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Journal of Solid State Chemistry 171 (2003) 217–220

JOURNAL OF
SOLID STATE
CHEMISTRY

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Determination of relative acid strength of La/paligorskyte by *n*-butylamine

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Received 5 May 2002; received in revised form 15 August 2002; accepted 1 September 2002

Abstract

The relative acid strength of lanthanum catalysts supported on paligorskyte was determined by thermodesorption of *n*-butylamine and infrared absorption spectroscopy. The results indicated that the desorption reaction took place in four temperature ranges. The catalyst containing 2% lanthanum particularly showed a considerable number of acid sites probably as a result of the relatively high specific area of the material.

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Keywords: Catalysts; Paligorskyte; Lanthanum; Thermodesorption, Acid sites

1. Introduction

Clay minerals have long been used as both catalysts and support, due to their ability to exchange ions, high surface area, and superior adsorption capability [1]. The exchange of specific cations can create active centers in clay minerals, granting catalytic properties which make them useful materials in a number of chemical reactions of industrial interest [2]. Paligorskytes are clay minerals of the hormitas group. These are naturally formed by chemical precipitation that took place in lakes and closed seas, frequently where volcanic acid ashes or esmectite-generator soluble salts had been deposited [3]. Paligorskytes consist of hydrated magnesium silicates that depict isomorphic replacements of magnesium by aluminum or iron. They are formed by two layers of SiO_4 tetrahedra with an inter-layer of $Mg(OH)_2$ and $Al(OH)_3$ octahedra. They are classified as a type 2:1 clay mineral [4] and depict fibrous texture and chained structure with microcanals. Different kinds of water can be found and account for 20 wt.% of the structure [5].

Lanthanides exhibit a vast range of technological applications, including catalysts for the petrochemical (lanthanum) and automotive industry (cerium). In Y-zeolites modified by rare earth elements, improvements in the catalytic behavior of the material were attributed to the formation of hydroxylic species within the canals of the structure, followed by induced thermal hydrolysis of $RE(H_2O)_n^{3+}$ cations upon calcination [6].

Adding lanthanum to paligorskytes results in the formation of active sites which improve the catalytic properties of the material as well as its thermal stability. The description of the acid properties of a solid with relatively high surface area involves the determination of the acid density, strength and nature of the sites. The adsorption of *n*-butylamine is widely used as a molecular probe in the characterization of acid character of solids surface [7,8]

In order to tailor a material for a given catalytic application, it is essential to establish whether the active sites present are basic or acid. The total acidity of the material is an important parameter that assists in the interpretation of the activity and selectivity of a catalyst [9]. A full description of the acid properties of a solid requires knowledge not only of the nature of the acid sites but also of the acid strength and density.

The present study presents thermogravimetric results on the total acidity of La/paligorskyte catalysts by thermodesorption of *n*-butylamine . The nature of the acid sites was identified by infrared (IR) spectroscopy. The effect of surface acid properties of La/paligorskyte

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0022-4596/03/$ - see front matter © 2003 Elsevier Science (USA). All rights reserved.
doi:10.1016/S0022-4596(02)00154-8

was studied for different La-contents, i.e., 2%; 3,6%; 6% and 9.8% (w/w). Samples were labeled according to the La-contents as S1, S2, S3, and S4, respectively. Samples with the same composition but adsorbed with *n*-butylamine were labeled S1A, S2A, S3A, and S4A, respectively.

2. Experimental

The paligorskyte clay was obtained from the Brazilian state of Piauí, located in the northeastern region of the country. It was leached with 6 N HCl solution for 5 h. Subsequently, the sample was filtered and rinsed with deionized water until full chloride elimination.

The La^{3+} cations were introduced on paligorskyte by ion exchange carried out in a water suspension containing 10% solids and lanthanum nitrates: La $(NO_3)_3 \cdot 7H_2O$ in concentrations of 2.0%, 3.6%, 6% and 9.8% w/w La^{3+}/paligorskyte resulting in the samples labeled S1, S2, S3, and S4.

La/paligorskyte samples were characterized by chemical analysis, FTIR, TG/DTG, BET surface area and XRD. They were heated and treated at 400°C for 1 h under flowing N_2 in order to activate the catalyst. Subsequently, the material was heated to 100°C for 1 h under a N_2 flow saturated with *n*-butylamine. Next, pure N_2 percolated the sample to remove any physiosorbed *n*-butylamine molecules. Samples containing *n*-butylamine were characterized by IR absorption spectroscopy, thermal analysis, and BET surface area, in order to establish the number of adsorbed molecules and qualitatively determine the driving force responsible for chemical adsorption.

IR absorption was carried out in a Bomen FTIR spectrophotometer using autosupported KBr pellets. The range between 4000 and 300 cm^{-1} was investigated. Thermogravimetric curves were obtained under flowing N_2 (50 mL min^{-1}) in the temperature range 30–900°C using a Perkin–Elmer TGA-7 thermobalance. The mass of each sample was approximately 2.5 mg.The heating rate was set to 10°C min^{-1}.

The surface area of the compounds was estimated using a Micromeritics Flowsorb 2300 BET system operating with gaseous N_2 adsorbed on the surfaces of the material cooled down to 77 K.

3. Results and discussions

IR absorption patterns corresponding to samples S1–S4 (Fig. 1) did not reveal the presence of acid sites within the range 1700–1300 cm^{-1}. On the other hand, samples S2A–S3A shown in the Fig. 1 are very similar and depicted a behavior typical of the presence of acid sites (Lewis or Brønsted), indicating that the material can be used as acid catalyst.

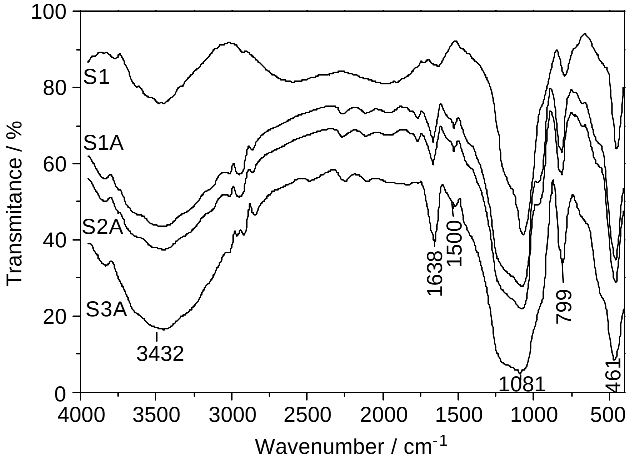

Fig. 1. IR absorption patterns of samples S1 and S1A–S3A, respectively.

The IR patterns showed peaks at 1638 cm^{-1} corresponding to Lewis acid sites [9]. Brønsted sites were observed at the 1530 cm^{-1} region [10]. Comparing these results to those obtained by Melo et al. [11], it could be seen that Tb^{3+}/paligorskyte depicted a better resolved band with respect to Lewis sites. This could be attributed to the lower ionic radius of Tb^{3+} compared to La^{3+}, thus resulting in a more efficient ionic exchange of the former. The results from IR absorption spectroscopy and thermal analysis assisted in evaluating the total acidity of the compounds by monitoring the types of acid sites present in the material.

The results obtained from thermal analysis were evaluated based on the investigation carried out by Barrios et al. [12], who identified weight losses characteristic of raw paligorskyte in addition to paligorskytes treated with hydrochloridric acid in different concentrations. La/paligorskyte catalysts depicted loss of adsorbed water in the temperature range 30–110°C, followed by loss of zeolitic water as well as water trapped in the canals of the structure at 110–210°C. Water molecules bound to octahedral cations were released in two stages: 210–330°C and 330–600°C. The characteristics of the weight losses were similar for all samples investigated. Thermogravimetric curves along with their derivatives corresponding to samples S1–S4 are depicted in Fig. 2(a) and (b), respectively.

The thermogravimetric curves of samples adsorbed with *n*-butylamine (S1A–S4A) suggested the desorption of the compound in four stages: (a) desorption of physiosorbed *n*-butylamine (30–110°C); (b) desorption of *n*-butylamine adsorbed in weak sites (110–210°C); (c) medium sites (210–330°C); and (d) strong sites (330–720°C). Weight losses and first derivatives corresponding to samples S1A to S4A are illustrated in Fig. 3.

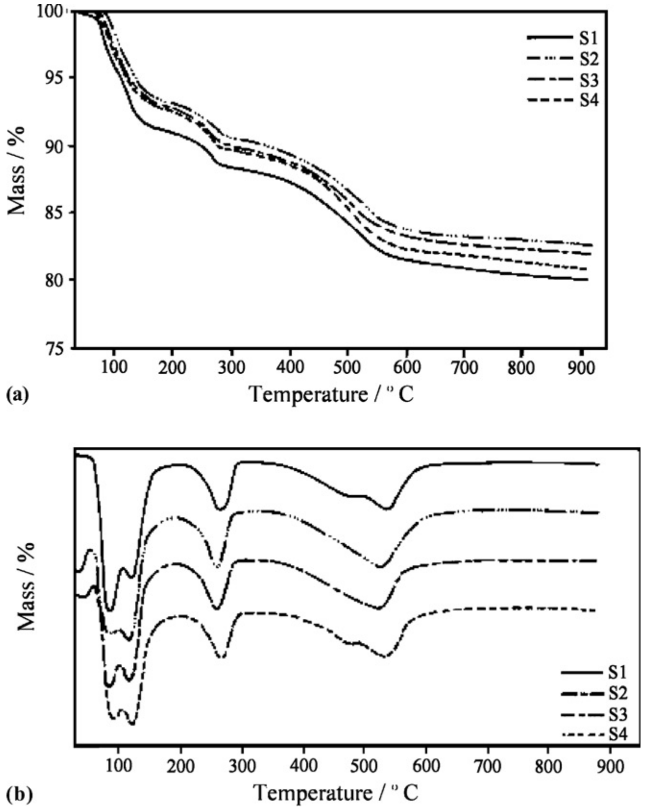

Fig. 2. (a) Thermogravimetric curves of samples S1–S4 and (b) first derivatives.

Total acidity was estimated considering that 1 mol of *n*-butylamine chemisorbed on the samples corresponded to 1 mol of acid sites. Determining the initial mass of the catalyst made it possible to represent the acidity in mmol of sites per gram of catalyst. Considering that the samples adsorbed with *n*-butylamine underwent a thermal pretreatment up to 400°C, it was reasonable to assume that the weight loss encountered between 30°C and 400°C corresponded exclusively to adsorbed *n*-butylamine molecules.

The types of adsorption sites and their relative strength as a function of the temperature are summarized in Table 1. Using the thermogravimetric data obtained from samples with and without *n*-butylamine it was possible to estimate the total acidity of each sample in units of mmol of sites per gram of catalyst.

The total acidity considering all the chemisorption that took place was plotted using the results from Table 1 for each catalyst (Fig. 4). As it can be seen, the maximum number of acid sites was obtained from the catalyst containing 2% lanthanum. This was probably a consequence of the relatively high surface area depicted by that material. Samples containing 3.2%, 6%, or 9.8% lanthanum showed a slight increase in the number of acid sites as the contents of lanthanum increased.

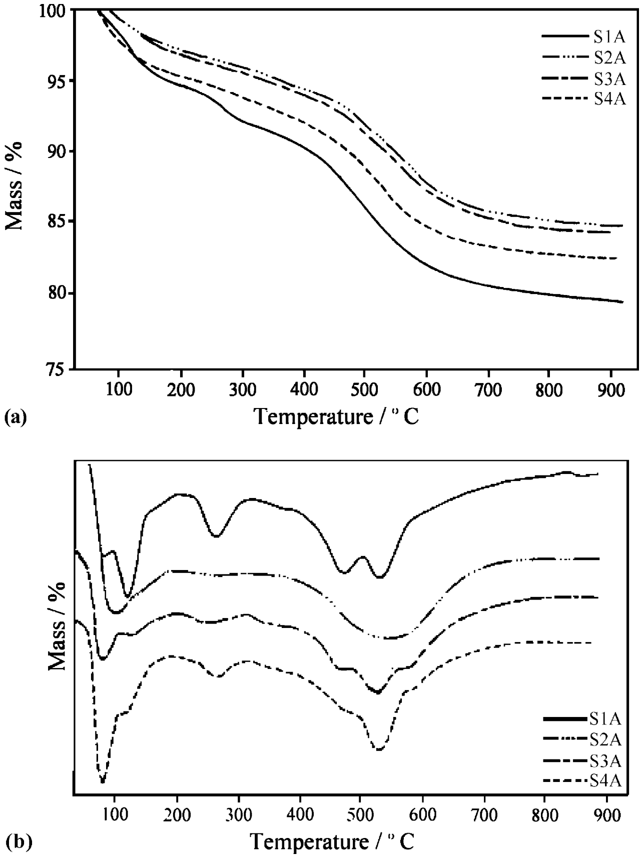

Fig. 3. (a) Thermogravimetric curves of samples adsorbed with *n*-butylamine S1A–S4A and (b) first derivatives.

Table 1
Number of acid sites per stage of thermodesorption for samples S1–S4.

Type of adsorption site/ΔT	S1	S2	S3	S4
	mmol g^{-1}			
Physiosorption/30–110°C	0.152	0.174	0.186	0.3695
Weak chemisorption/110–210°C	0.571	0.226	0.254	0.269
Medium chemisorption/210–330°C	0.386	0.214	0.243	0.253
Strong chemisorption/330–720°C	0.617	0.422	0.542	0.454

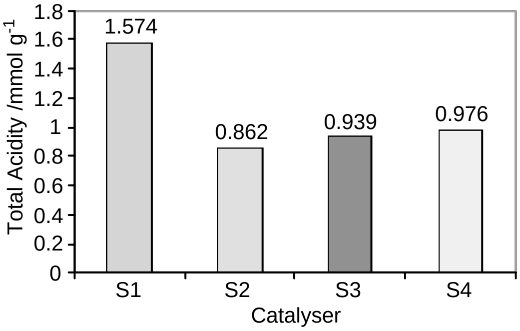

Fig. 4. Total acidity as a function of the lanthanum contents in paligorskyte.

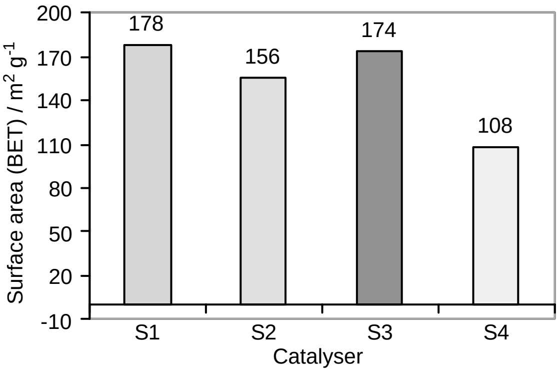

Fig. 5. BET surface area as a function of lanthanum contents in paligorskyte.

The results of BET surface area (Fig. 5) suggested that most of the lanthanum added to samples S2 and S4 were located in the canals of the paligorskyte structure obstructing pores. The addition of lanthanum was not successful for sample S2 and exceeded the capability of the paligorskyte to exchange cations for sample S4.

Lewis and Brønsted acid sites (weak, medium, and strong) were observed in samples S1–S4 as a result of the thermodesorption of previously adsorbed *n*-butylamine. Paligorskyte containing 2% La^{3+} depicted the highest specific area and the greatest number of both Lewis and Brønsted acid sites. The former was more pronounced in the material according to IR absorption spectroscopy. When added in appropriate amounts, lanthanum acted as a superior Lewis site former resulting in useful catalysts for dehydration reactions. These results can be compared with terbium on paligorskyte [11]

Acknowledgments

CNPq—National Research Council of Brazil is acknowledged for financial support for this work.

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