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Evaluation of the relative acid strength of cerium and calcium exchanged Y zeolite by TG and DSC

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Abstract

The relative acid strength of cerium and calcium Y zeolite was evaluated by thermogravimetry (TG) and differential scanning calorimetry (DSC) methods, using *n*-butylamine as a molecular probe. The total acidity was calculated from TG curves whereas the relative acid strength given in J per acid site was determined by the DSC curves, using the Borchardt–Daniels kinetic model. The enthalpies of these processes are proportional to the acid-site strength in each specific temperature range.

INTRODUCTION

Zeolites are crystalline aluminosilicates containing alkaline and alkaline earth metal elements. Structurally, they comprise a three-dimensional network of SiO_4 and AlO_4 tetrahedra linked together through common oxygen atoms [1]. The isomorphic substitution of Si by Al results in a negative charge density in the zeolite lattice. The neutralization of this charge is achieved by the introduction of exchanged di- or trivalent cations in the structural sites of the zeolite. This is of a great importance in the generation of protonic acidity.

A solid acid is capable of converting an adsorbed basic molecule into its conjugated acid form. The acid site is able to transfer a proton from the solid to the adsorbed molecule (Brønsted acid site) or an electron pair from the adsorbed molecule to the solid surface (Lewis acid site). Dehydrated zeolites can exhibit Brönsted and Lewis acid active sites, depending on the ion exchange and thermal treatment conditions [2, 3].

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The protonation of a zeolite through polyvalent ion exchange occurs according to the equation [4]

$$M^{n+}(H_2O)_{(n-1)} \xrightarrow{T_1} M(OH)^{+}_{(n-1)} + (n-1)H^{+} \xrightarrow{T_2}$$

$$M(OH)^{2+}_{(n-2)} + (n-2)H^{+} + H_2O \qquad (T_2 < T_1)$$

The protons react with the oxygen lattice of the zeolite giving rise to very strong acid sites.

The description of the acid properties of a solid with a reactively high surface area must involve the determination of the acid density, the strength and the nature of the sites.

The adsorption of weak bases has been used extensively for the determination of zeolite acid sites, with the adsorbed base being studied by non-linear and linear thermo-programmed desorption (TPD) [5–7].

The aim of this work is to evaluate the acid properties (density and strength) of Ce,Ca-exchanged NaY zeolite by TG and DSC techniques using *n*-butylamine as the molecular probe. The acid strength kinetic parameters are determined by the Borchardt and Daniels kinetic model [8].

EXPERIMENTAL

Cerium and calcium exchanged NaY zeolite, $(Ce,Ca)^{ex}NaY$, was synthesized by refluxing NaY zeolite (SAR = 2.4) with calcium chloride and cerium chloride solutions, followed by thermal treatment at 693 K under nitrogen flow.

The chemical composition of the sample was determined by atomic emission spectroscopy. Structural analysis was carried out by infrared spectroscopy, using an FT-IR Bomem MB-102 instrument. The crystallinity was determined by X-ray diffraction patterns.

The acidity of the $(Ce,Ca)^{ex}NaY$ zeolite was evaluated as follows. The sample (0.01 g) previously saturated with *n*-butylamine, was transferred to a thermobalance (Du Pont 910, TA-2000), and submitted to the following programmed thermodesorption: an isothermal heating at 368 K for one hour, then 15 K min^{-1} heating under dry air flowing at 50 ml min^{-1}. The total acidity was defined as the absolute mass of *n*-butylamine desorbed from the acid sites of the catalyst, being expressed in acid sites per g.

The estimate of the relative acid strength by DSC, using the Borchardt and Daniels kinetic model, was made by monitoring the thermal decomposition of *n*-butylamine in three specific temperature ranges. These decompositions are exothermic and were used for the calculation of the kinetic parameters involved in the process, including the activation energy, reaction order and heat of reaction.

RESULTS AND DISCUSSION

The unit cell chemical composition of the (Ce,Ca)^{ex}NaY zeolite was $Ce_{12.3}Ca_{6.0}Na_{8.1}(AlO_2)_{57}(SiO_2)_{135}$, with about 65% cerium exchanged and the silicon:aluminum ratio being 2.4.

Infrared spectroscopy and X-ray diffraction measurements showed that the (Ce,Ca)^{ex}NaY zeolite is crystalline, with a well-defined structure. The IR spectra also revealed the existence of [$CeOH^{2+}$] and [H · · · O–Si] in the zeolite cages after thermal treatment [9].

The TG and DTG curves of the (Ce,Ca)^{ex}NaY zeolite are shown in Fig. 1. One can see that there are five peaks in the DTG curve and corresponding weight loss steps in the TG curve. The peaks were assigned as peaks 1 and 2, 368–539 K, desorption of physisorbed water and *n*-butylamine from weak acid sites, respectively; peak 3, 539–700 K, dissociation of *n*-butylamine to ammonia and butene from medium acid sites; peaks 4 and 5, 700–971 K, degradation of diamines from strong acid sites in the supercage and sodalite cages, respectively.

The possibility of *n*-butylamine decomposition by the medium and strong acid sites is now considered. The products would be formed according to the Hoffmann degradation [10, 11]

$$CH_3CH_2CH_2CH_2NH_3^+ \cdots \bar{O}Zeol \rightarrow$$

$$NH_3 + CH_3CH_2CH_2CH{=}CH_2 + HOZeol$$

This mechanism has been verified in the decomposition of *n*-butylamine

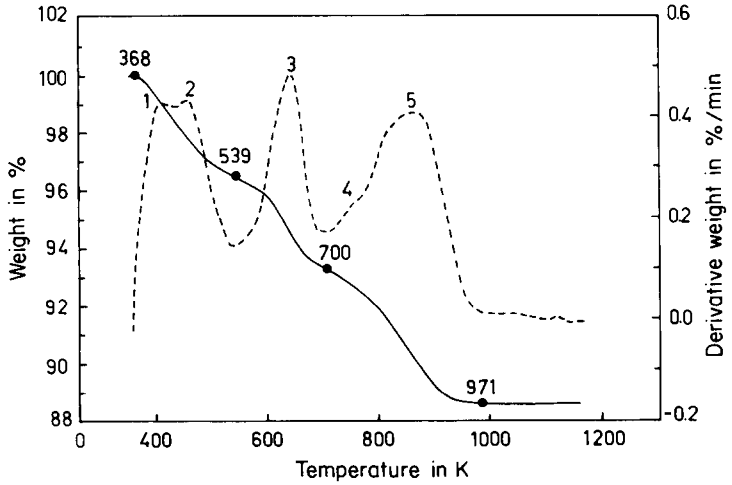

Fig. 1. TG/DTG curves for (Ce,Ca)^{ex}NaY zeolite adsorbed with *n*-butylamine, showing weight losses from the different acid sites.

over silica–alumina catalyst [12]. It is known that primary amines can be convered to diamines over acid catalysts at high temperatures. In the DTG curve, the peak observed in the 700–971 K temperature range was attributed to the reaction between *n*-butylamine and the protonated amine

$$CH_3CH_2CH_2CH_2NH_2 + CH_3CH_2CH_2CH_2NH_3^+ \cdots \bar{O}Zeol \rightarrow$$
$$NH_3 + (CH_3CH_2CH_2CH_2)_2NH_2^+ \cdots \bar{O}Zeol$$

The formation of butene, ammonia and diamine over acid zeolites has been demonstrated by other authors using NMR [13], infrared spectroscopy [14] and mass spectrometry [15, 16]. Thus, it was suggested that the formation of diamines should occur in the bulk of the $(Ce,Ca)^{ex}NaY$ zeolite. From the calculations of the total acidity of the catalyst, it is assumed that one molecule of *n*-butylamine adsorbs selectively on one acid site.

The DSC curve of the $(Ce,Ca)^{ex}NaY$ zeolite showing the isotherms relative to acid site distribution is illustrated in Fig. 2. There are three exotherms, corresponding to the desorption and thermal decomposition of *n*-butylamine in the weak, medium and strong acid sites, respectively. It is suggested that the enthalpies and activation energies relative to each process are directly proportional to the acid site strength in each specific temperature range.

From the application of the Borchardt and Daniels kinetic model programs, 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 curves of time conversion show the desorption and degradation of *n*-butylamine in the acid sites of different strength. The

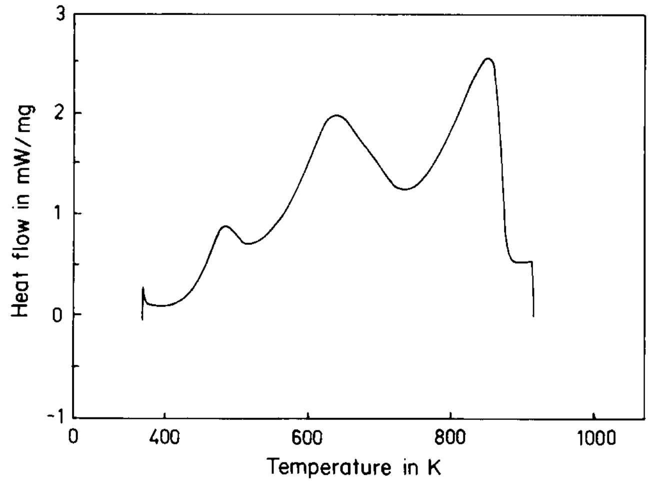

Fig. 2. DSC curve of $(Ce,Ca)^{ex}NaY$ zeolite adsorbed with *n*-butylamine, showing exotherms relative to different acid site strengths.

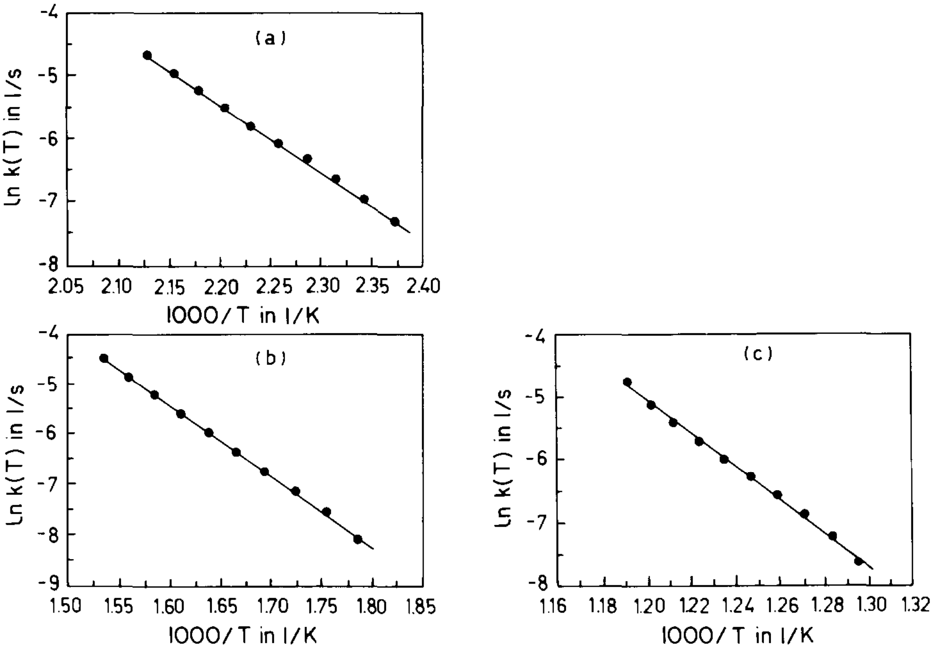

Fig. 3. Arrhenius plots used to obtain the activation energy relative to the deamination process from (a) weak, (b) medium and (c) strong acid sites in the (Ce,Ca)^{ex}NaY zeolite.

$\ln k(T)$ versus $1/T$ plot results in straight lines, as seen in Fig. 3 (a) weak, (b) medium and (c) strong acid sites. The activation energies of the deamination processes referring to the three exotherms can be obtained from the slope of the straight lines, demonstrating that the Borchardt–

TABLE 1

Total acidity and acid strength kinetic parameters of the (Ce,Ca)^{ex}NaY zeolite

	Acid sites		
	Weak	Medium	Strong
TG/DTG			
Total acidity/(acid sites per g) × 10^{20}	3.7	4.3	5.7
Temperature range/K	368–539	539–700	700–971
DSC/Borchardt–Daniels kinetic model			
Reaction order	0.9	2.1	1.3
Activation energy/kJ mol^{-1}	89.9	118.0	221.8
$\log Z/\mathrm{min}^{-1}$	9.7	9.3	13.5
Heat of reaction/J g^{-1}	72.9	378.0	464.0
TG/DSC			
Acid strength/(J per acid site) × 10^{-19}	2.0	8.9	8.2

Daniels kinetic model can be applied satisfactorily for the evaluation of the relative acid site strength in solid acids. The kinetic parameters related to desorption of *n*-butylamine from the acid sites in the exchanged zeolite are summarized in Table 1.

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