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Thermokinetic investigation of acid sites of the vermiculite doped lanthanum

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ABSTRACT

It is widely recognised that the activation energy (E_a) is involved in the process of thermal decomposition; it allows the stability of the material to be better understood. The Ozawa method is an efficient tool for obtaining the kinetic parameters involved in the process of thermal decomposition. This method is based on measuring the thermal energy associated with the decomposition mass percentage related to temperature that is obtained using thermogravimetric analysis (TGA) at different temperatures. The thermogravimetric curves of vermiculite samples at different temperatures showed a shift at higher temperature associated with increased heating rate values. However, when a small heating ratio is used, this energy is released in the system on a larger time interval, allowing the sample to absorb this energy more efficiently, which results in a greater mass removal at lower temperatures. The interactions of acid sites with the probe molecule showed a quantitative relation to increasing the lanthanum doping, and the samples with higher doping lanthanum showed higher value of activation energy associated with the desorption of the probe molecule.

1. Introduction

From TG and DTG (differential thermogravimetric) curves, characteristic parameters, which distinctly reveal the thermal decomposition process, could be deduced. These parameters are very important to understand the physical and chemical conversion of the tested sample and to design or operate a conversion system to achieve high efficiency [1].

The specific doping lanthanum is due to its oxidation state (3+) similar to aluminum and high acidity which explains its wide use in catalytic processes [2].

The Ozawa method is well reported in previous studies of decomposition reactions involving kinetic parameters [3]. The activation energy is calculated by this method using the average slope of the line between the points which is obtained by linear regression and extrapolation of this line also provides the pre-exponential factor (A) [4].

The many methods proposed for obtaining the kinetic parameters from the thermogravimetric data, though rather complicated, may be classified into two classes, in both of which the rates of decomposition must have the following form:

$$-\frac{dW}{dt} = A\exp\left(-\frac{Ea}{RT}\right)W^n \qquad (1)$$

where W is the fractional residual weight of the sample; T, the absolute temperature; R, the gas constant; t, the time, and A, Ea and n, the pre-exponential factor, the activation energy and the order of the reaction respectively [5].

This work aims to assess the stability of the acid sites of the thermokinetic structure of vermiculite samples doped with different ratios lanthanum and obtain the activation energy of thermodecomposition by using the method of Ozawa.

2. Experimental procedure

2.1. Sample preparation

Samples mesoporous vermiculite (Al_{13}PILV, $LaAl_{12}$PILV e La_2Al_{11}PILV) were obtained from a natural vermiculite (VERM) previously treated and intercalated with an aluminum doped lanthanum oligomer was obtained from solutions of 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 ratios $[OH^-]/[Al^{3+}]$=2.4 and La_xAl_{13-x} (where x =0, 1 or 2) , then calcined at 823 K for 3 h.

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2.2. Acidity characterization of samples

Lewis and Bronsted-Lowry acids sites of mesoporous vermiculite was carried out using pyridine as a probe molecule by means of absorption spectroscopy in the infrared (FT-IR). Pure tablet samples format different temperatures 373 K, 473 K, 573 K and 673 K were obtained using a ABB model FTLA2000 spectrometer. The weight W(g) and the diameter D(cm) of each sample were recorded by the measurement Brönsted and Lewis acid sites ($q_{B,L}$) by using Eq. (2) as [6,7]:

$$q_{B,L} = (A_{B,L}\pi D^2)(4w\varepsilon_{B,L})^{-1} \tag{2}$$

where D = tablet diameter (cm), W = sample weight (g) $A_{B,L}$=absorbance bands integration in characteristic mode, obtained with the aid of appropriate software after optimization of the baseline; $\varepsilon_{B,L}$=extinction coefficient of the interaction of pyridine with Brönsted acid sites =1.67 ± 0.12 cm mol^{-1} and Lewis =2.22 ± 0.21 cm mol^{-1}[8].

Thermogravimetric analysis (TGA) were performed on a TA Instruments TGA Q series Q50-0915 model, where samples (10.0 mg) were analyzed and subjected to heating with ratio of 5, 10, 15, 20 and 25 °C min^{-1}, and the temperature of 900 K in synthetic air atmosphere.

According Lopes et al. [9], the study of thermal decomposition by the Ozawa method, consists of the heating of specimens, each at a different temperatures, through their decomposition region. The specimen mass is recorded continuously as a function of temperature. The temperatures for constant conversion are determined from the resultant mass loss curves. After lots mathematical development, the Arrhenius activation energy (*Ea*) is then determined from a linear regression of the logarithm of the heating rate (*log β*) versus the reciprocal of the absolute temperature (*1/T*) at constant conversion level. Where *b* is the slope (Eqs. (3) and (4)).

$$\log\beta = b \times \left(\frac{1}{T}\right) + a \tag{3}$$

$$E_a = b \times -18.2045 \tag{4}$$

3. Results and discussion

3.1. Relationship lanthanum structure

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.

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.

3.2. Infrared spectroscopy and acidity characterization

Palkova et al. [10] suggest that acidic surfaces in pillared clays are associated to the SiOH groups or AlOH composition (Fig. 1a). According Chmielarz et al. [11] an efficient way to investigate the acid properties of porous solid based on aluminum silicates, magnesium and/or iron is the use of pyridine as the probe molecules.

Fig. 1a, b and c show spectra of pyridine adsorbed on oligomers modified with vermiculite Al_{13}, $LaAl_{12}$ and La_2Al_{11} at different temperatures 373 K, 473 K, 573 K and 673 K respectively. The stretch regions 1580–1550 cm^{-1} and 1455–1440 cm^{-1} spectral characteristics are related to the Brönsted and Lewis sites respectively.

According Gyftopoulou et al. [12] the acid character of the pillared vermiculites are derived from both sites of Brönsted (proton donor) and Lewis (receiver pair of electrons). The Brönsted acidity appears to be associated with the release of protons during the dehydroxylation of the pillars and the vermiculite lamellae, while the Lewis acidity of metal oxides is attributed to the pillars. It is observed in Fig. 1a, b and c that the band at 1445 cm^{-1} on Lewis sites, increases significantly as the amount of lanthanum incorporated into abutment also increases. Bands at 1490 cm^{-1} are the contributions of the acidic Brönsted and Lewis sites and undergo changes in their relative intensities [13].

The values of the thermal desorption of the pyridine according to the calcination temperature indicate that mesoporous vermiculite doped lanthanum had both high acidity of Bronsted and Lewis, and La_2Al_{11}PILV (at 673 K 32.11 and 12.31 μmol Py g^{-1} respectively) confirm that an increase in the amount of lanthanum in pillars effectively raises the Lewis acidity.

The changes in the acid sites of Lewis and Brönsted (Fig. 1c) appear to be related to a possible displacement of the lanthanum which is not in a central position in relation to the oligomer, as expected, since the structure of symmetry of the central element ion with a Keggin-type structure presents coordination index smaller than metal species in their vicinity. The highest stability of Lewis sites was associated with the fact that these are located on the lanthanum, favored over contraction related to lanthanum that this species is subject.

3.3. Thermokinetics parameters obtained using Ozawa method

Fig. 2a, b and c show the thermogravimetric curves of vermiculite mesoporous samples in an air synthetic atmosphere (Al_{13}PILV, $LaAl_{12}$PILV and La2Al_{11}PILV) with pyridine adsorbed. The curves obtained for different ratios of heating revealed a shift in high temperature due to thermal decomposition of pyridine related desorption of acid sites, which according to the results obtained in the infrared range, is 373–673 K for Al_{13}PILV and $LaAl_{12}$PILV, extending values greater than 673 K for the sample La2Al_{11}PILV. The shift can be explained as follow: the energy added to the system is the same, independent of the velocity. However, when lower temperature is used the energy remains longer in the system allowing clay to absorb this energy more efficiently, resulting in elimination of mass at lower temperatures than higher.

$LaAl_{12}$PILV (Table 1), demonstrates higher values of activation energy, which indicates great thermal stability of the interactions between the acid sites and pyridine. Although, La2Al_{11}PILV had a great Lewis acidity, the activation energies (Fig. 2d) were lightly lower for Al_{13}PILV and $LaAl_{12}$PILV short percentage of mass loss.

Fig. 2d shows that doping with lanthanum is directly related to the increased acidity evidenced by increased activation energy related to thermal decomposition of interaction between pyridine-sites acids.

The variation and magnitude of the activation energy indicates that the samples have a higher lanthanum doping have higher acidity, but smaller thermal stability justified by the high variation in activation energy for the same sample, may be due to a reduced interaction between the probe molecule and acid sites.

Acidity and activation energy can be related to the size difference between the oligomers of the samples inserted in the precursor structure, and it also may show upon the infrared results, that with increasing lanthanum doping, the basal interplanar basal structure did not reach the homogeneity of the pillars, possibly due to the larger size of lanthanum.

4. Conclusions

Brönsted acid sites are present in greater quantity and higher thermal stability in all samples of modified vermiculite, but the Lewis acid sites showed similar decay curves, possibly due great homogeneity of interaction with probe molecule (pyridine).