

The acidity of dealuminated clinoptilolite investigated by DSC, DTA and TG methods

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Abstract

Dealuminated NH_4^+ -clinoptilolite samples, prepared using $(\text{NH}_4)_2\text{SiF}_6$ and calcined at various temperatures, were used for the investigation of acidity properties. The strength of the acid sites was measured by a combination of TG and DSC measurements. It was found that the dealumination process starts preferentially at the weak acid sites. The intensive removal of aluminium from the strong acid sites started at the highest extent of dealumination.

INTRODUCTION

In 1978 Breck investigated zeolite dealumination using an aqueous solution of ammonium hexafluorosilicate [1]. The acid sites in the structure of zeolite have been investigated by many authors, using various methods: for example, Aboul-Gheit used differential scanning calorimetry (DSC) for the investigation of the acid-site strength distribution in zeolites [2]. He investigated the adsorption of triethylamine and ammonia on monoionic Na- and H-mordenite. Temperature-programmed desorption (TPD) was performed by DSC. These types of basic adsorbates were used to indicate the adsorption potential from the effective pore size diameter and the acid-site strength of the adsorbents. DSC can provide ΔH values for desorption, which are proportional to the number of acid sites. Activation energy values of desorption have been taken as a numerical criterion for comparing acidity strengths [2].

Karge et al. [3] have determined the acidity of dealuminated hydrogen forms of mordenites and Y-zeolites by TPD of ammonia and pyridine, the desorption of which was monitored using mass spectrometry. Four types of acid site were indicated using ammonia: weak Brønsted and/or Lewis

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centres, medium Brönsted, strong Brönsted and strong Lewis acid sites. However, pyridine indicated only medium and strong Brönsted acid sites. It was suggested that the estimated difference occurred due to the different accessibility of the sites for the individual probe molecules.

Kojima et al. [4] investigated various ammonium–sodium exchange levels in synthetic mordenite, measuring the changes in the number and strength of the acid sites by TPD of pyridine. The number of acid sites increased with increasing NH_4^+ exchange level.

The acidity of zeolite Beta [5] has been characterized by TPD of ammonia and of other bases of various kinetic diameters and basicity strengths. TPD analysis was carried out using simultaneous TG/DTA analysis. Four distinct zones of exothermal weight loss were distinguished.

The acidity of NH_4^+ -ZSM-5, H-mordenite, NH_4^+ -Y and NH_4^+ -LZ-105 zeolites was investigated using NH_3 -TPD [6]. A Sartorius electronic microbalance was used for the TPD studies. The peak temperature was related to the activation energy of decomposition and the peak area was related to the number of acid sites.

Ammonium-exchanged forms of synthetic zeolites [7] have been analysed using DSC. The samples were heat treated in static air at 350, 400, 450, 500 and 550°C, and then studied by DSC. Three exothermal peaks, with maxima at 150, 225 and 560°C, indicated that the NH_4^+ ions were bonded in the structure of Zeolon 400 in different modes of varying strengths.

The aim of the present work was to investigate the dealumination of dealuminated NH_4^+ -clinoptilolite samples prepared under various conditions in order to compare the NH_4^+ bonding in the clinoptilolite structure, related to the different acid sites, using DSC and TG.

EXPERIMENTAL

Materials

Natural clinoptilolite from Nižný Hrabovec (eastern Slovakia) was used as a starting material. The clinoptilolite content (70 ± 5 mass%) was determined by X-ray diffraction (XRD), as previously described [8]. A similar method was used in the evaluation of the loss in crystallinity during the dealumination process. The NH_4^+ forms of clinoptilolite were prepared by treatment with 3 M NH_4Cl , using the standard cation exchange method. Dealumination was carried out in 2.5 M $\text{CH}_3\text{COONH}_4$, buffered to pH 6 using a 0.75 M aqueous solution of ammonia hexafluorosilicate, at a constant $\text{SiF}_6^{2-}/\text{NH}_4^+$ -clinoptilolite ratio of 0.3 and at 95°C [1]. Dealuminated samples were washed with boiling water and dried at ambient temperature.

The characterizations of the natural and dealuminated samples of clinoptilolite are given in Table 1. The composition was determined by the method of Barrer et al. [9].

TABLE 1

Characterization of samples of clinoptilolite before and after dealumination

Sample	τ^a (h)	Composition [9]	Crystallinity ^b (%)	Si/Al
D	0	$\text{Ca}_{2.0}\text{Mg}_{0.1}\text{Na}_{0.6}\text{K}_{1.9}\text{Al}_{6.7}\text{Si}_{29.3}\text{O}_{72}$	70 ± 5.0	4.37
D ₀	0	$(\text{NH}_4)_{6.7}\text{Al}_{6.7}\text{Si}_{29.3}\text{O}_{72}$	100	4.37
D ₁	1	$(\text{NH}_4)_{6.03}\text{Al}_{6.03}\text{Si}_{29.97}\text{O}_{72}$	94 ± 4.5	4.97
D ₃	3	$(\text{NH}_4)_{5.27}\text{Al}_{5.27}\text{Si}_{30.73}\text{O}_{72}$	78 ± 5.1	5.83
D ₆	6	$(\text{NH}_4)_{4.21}\text{Al}_{4.21}\text{Si}_{31.79}\text{O}_{72}$	48 ± 5.5	7.55

^a Time of dealumination.^b According to ref. 1.

Thermal deammoniation

Dealuminated NH_4^+ -clinoptilolite samples were treated at 150, 250, 350, 400, 450, 500 and 550°C, respectively, in the electric oven under static air for 5 h. The samples were then put in the desiccator above P_2O_5 , cooled to room temperature and studied by TG, DTA and DSC.

Methods

A Philips diffractometer (PW 1050) with Ni-filtered Cu $K\alpha$ radiation, at 30 kV and 40 mA was used. Before XRD measurement, the samples were equilibrated in a desiccator at 35% relative humidity for 5 h.

A Du-Pont 990 thermal analyser and 990 DSC cell were used for the DSC measurements. Samples (10 mg) were measured in static air in the temperature range 30–720°C and at a heating rate of 10 K min⁻¹.

A Q-1500 derivatograph (MOM, Budapest) was used for the DTA, TG and DTG measurements. Samples were investigated under static air in the temperature range 20–750°C, at a heating rate of 10 K min⁻¹.

RESULTS AND DISCUSSION

The extent of the NH_4^+ exchange in NH_4^+ -clinoptilolite was analysed using two methods.

(1) The experimental values of cation exchange capacity (CEC) were measured by the method of Hudec et al. [10] (see Table 2).

(2) The results of the CEC determination were calculated from the mass losses of the dealuminated NH_4^+ -clinoptilolite samples, investigated by TG measurements in the temperature region 230–500°C (exothermal part of the DTA curve) (see Table 2).

The results in Table 2 demonstrate that the exchange of the original cations for NH_4^+ , taking into account the accuracy of the CEC determination, is complete.

TABLE 2

Theoretical and experimental CEC values (mmol g^{-1}) of clinoptilolite samples

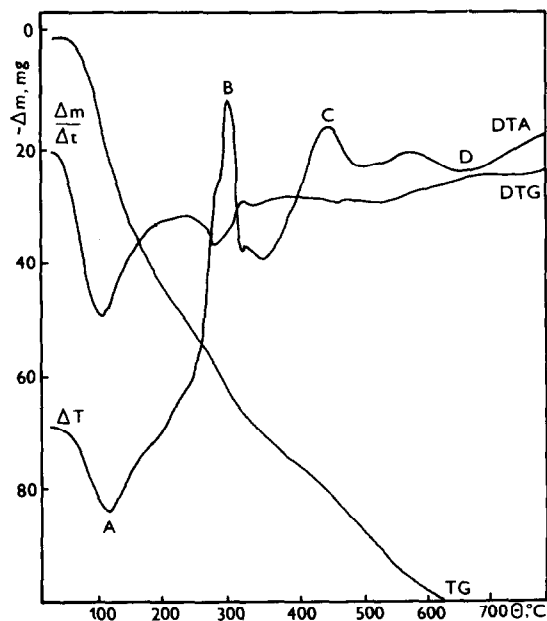
Sample	CEC _{theor} ^a	CEC _{theor} ^b	CEC _{exp} [10]	CEC _{exp,TG}
D ₀	2.45	1.76	1.63	1.69
D ₁	2.21	1.59	1.40	1.42
D ₃	1.80	1.29	1.17	1.19
D ₆	1.57	1.13	1.02	0.92

^a Theoretical CEC, calculated from the crystallochemical formulae.^b Theoretical CEC, recalculated for the 70 mass% of clinoptilolite content.

Typical DTA, TG and DTG thermograms of NH_4^+ -clinoptilolite samples that have not been thermally treated are shown in Fig. 1; the DTA curve can clearly be divided into exothermal and endothermal regions. The individual temperature regions in the DTA curve correspond to the various types of NH_4^+ -clinoptilolite reactions. In the temperature region A (20–230°C), desorption of zeolitic water is assumed to occur according to the scheme



The endothermal DTA region, in the range of 80–230°C, corresponds to an intensive mass loss (Fig. 1).

Fig. 1. DTA, TG and DTA curves of NH_4^+ -clinoptilolite with no thermal treatment.

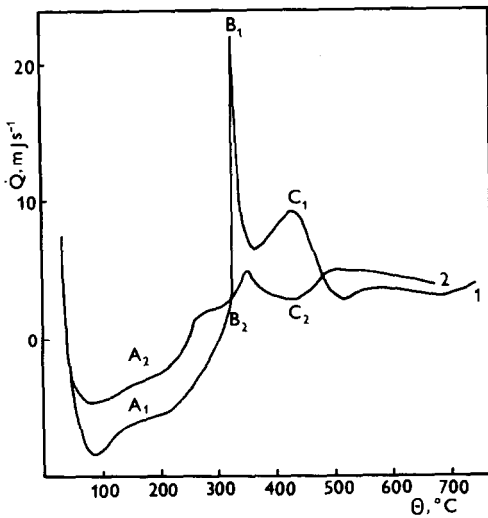
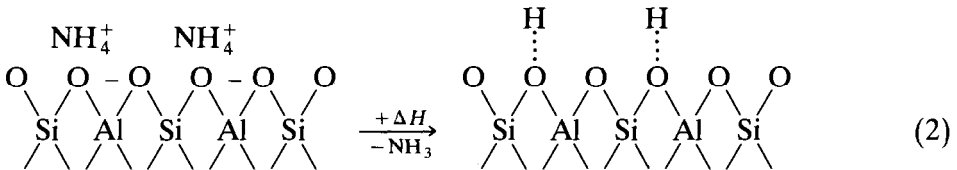


Fig. 2. DSC thermograms of NH_4^+ -clinoptilolite with no thermal treatment: curve 1, in static air; curve 2, in N_2 .

The exothermal region in the DTA (Fig. 1) and/or DSC curves (Fig. 2) can be divided into two exothermal parts, B and C. Peak B represents the desorption and oxidation of ammonia in the temperature interval 230–350°C, according to the following scheme



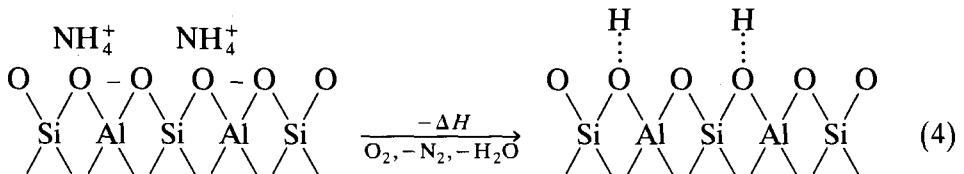
and



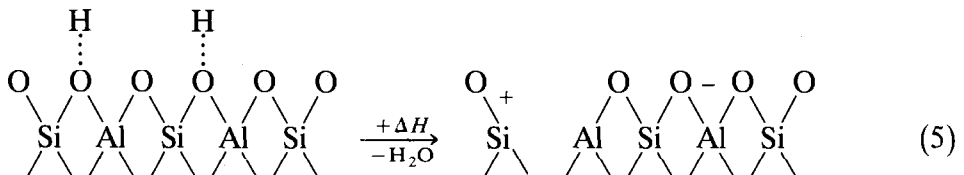
It is assumed that this process corresponds to the decomposition of the weakly bonded NH_4^+ ions in the clinoptilolite structure (peaks B, B_1 and B_2 in Figs. 1 and 2 respectively). Weak Brönsted acid sites are formed from NH_4^+ -clinoptilolite as a precursor, according to reaction (2). Two steps in the reaction of the weakly bonded NH_4^+ have been determined using DSC measurements (Fig. 2). The DSC thermograms of NH_4^+ -clinoptilolite, measured in N_2 , displayed three endothermic peaks (Fig. 2). The peak temperature corresponding to the weakly bonded NH_4^+ (B_2) was shifted to a lower temperature, compared to the peak B_1 (Fig. 2). Obviously some NH_3 is desorbed (reaction (2)) before the oxidation reaction has started. It is evident that the oxidation of the weakly bonded NH_3 occurs in a narrow temperature range (Fig. 1). This may be connected with a small diffusion

barrier for NH_3 release during this reaction. Accordingly, the location of weak acid sites may be considered to be close to the crystal surface.

The second exothermal region (peaks C and C_1 in Figs. 1 and 2, respectively) beginning at 340–350°C represents the decomposition of the strongly bonded NH_4^+ (the strong Brönsted acid site precursors) in the clinoptilolite structure. The broad temperature range of the exothermal region C can be explained by a diffusion-controlled oxidation of NH_4^+ or by a broad dispersion of stability of NH_4^+ bonds in the clinoptilolite structure. In the case of the diffusion-controlled reaction, peak C corresponds to the intraporous acid sites. No significant shift of peak temperatures was found between the DSC measurements in static air and in N_2 . Therefore, a two-step reaction as shown in reactions (2) and (3) was not confirmed, and the decomposition could be described by the scheme



The weak endothermal peak D, with peak temperature 620–640°C, was found in the temperature range 560–730°C. This represents a dehydroxylation reaction with the formation of Lewis acid sites according to the scheme



In the same way, the corresponding regions on the TG curves were evaluated from the mass losses corresponding to the individual exothermal reactions. Accordingly, the mass losses of ammonia from weak and strong acid sites can be determined. The mass loss data for the first exothermal region B are shown in Fig. 3 with respect to the calcination temperature. The mass loss maxima of region B coincide with the calcination temperature range 250–350°C. This region corresponds approximately to the exothermal peak B in the DTA curve, reflecting the reactions (2) and (3).

The curves in Fig. 4 represent the mass losses for the second exothermal region C. The mass loss maxima of this region coincide with the calcination temperatures 350–500°C. The shape of the curves in Fig. 3 (broad temperature region of mass loss maxima) can be explained by diffusion control of the exothermal reaction. TG data for the weak and strong Brönsted acid sites are given in Table 3.

It was found that the mass losses corresponding to both the strong and weak acid sites decrease when the extent of dealumination increases. From

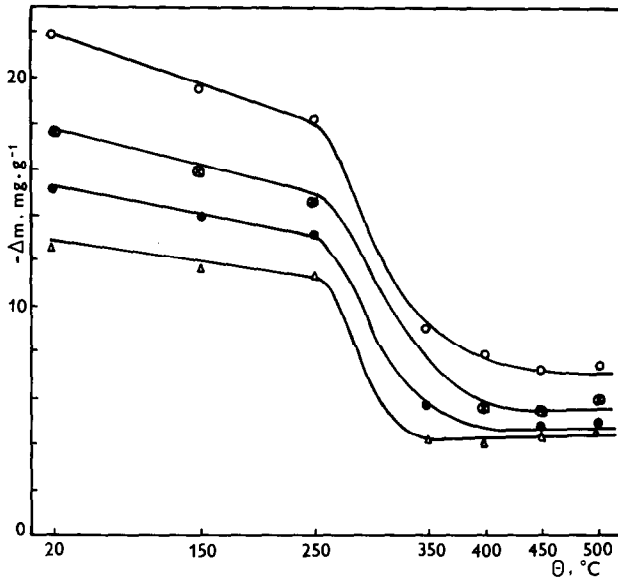


Fig. 3. Dependence of the mass losses corresponding to the decomposition of the weak NH_4^+ -clinoptilolite bonds, on the calcination temperatures: \circ , D_0 ; \otimes , D_1 ; \bullet , D_3 ; \triangle , D_6 .

the values in Table 3, it can be suggested that the dealumination process starts preferentially at the weak acid sites and at the surface layers of the clinoptilolite crystals. The mass losses connected with the strong acid site formation do not decrease so markedly with the extent of dealumination.

The DSC thermograms of calcined samples are shown in Fig. 5. Exothermal DSC peaks provide information on the reaction heats of NH_4^+ -clino-

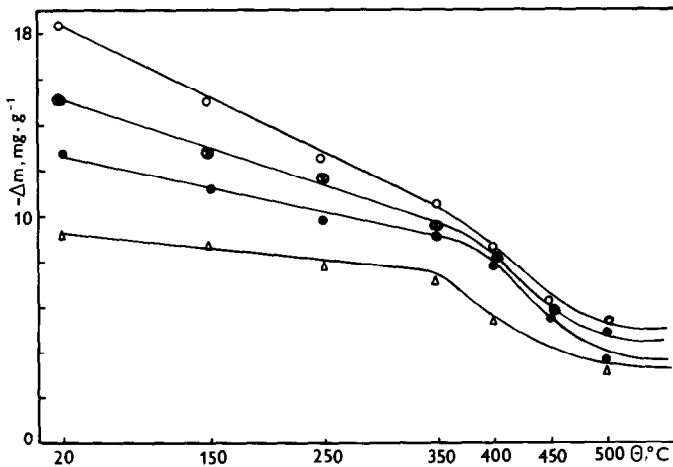


Fig. 4. Dependence of the mass losses corresponding to the decomposition of the strong NH_4^+ -clinoptilolite bonds on the calcination temperatures: \circ , D_0 ; \otimes , D_1 ; \bullet , D_3 ; \triangle , D_6 .

TABLE 3

Mass losses, corresponding to the individual exothermal reactions of NH_4^+ -clinoptilolite

Sample	Mass loss corresponding to	
	Weak sites (mg g^{-1})	Strong sites (mg g^{-1})
D_0	12.0	5.0
D_1	9.5	4.9
D_3	8.5	4.8
D_6	6.5	4.0

ptilolite decomposition (ΔH) which represent a value (Table 4) given by the superposition of (1) the exothermal reaction of NH_3 oxidation (reaction (3) and reaction (4)), (2) the endothermal decomposition of NH_4^+ -zeolite bonds (reaction (2)), and (3) the endothermal desorption of gases from the structure.

From a comparison of the thermoanalytical curves shown in Fig. 5, it can be concluded that the exothermal peak B (Fig. 2) disappears when the

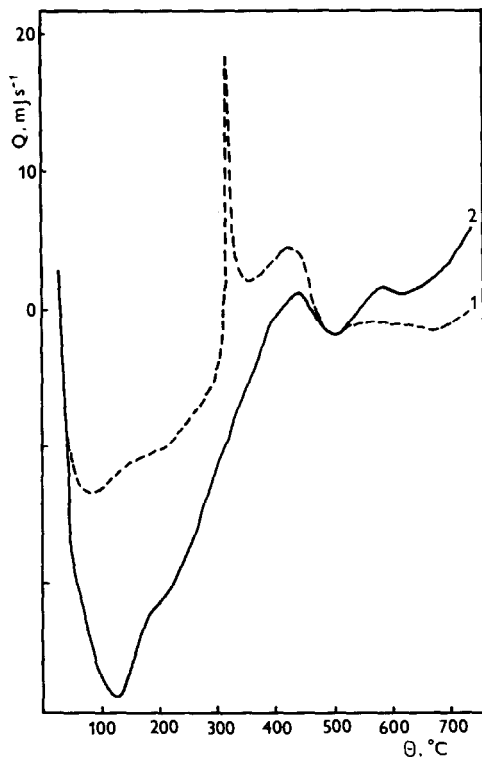


Fig. 5. DSC thermograms of the sample D_0 after calcination at 250°C (curve 1) and 350°C (curve 2).

TABLE 4

Reaction heats $-\Delta H$ (J g⁻¹) of the calcinated NH₄⁺-clinoptilolite samples

Sample	Reaction heat $-\Delta H$ of samples calcined at		
	150°C	250°C	350°C
D ₀	51.8	50.7	10.4
D ₁	41.0	37.5	7.8
D ₃	30.4	26.7	3.9
D ₆	21.5	18.3	1.2

samples are heated at 350°C, i.e. experimental ΔH values measured after calcination at 250°C may be considered as the enthalpies of decomposition of both the weakly and the strongly bonded NH₄⁺. The ΔH values for the samples calcined at 350°C represent the enthalpies of decomposition of the strongly bonded NH₄⁺.

It was found that both B and C peak areas decrease with increasing dealumination. Two energetic types of NH₄⁺ bond in NH₄⁺-clinoptilolite samples are revealed by the TG and DSC measurements. The dealuminated NH₄⁺-clinoptilolite samples exhibited a more significant decrease of the weak acid sites than of the strong ones. Consequently, the relative number of strong acid sites increases in the dealuminated samples.

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