O}$ 0.2 mol.L^{-1} , seeing x equals to 1 or 2. Oligomers were obtained by considering the ratio $\text{OH}^- / (\text{Al} + \text{La}) = 2.4$. Oligomer solution with stirring at 353K was added to the sample VNa dispersed in deionized water (10% m.V⁻¹) under stirring for 24 hours, obtaining the interleaved samples, which were washed with deionized water and dried at 373K, crushed and calcined at 773K for 3 hours.

Lewis and Bronsted-Lowry acidity study of pillared vermiculites was carried out using pyridine as a probe molecule by infrared spectroscopy absorption (FT-IR) of samples tablets form at different temperatures

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(373K - 673K). Weight W (g) and diameter D (cm) of each sample were recorded for the measurement of the Brönsted and Lewis acid sites ($q_{B,L}$) using an equation:

$$q_{B,L} = (\pi \cdot A \cdot D^2) \cdot (4 \cdot W \cdot \epsilon_{B,L})^{-1}$$
 (1)

where A is the integrated area of the band (a) and $\epsilon_{B,L}$, molar extinction coefficient ($\mu\text{mol} \cdot \text{g}^{-1}$)^{19,20}.

Mössbauer spectra were recorded in transmission mode at room temperature with a radioactive source ⁵⁷Co rhodium matrix mounted in a speed control operating mode sine ranging from -4 to +4 mm.s⁻¹, to observe all transitions possible energy hyperfine parameters of structural iron (⁵⁷Fe) nuclei.

3. Results and Discussion

3.1. Acidity characterization

Some authors, such as Pálkova et al.¹³ and Nunes et al.²¹ suggest that acidic properties of pillared clays are attributed to the presence of SiOH or AlOH groups. An efficient way to investigate this association is the use of organic bases such as pyridine, which second Chmielarz et al.²², has frequently been used in the study of acidic sites.

According Akçay¹¹ and Benvenuti et al.²³, distinction between the of Lewis and Bronsted acidity is based on the position of certain vibrational modes (Table 2) of pyridine molecule known as 8a and 19b. Pyridine is a strong base and a proton transfer, resulting in the formation of ions when the pyridinium molecules interact with Brönsted acid sites.

Figures 1, 2 and 3 show pyridine spectra adsorbed on samples of the oligomers modified with vermiculite Al₁₃, LaAl₁₂ and La₂Al₁₁ respectively, at different temperatures: 373K, 473K, 573K and 673K. Stretch region in the spectra of 1580-1550 cm⁻¹ and 1455-1440 cm⁻¹ band 19b are characteristics to the Brönsted and Lewis sites (Table 2), respectively.

Table 1. Description of the samples.

Sample	Description
VERM	Natural vermiculite
VNa	Sodium vermiculite
Al ₁₃ PILV	Al ₁₃ -Pillared vermiculite
LaAl ₁₂ PILV	LaAl ₁₂ -Pillared vermiculite
La ₂ Al ₁₁ PILV	La ₂ Al ₁₁ -Pillared vermiculite

Table 2. Pyridine bands adsorbed on the solid surface according Benvenuti et al.²³ and Akçay¹¹.

Modes	Wave number (cm ⁻¹)			
	FA	LH	CSL	PSB
8a	c.a. 1580	c.a. 1595	1600-1630	c.a. 1640
19b	c.a. 1438	c.a. 1444	1447-1465	1530-1550

Gyftopoulou et al.²⁴ report the samples acidic character of pillared vermiculites derived from both Brönsted sites (proton donor) and Lewis sites (receiver pair of electrons). Brönsted acidity may be associated with the protons release during pillars and the vermiculite lamellae dehydroxylation, whereas the Lewis acidity is assigned to metal oxides pillars.

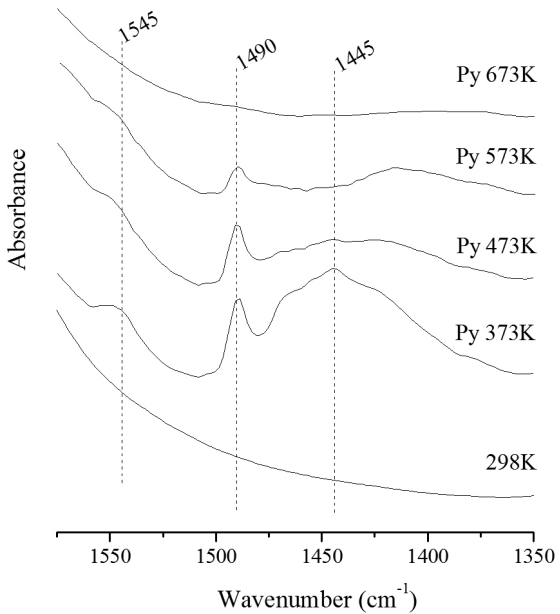


Figure 1. FT-IR spectra of pyridine adsorbed on the sample Al₁₃PILV.

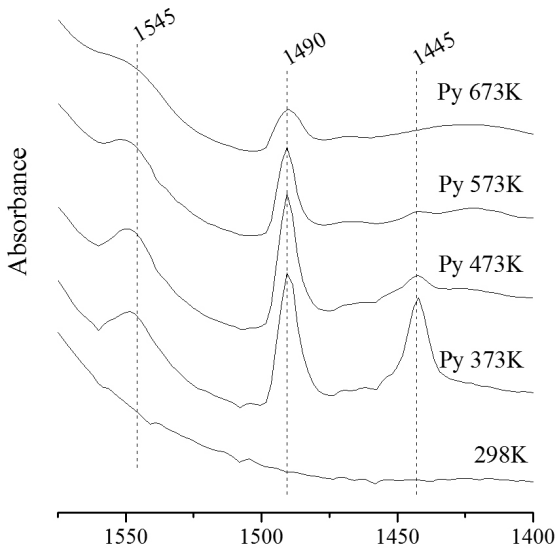


Figure 2. FT-IR spectra of pyridine adsorbed on the sample LaAl₁₂PILV.

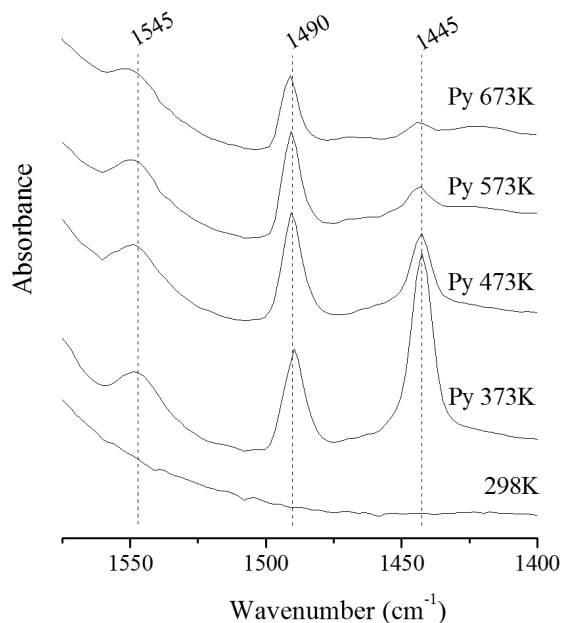


Figure 3. FT-IR spectra of pyridine adsorbed on the sample $\text{La}_2\text{Al}_{11}\text{PILV}$.

Figures 1, 2 and 3, the band at 1445cm^{-1} on Lewis sites increases significantly as the amount of lanthanum incorporated increases. Layman et al.²⁵, Shimizu et al.²⁶ and Yazıcı et al.²⁷ noted that the region in 1490cm^{-1} correspond Lewis and Brönsted acid sites, who also undergo changes in their intensities. However, these changes and thermal degradation of Lewis and Brönsted acid sites (Figure 4), are not as significant, and appear to be related to the fact that the lanthanum is not in a central position in the oligomer, and also the greater stability than Lewis sites acquire when they are located in this specie.

Figure 4 shows a significant increase in Lewis acidity, related to the higher percentage (% w/w) of lanthanum in the oligomer, which shows that the concentration of Lewis sites triples. Twice lanthanum the oligomer, the concentration of sites increases approximately eight times.

3.2. Mössbauer spectroscopy

Parameter values hyperfine obtained by adjusting the Mössbauer spectra are shown in Table 3. All Mössbauer spectra (Figure 5a-d) obtained from samples in powder of natural and pillared clay with aluminum and aluminum - lanthanum, show the presence of Fe^{3+} , and still observing (Figure 5a) that only natural vermiculite (VERM) presented Fe^{2+} .

Mössbauer spectra (Figure 5) may elucidate doubt as iron may affect the thermal stability of the obtained material and possibly iron and interacts only with pillared aluminum oligomer (Al_{13}) and aluminum-doped lanthanum oligomers (LaAl_{12} and $\text{La}_2\text{Al}_{11}$).

$\text{Al}_{13}\text{PILV}$, and $\text{LaAl}_{12}\text{PILV}$ $\text{La}_2\text{Al}_{11}\text{PILV}$ showed quadrupole splitting values (Δ) * significantly different

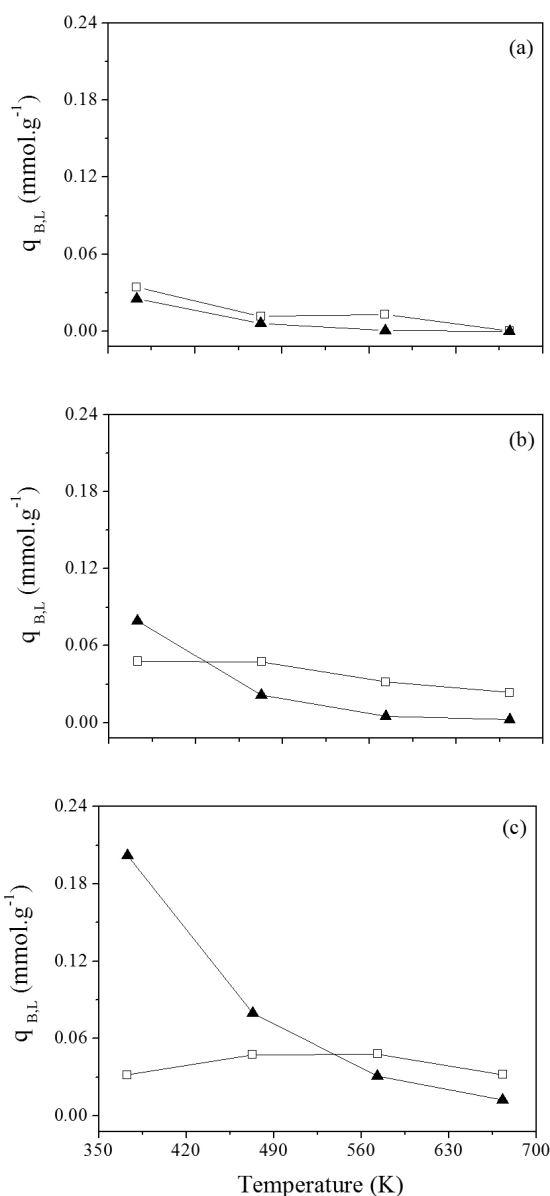


Figure 4. $q_{B,L}$ (mmol.g^{-1}) vs. Temperature (K) of measurement of the Brönsted acid sites ($\square$) and Lewis ($\blacktriangle$) of the samples: (a) $\text{VAl}_{13}\text{PIL}$, (b) $\text{VLaAl}_{12}\text{PIL}$ and (c) $\text{VLa}_2\text{Al}_{11}\text{PIL}$.

(1.28, 1.21 and 1.14mm.s^{-1}), respectively, as shown in Table 3, decreasing values show an increase in the organization octahedral site iron could be related growing pillars doping with lanthanum and increased acidity.

According Carriazo et al.²⁸ may be slight variations in the parameters δ and Δ_{EO} , especially considering the chemical environment of Fe^{3+} in the mineral structure may vary slightly, and distortion may occur in the geometry sites of Fe^{3+} due loss of water or OH groups in the calcination step.

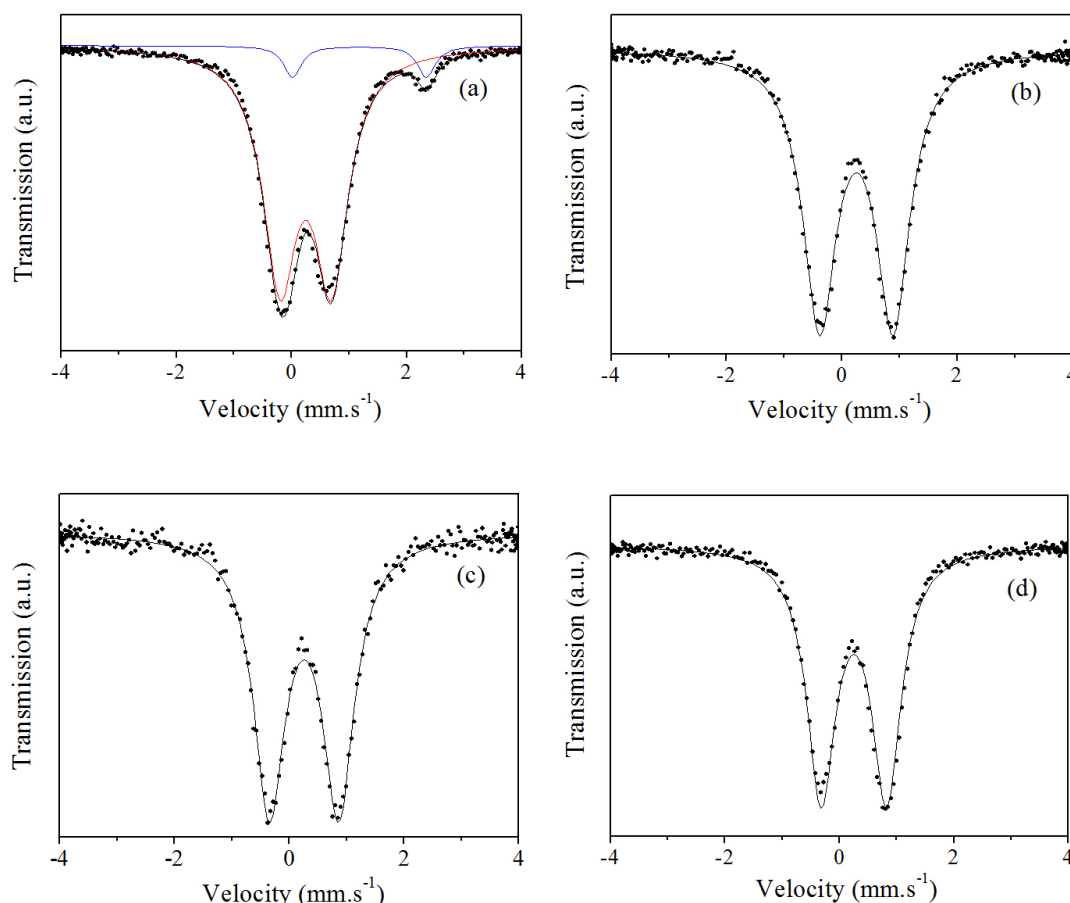


Figure 5. Mössbauer spectra of (a) VERM, (b) $\text{Al}_{13}\text{PILV}$, (c) $\text{LaAl}_{12}\text{PILV}$ and (d) $\text{La}_2\text{Al}_{11}\text{PILV}$.

Table 3. Hyperfine parameters vermiculite at different steps.

Sample	Assignment	δ (mm.s^{-1})	ΔE_Q (mm.s^{-1})	Γ (mm.s^{-1})
VERM	Fe^{3+}	0.34	0.89	0.71
	Fe^{2+}	1.28	2.33	0.37
$\text{Al}_{13}\text{PILV}$	Fe^{3+}	0.37	1.28*	0.70
$\text{LaAl}_{12}\text{PILV}$	Fe^{3+}	0.38	1.21*	0.67
$\text{La}_2\text{Al}_{11}\text{PILV}$	Fe^{3+}	0.37	1.14*	0.61

δ : isomer shift (measured relative to $\alpha\text{-Fe}$); ΔE_Q : quadrupole splitting; Γ : line width.

4. Conclusions

Aluminum doped lanthanum oligomer ($\text{LaAl}_{12}\text{PILV}$ and $\text{La}_2\text{Al}_{11}\text{PILV}$) showed Lewis and Brönsted sites predominance at temperatures up to 373K and 573K respectively. The Brönsted sites showed greater thermal stability in all modified clay samples. Mössbauer spectra indicated a possible relationship between increased

octahedral site Fe^{3+} symmetry, lanthanum/aluminum doped oligomer and higher acidity.

Acknowledgements

This work was financially supported by the CNPQ, CAPES and Policlay NT.

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