

DETERMINATION OF Ca/NaY ZEOLITE ACIDITY BY TG AND DSC

A. S. de Araujo, V. J. Fernandes Jr. and G. J. T. Fernandes

UFRN, Dept. Química, CP 1662, 59078-970, Natal, RN Brazil

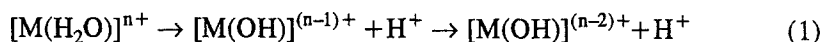
Abstract

The acid properties of the Ca/NaY zeolite were investigated by means of *n*-butylamine desorption and thermal decomposition, using both thermogravimetry (TG) and differential scanning calorimetry (DSC). The total acidity of the zeolite was calculated from the TG data, while DSC was used with the Borchardt-Daniels kinetic model to determine the relative acid strength of the catalyst, given in J per acid site. The enthalpies of these processes are proportional to the acid site strength in each specific temperature range.

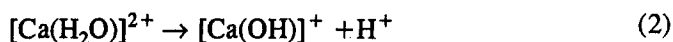
Keywords: acid solid catalyst, Ca/Na zeolite, heterogeneous catalysis

Introduction

An acidic solid catalyst in a material capable of converting an adsorbed basic molecule into its conjugated acid form. The acid site is able to transfer a proton from the adsorbed molecule to the adsorbed molecule (Brönsted acid site) or an electron pair from the solid to the solid surface (Lewis acid site). Dehydrated zeolites can exhibit both Brönsted and Lewis acid sites, depending on the ion-exchange and thermal treatment [1, 2]. The catalysis effected by acid zeolites is a function of the nature, density and strength of the acid sites, as well as the chemistry of the reaction intermediates. Structurally, zeolites comprise a three-dimensional network of SiO₄ and AlO₄⁻ complexes, linked together through common oxygen atoms. The neutralization of the negative charge is achieved by the introduction of polyvalent cations into the structural zeolite sites. This is of great importance in the generation of protonic acidity. The selectivity depends on the ionic ratio of the exchanged cations [3]. The protonation of a zeolite through a polyvalent ion (Mⁿ⁺) occurs according to Eq. (1):



The protons react with the oxygen lattice of the zeolite, giving rise to strong acid sites. In this way, divalent Ca-exchanged NaY zeolite, after thermal treatment, is a suitable catalyst in terms of the acidity of the solid [4]. The protonation of a zeolite through Ca²⁺ ion-exchange occurs according to Eq. (2):



The thermoanalytical methods and infrared spectroscopy are the most valuable techniques for the characterization of an acidic surface. Organic bases such as pyridine ($pK_b=8.75$) and ammonia ($pK_b=4.75$) have frequently been used to determine the nature (Brönsted or Lewis) of the acid sites. The *n*-butylamine ($pK_b=3.23$), which is a relatively strong base, is commonly used to determine the total acidity; it will react with weaker acid sites than either pyridine or ammonia.

The aim of this work is to evaluate the acid properties of Ca/NaY by means of TG and DSC techniques, using *n*-butylamine as the molecular probe. The use of *n*-butylamine for the characterization of solid surfaces such as silica, alumina, silica-alumina and montmorillonite has been reported [5, 6]. The acid strength kinetic parameters are determined via the Borchardt-Daniels kinetic model. As the acid properties (strength and total acidity) of zeolite catalysts are related to the activity and selectivity of several reactions, measurements of these properties are of interest in catalytic research.

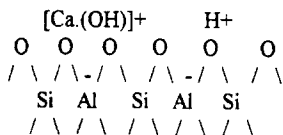
Experimental

Calcium-exchanged NaY zeolite (Ca/NaY) was synthesized by refluxing a NaY zeolite (Si/Al=2.4) with calcium chloride solution, followed by thermal treatment at 693 K under a nitrogen flow [7]. The physicochemical characterization of the NaY and Ca/NaY samples was carried out by analytical methods, such as ICP-AES, FT-IR and XRD patterns. From ICP-AES, the unit cell chemical composition was determined. Structural analysis was determined by Fourier transform infrared spectroscopy, using a Bomem MB-102 instrument. Crystallographic properties of the samples were investigated by X-ray diffraction.

To determine the total acidity, an exchanged sample (0.01 g) previously saturated with *n*-butylamine was transferred to a thermobalance (DuPont 910, TA-2000) and was submitted to the following programmed thermodesorption: isothermal heating at 368 K for 1 h, followed by heating at 15 K min⁻¹ under dry air flowing at 50 ml min⁻¹. The total acidity was defined as the absolute mass of base desorbed from the acid sites of the catalyst, expressed in acid sites per g [8].

Results and discussion

The unit cell chemical compositions of NaY and Ca/NaY are $\text{Na}_{57}(\text{AlO}_2)_{57}(\text{SiO}_2)_{135}$ and $\text{Ca}_{17.9}\text{Na}_{21.2}(\text{AlO}_2)_{57}(\text{SiO}_2)_{135}$, respectively. The FT-IR and XRD data showed that Ca/NaY is crystalline, with a well-defined structure. The infrared spectrum of Ca/NaY revealed the existence of $[\text{Ca}(\text{OH})]^+$ and $[\text{H}---\text{O}-\text{Si}]$ in the zeolite cages after thermal treatment. The structural features can be depicted as:



To study the acid properties of the Ca/NaY zeolite, it was considered that the basic molecule enters the pores of the zeolite to interact with all the acid sites, and the number of acid sites was determined from the amount of base required to reach the saturation point. The decomposition of *n*-butylamine by the medium and strong acid sites was analysed. The results from the TG and DTG curves (Fig. 1) showed that the thermal behaviour of [*n*-butylamine-Ca/NaY] was as follows: (i) desorption of physically adsorbed water and *n*-butylamine below 498 K; (ii) dissociation of the *n*-butylamine from medium acid sites at 516–676 K, and from strong acid sites at 676–955 K. The ammonia and butene products of dissociation of *n*-butylamine would be formed according to Hoffman degradation [9, 10], as shown in Eq. (3). This mechanism has been verified in the decomposition of *n*-butylamine on a silica-alumina catalyst [11].

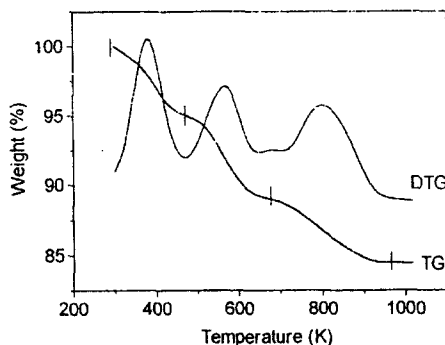


Fig. 1 TG/DTG curves for Ca/NaY zeolite adsorbed with *n*-butylamine, showing weight from the different acid sites

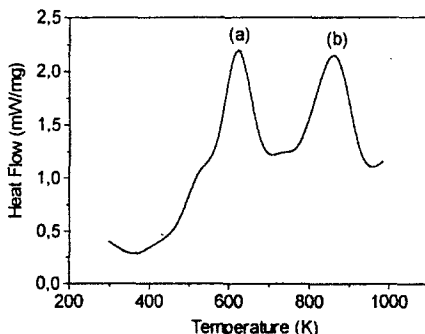
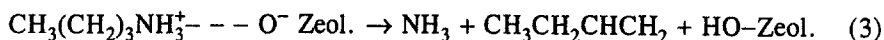
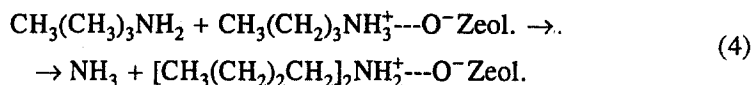


Fig. 2 DSC curve of Ca/NaY zeolite adsorbed with *n*-butylamine, showing exotherms related to: (a) medium and (b) strong acid sites



It is known that primary amines can be converted to diamines over acid catalysts at high temperatures. In the DTG curve, the peak observed in the temperature range 676–955 K was attributed to the reaction between *n*-butylamine and its protonated form, as shown in Eq. (4):



The presence of butene, ammonia and diamine as decomposition products on *n*-butylamine over acid zeolite catalysts was demonstrated by infrared spectroscopy [12], proton nuclear magnetic resonance [13] and mass spectrometry [14]. It was suggested that the formation of diamines should occur in the bulk of the Ca/NaY zeolite. However, for calculation of the total acidity of the catalyst, it was assumed that one molecule of *n*-butylamine adsorbs selectively on one acid site.

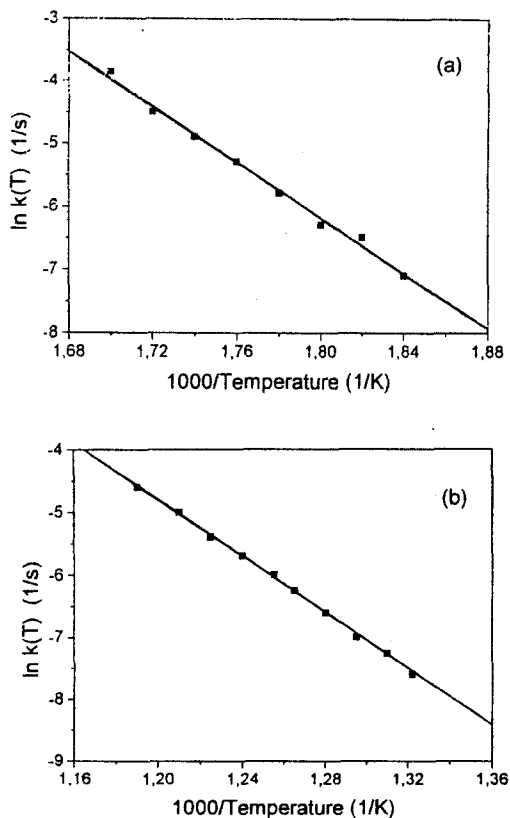


Fig. 3 Arrhenius plots used to determine the activation energy relative to the deamination process from (a) medium and (b) strong acid sites

Table 1 Acid sites density and strength kinetic parameters of the Ca/NaY zeolite

Parameter	Acid sites	
	Medium	Strong
TG-DTG		
Total acidity (acid sites per g) $\times 10^{20}$	7.8	7.0
Temperature range/ $^{\circ}\text{C}$	243–403	403–682
DSC/Borchardt-Daniels kinetic model		
Reaction order	2.8	1.8
Activation energy/ kJ mol^{-1}	195.8	211.0
Heat of reaction/ J g^{-1}	238.2	371.5
Simultaneous TG/DSC		
Acid strength/ $(\text{J per acid site}) \times 10^{-19}$	3.0	5.3

The DSC curve of the Ca/NaY zeolite (Fig. 2) exhibited two exothermic peaks, relating to each acid site strength. The first peak corresponds to the desorption of *n*-butylamine and probable dissociation of the base from the medium acid sites, according to Eq. (3), whereas the second is related to amine decomposition from the strong acid sites. It is suggested that the enthalpies and activation energies relating to each process are directly proportional to the acid site strength in each specific temperature range.

On the basis of the Borchardt-Daniels kinetic model [15], software developed by DuPont was used to determine the kinetic parameters of *n*-butylamine desorption from the Ca/NaY zeolite. In this way, curves were plotted showing the time conversion (min) as a function of the temperature (K), and $\ln k(T)$ as a function of the inverse of the temperature ($1/K$). The time-conversion curves present the desorption and degradation of *n*-butylamine at acid sites of different strengths. The $\ln k(T)$ vs. $1/T$ plot is a straight line, as illustrated in Figs 3(a) and 3(b). The activation energies of the deamination process relating to the two exotherms can be obtained from the slopes of the straight lines, demonstrating that the Borchardt-Daniels kinetic model can be applied for the evaluation of the relative acid strength in solid acids [6]. The total acidity (from TG/DTG) and the kinetic parameters (from DSC) relating to the desorption of *n*-butylamine from the medium and strong acid sites are given in Table 1.

* * *

This work was supported by Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq). The authors are very grateful to M. L. C. Rodrigues and C. I. Braga, from D. P. Instrumentos Científicos.

References

- 1 J. W. Ward, *J. Catal.*, 11 (1968) 259.
- 2 P. A. Jacobs, *Carboniogenic Activity of Zeolites*, Elsevier, Amsterdam 1977, p. 2.

- 3 S. Csicsery, *Zeolites*, 4 (1984) 202.
- 4 R. Carvajal, P. Chu and J. H. Lunsford, *J. Catal.*, 125 (1990) 123.
- 5 T. Morimoto, J. Imai and M. Nagao, *J. Phys. Chem.*, 78 (1974) 704.
- 6 R. Bezman, *J. Catal.*, 68 (1981) 242.
- 7 A. S. Araujo, DSc. Thesis, Universidade de Sao Paulo, Sao Paulo, Brazil 1992.
- 8 A. S. Araujo, V. J. Fernandes Jr., I. Giolito and L. B. Zinner, *Thermochim. Acta*, 223 (1993) 29.
- 9 P. A. Jacobs and Uytterhoeven, *J. Catal.*, 26 (1972) 175.
- 10 L. M. Parker, D. M. Bibby and J. Patterson, *Zeolites*, 4 (1984) 168.
- 11 M. Takahashi, Y. Iwasawa and S. Ogasawara, *J. Catal.*, 45 (1976) 15.
- 12 A. K. Gosh and G. Curthoys, *J. Chem. Soc. Faraday Trans. I*, 80 (1984) 99.
- 13 I. Mochida, A. Yasutake, H. Fujitsu and K. Takeshita, *J. Catal.*, 82 (1983) 313.
- 14 L. M. Parker, D. M. Bibby and R. H. Meinhold, *Zeolites*, 5 (1985) 384.
- 15 H. Borchardt and F. Daniels, *J. Amer. Chem. Soc.*, 79 (1965) 41.