MASS SPECTRAL STUDIES ON THE THERMAL DESORPTION OF ALIPHATIC AMINES FROM THE SURFACE OF Y-TYPE ZEOLITES *

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(Received 25 August 1987)

ABSTRACT

Thermogravimetric and thermal desorption mass spectroscopic studies of some amines from the surface of NaY, CaY and HY zeolites are reported. The amines studied include, n-propylamine, isopropylamine and n-butylamine. Mass spectral data show that the amines decompose on the zeolitic surface to give rise to various reactions on the zeolite surface typical of those on an acid catalyst. From the ease with which aliphatic amines are decomposed even on residual acid sites of NaY, it is concluded that the characterisation of the surface acidity of zeolites by thermal methods should be accompanied by a simultaneous identification of the desorbed species.

INTRODUCTION

The important industrial applications [1] of zeolites are in hydrocarbon transformations, namely, catalytic cracking, hydro-isomerisation, selective forming, hydrocracking and transformation of aromatic hydrocarbon. Catalytically active sites in zeolites may involve separate phases, e.g. metals, oxides, complexes and other occluded species or countervalent ions. However, the majority of the applications make use of the acidity in zeolites. It is, therefore, important to determine the nature, number, strength and distribution of acid sites in order to evaluate, as well as to understand, the catalytic activity of zeolites. A variety of techniques [2] including base titration using Hammett indicators, thermometric titrations, temperature programmed desorption of bases, nuclear magnetic resonance (NMR) spectroscopy and infrared (IR) spectroscopy have been employed for characterisation of acid sites. Differential thermal analysis in combination with thermogravimetry, hitherto less used, is shown [3] to be a useful method for acidity determination in solids. Ghosh and Curthoys [4], employing this

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* IPCL communication No. 118
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technique with n-butylamine and ammonia as bases, have characterised the acidity in mordenite. In this work, we have attempted to characterise the acidity of Y-type zeolites, employing n-propylamine, isopropylamine and n-butylamine as basic probes. In their studies, Ghosh and Curthoys [4] remarked that n-butylamine was decomposed on the mordenite surface into butene and ammonia at elevated temperature (678 K). In order to investigate the possibility of such reactions on Y-type zeolites we have also carried out temperature programmed desorption employing mass spectrometry as a means of identifying transient or reaction products.

EXPERIMENTAL

Y zeolite (SK-40) powder was obtained from Union Carbide Co. Calcium exchanged Y was prepared by refluxing this powder with 10% calcium chloride solution for 8 h. The HY form was obtained by first preparing the ammonium form by refluxing with 10% ammonium chloride solution and then calcinating NH_4Y at 723 K for 4–5 h. The extent of exchange in each case was determined from atomic absorption spectroscopic analysis of the material. The percentage exchange values are 74 and 62 for HY and CaY, respectively. Zeolite samples were activated at 623 K for 3 h under constant evacuation and were cooled to ambient temperature under vacuum. These were then exposed to amine vapours which had previously been freeze dried and allowed to saturate. A small amount of this sample was quickly transferred to a Cahn balance. Temperature programmed desorption was carried out with TGA system 113 of Cahn Instruments Inc. Temperature programming was carried out with a microprocessor Micricon 823. Temperature was controlled with the help of a split shell furnace and a K thermocouple was used as a probe. Samples were heated under nitrogen atmosphere (50 cm^3 min^{-1}) which was dried by passing through a molecular sieve 13X column and anhydrous calcium chloride.

Mass spectral studies were carried out by GC–MS (Hewlett Packard model 5985 B). Zeolite samples were packed in a column (a stainless steel tube 6.2 mm in diameter). This column was connected in the HP 5840 GC oven. The outlet of this column was joined to a stainless steel tube of 3.1 mm diameter and this was connected to a mass detector through a transfer line heated at 523 K. Helium gas (30 cm^3 min^{-1}) was continuously purged through the system. Heating was carried out from 303 K to 623 K at a rate of 10 K min^{-1}. Amine samples (2–3 μl) were injected into the column and heating was started. Mass spectra of the desorbing products at different temperatures were recorded. For selected ion monitoring, the following conditions were maintained: scanning of mass, 30 a.m.u. s^{-1} scan time, 1.2 s; EMV 2000 V; mass range, 40–300. n-Butylamine, n-propylamine and isopropylamine of high grade quality were obtained from Fluka and E-Merck.

RESULTS AND DISCUSSION

From the thermogravimetric data the number of millimoles of base per gram of zeolite were calculated and are given in Table 1. The available literature values [5–7] are given in parentheses. These values have been corrected for the physisorbed amount of amines by subtracting the amount of amine desorbed up to the boiling point of the amine. Our values show reasonably good agreement with those in the literature. We see from these data that the amount of amine adsorbed follows a trend: n-propylamine > isopropylamine > n-butylamine. Figures 1–3 show differential thermo-gravimetry (DTG) curves for desorption profiles on NaY, CaY and HY zeolites. The desorption profiles on NaY consist of broad bands in the initial stages up to 500 K and then gradually approach zero. On HY, however, there are sharper bands in the inital stages and desorption does not reach completion even at 673 K. One would normally associate these trends with the cation distribution and acidity of HY, CaY and NaY. The larger number of cations available on NaY gives rise to broader bands than those of HY and CaY. However, the higher acidity of HY and CaY results in slower desorption of the amines at higher temperatures.

Thermal desorption mass-spectral profiles provide a better picture of the influence of the zeolite acidity and the basicity of the molecules on the behaviour of the amines on the surface. Figures 4–6 show these profiles for n-propylamine and n-butylamine on HY, CaY and NaY. The Y axis in these graphs gives the total ion count which, in practice, represents the cumulative desorption of molecules having a mass higher than 50. As expected from the well-known acidic behaviour of ion-exchanged Y zeolites, it is seen that the temperature at which amines are desorbed depends on the cations present. For the two amines, the marginal difference in the basicity of the two molecules is seen to influence considerably their desorption profiles. On the relatively non-acidic NaY surface, desorption sharply decreases as the

TABLE 1

Number of millimoles of amine per gram of zeolite

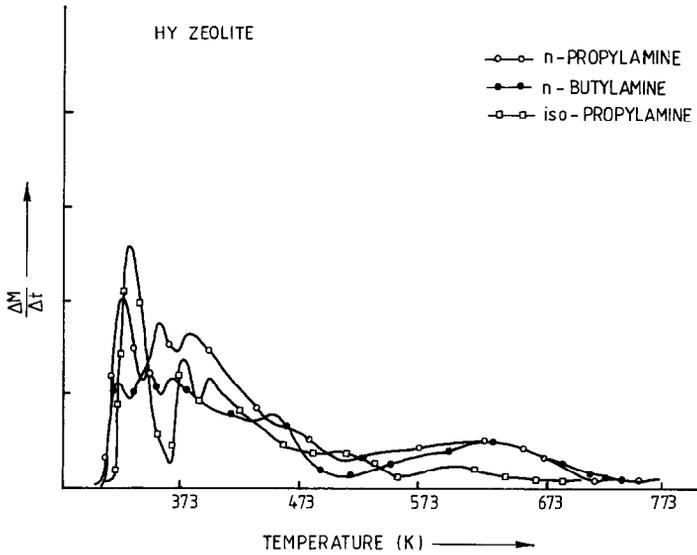| Zeolite	n-Butylamine	n-Propylamine	i-Propylamine
HY	2.0 (2.7 [a], 2.10 [b], 2.6 [b])	3.9	3.7
NaY	3.2	4.6	4.1
CaY	2.3 (1.9 [a], 2.7 [c])	3.1	3.2

[a] Ref. 5.
[b] Ref. 6.
[c] Ref. 7.

Fig. 1. Differential thermogravimetric curve for the desorption of amines from HY zeolite.

temperature is raised to above 600 K. On the HY zeolite surface the trend shows that the molecules are released only gradually.

Figures 7–9 give the fragmentation patterns of the molecules desorbing from HY, CaY and NaY zeolite surfaces at different temperatures. This gives an idea of the type of interactions occurring on the surface of the three
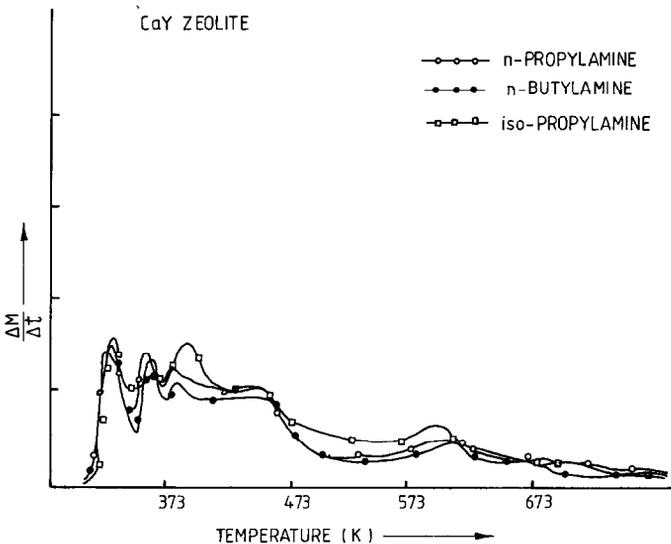

Fig. 2. Differential thermogravimetric curve for the desorption of amines from CaY zeolite.
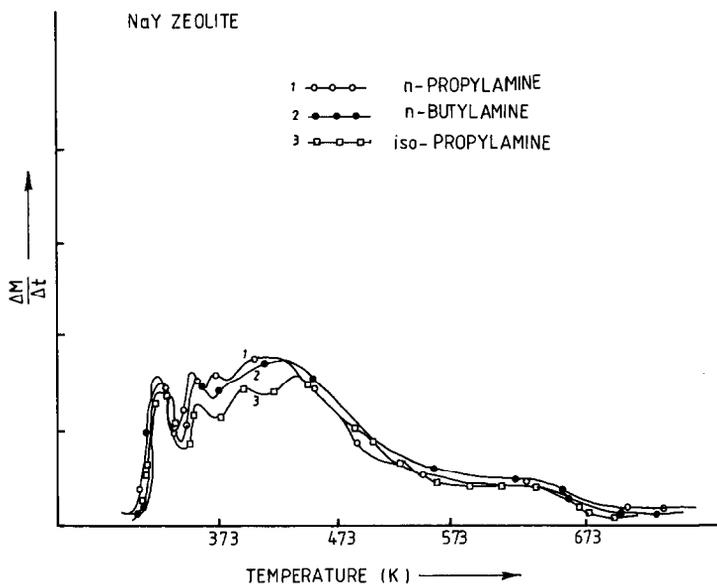
Fig. 3. Differential thermogravimetric curve for the desorption of amines from NaY zeolite.

zeolites. The desorption product of NaY is predominantly butylamine ($m/e = 73$), but in the case of HY the major fraction consists of butene ($m/e = 56$), higher olefins ($m/e = 184$), dienes ($m/e = 110$) and aromatics ($m/e = 91$). The products desorbing from CaY are similar to those of HY.

The progress of the different reactions taking place on the surface is shown more vividly by the desorption profiles obtained through the selected
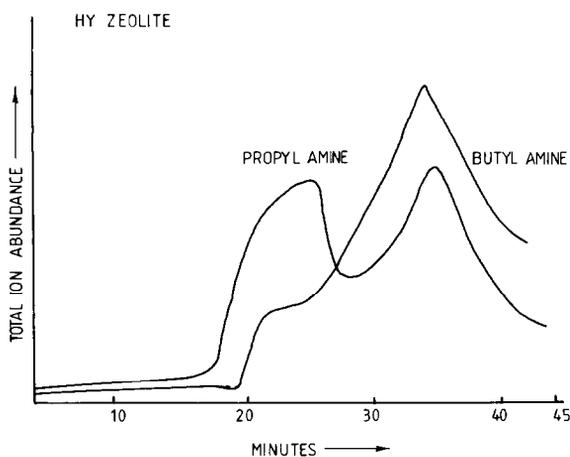
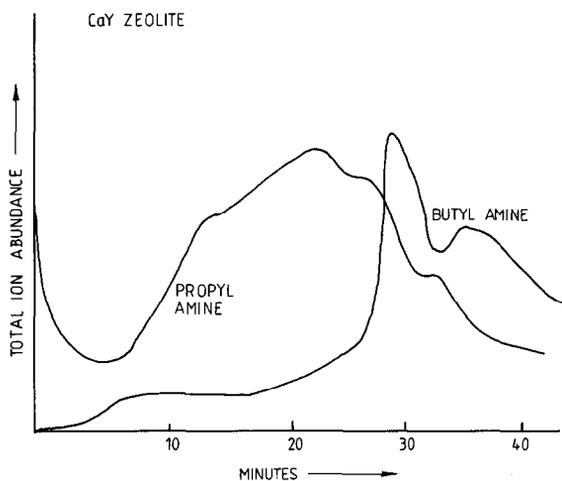Fig. 4. Thermal desorption mass spectra of n-propylamine and n-butylamine from the surface of HY zeolite.

Fig. 5. Thermal desorption mass spectra of n-propylamine and n-butylamine from the surface of CaY zeolite.

ion monitoring (SIM) programme of the computer (Figs. 10–12). In these figures, the desorption of the unconverted butylamine ($m/e = 73$), butene ($m/e = 56$), paraffins as a class ($m/e = 57$) and aromatics as a class ($m/e = 91$) together with the total ion profile are shown during the butylamine desorption experiment from HY, CaY and NaY surfaces. The presence of the dimerised butene ($m/e = 112$) is also indicated. On NaY (Fig. 12) the main molecule desorbing is seen to be n-butylamine, with traces of aromatics and C_8 olefin desorbing at higher temperatures. In contrast, on HY and even
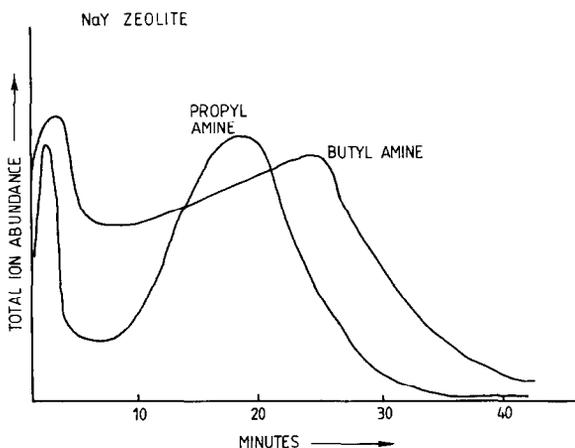

Fig. 6. Thermal desorption mass spectra of n-propylamine and n-butylamine from the surface of NaY zeolite.

n- BUTYL AMINE HY

RET. TIME : 32.15 MINUTES
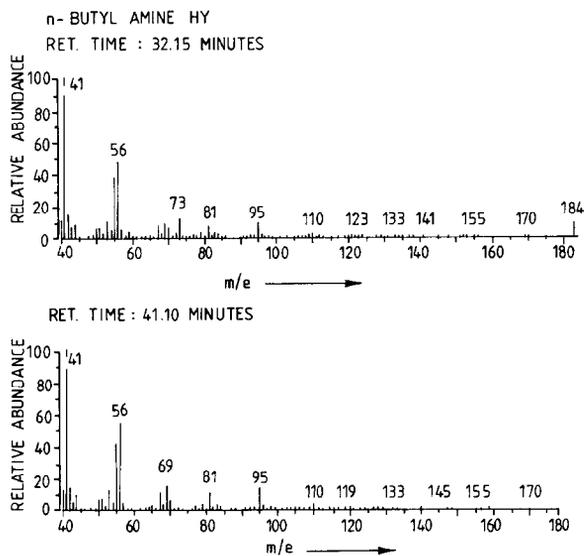

RET. TIME : 41.10 MINUTES

Fig. 7. Mass spectral fragmentation pattern of molecules desorbed from the surface of HY zeolite.

on CaY unconverted butylamine constitutes only a minor fraction of the total desorbed products. On CaY, the butene formed appears to desorb readily, whereas on HY the major part of the butene undergoes further reactions such as hydrogen transfer, dimerisation and aromatisation.

The formation of various products of degradation from chemisorbed amines may be explained in terms of acid catalysed conversions on zeolite
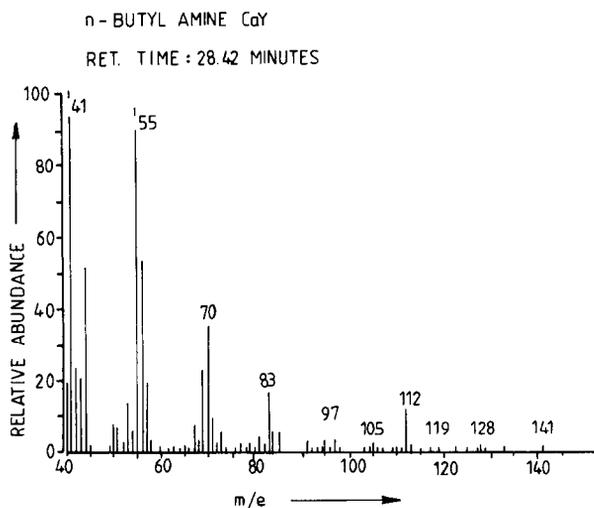
n – BUTYL AMINE CaY

RET. TIME : 28.42 MINUTES

Fig. 8. Mass spectral fragmentation pattern of molecules desorbed from the surface of CaY zeolite.
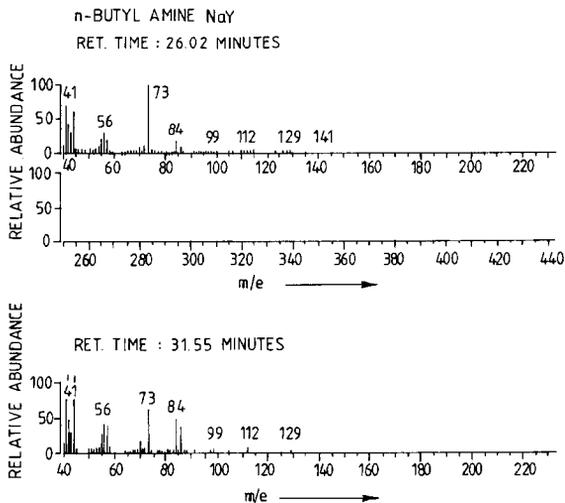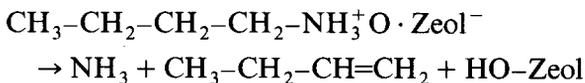
Fig. 9. Mass spectral fragmentation pattern of molecules desorbed from the surface of NaY zeolite.

surfaces. The amine molecule chemisorbed on the surface acid sites is protonated and may undergo Hofmann degradation giving rise to ammonia and the corresponding olefin.

$$CH_3-CH_2-CH_2-CH_2-NH_3^+O \cdot Zeol^-$$
$$\rightarrow NH_3 + CH_3-CH_2-CH=CH_2 + HO-Zeol$$

Such reactions of amines on mordenite and silica–alumina have also been reported [8–11]. The olefin generated by the above reaction, will then
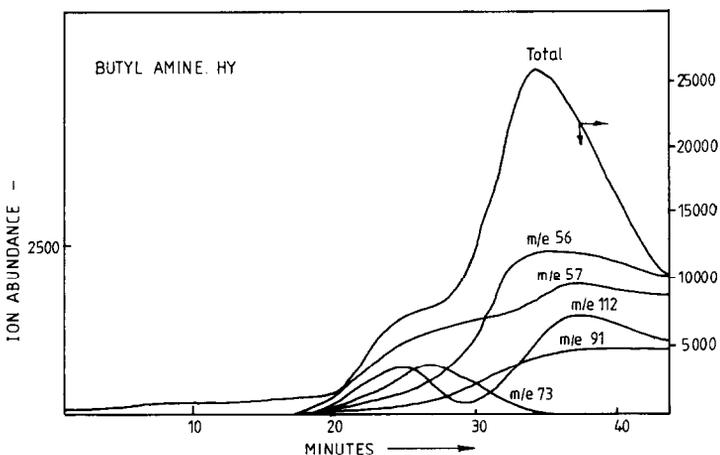

Fig. 10. Selected ion monitoring by mass spectrometry of the desorbed products from the surface of HY zeolite.
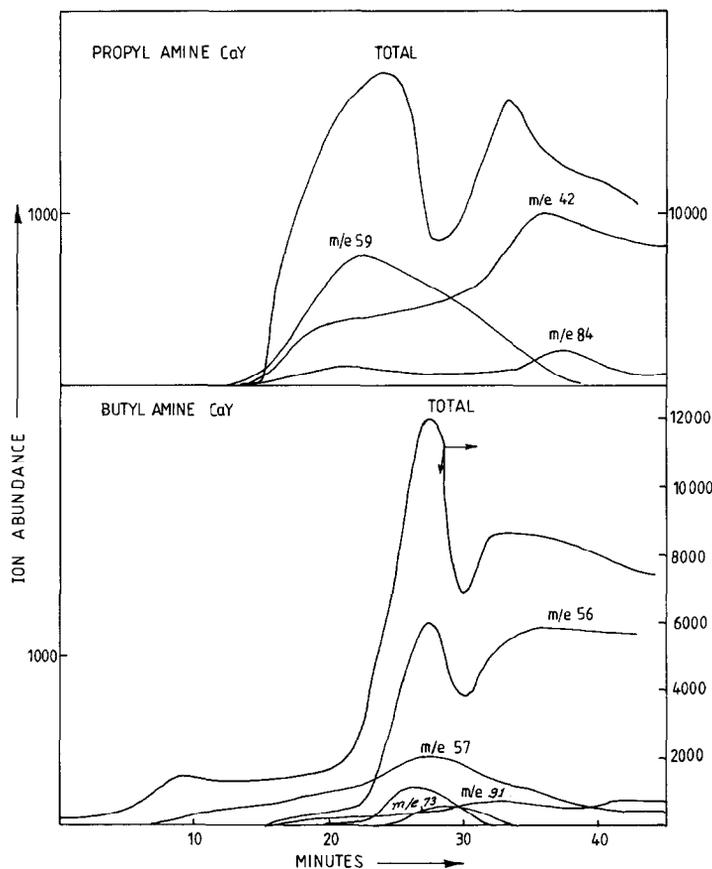
Fig. 11. Selected ion monitoring by mass spectrometry of the desorbed products from the surface of CaY zeolite.
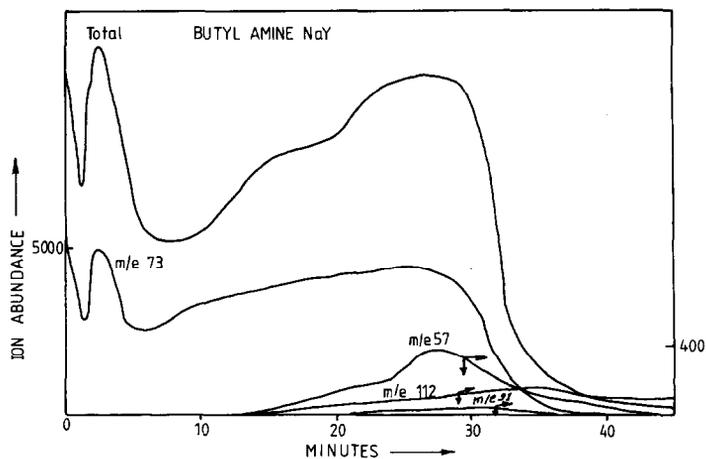

Fig. 12. Selected ion monitoring by mass spectrometry of the desorbed products from the surface of NaY zeolite.

undergo further reactions such as oligomerisation, hydrogen transfer and aromatisation typical of acidic catalysts [12]. Our mass spectral data have also provided evidence of the formation of secondary amines of the following types by the disproportionation of the primary amine.

$$2R-NH_2 \rightarrow R_2-NH + NH_3$$

The molecular ion of Bu_2NH ($m/e = 129$) has been observed during the desorption of butylamine on HY (Fig. 7).

Morishige et al. [11] have observed a high temperature desorption peak in the thermal desorption spectra of methylamines on alkaline earth zeolites. They attributed this peak to the interaction of the amine molecule with the S_{II} cation site of the zeolite. Our data suggest that this may occur in the case of NaY, but for CaY and HY the high temperature peak is essentially due to the decomposition of protonated amine molecule.

The thermogravimetric methods for acidity measurements using primary amine molecules as probes should be examined in the light of our present mass spectral data. Keeping in mind the ease with which amines are decomposed even on residual acid sites of NaY (Fig. 12) it is reasonable to conclude that all protonated amine molecules decompose on heating. Therefore a satisfactory characterisation of acidity of solid samples by amine desorption cannot be carried out unless accompanied by a simultaneous identification of the species being desorbed. One may attempt to calculate the number of surface sites by estimating the number of amine molecules decomposing during thermal desorption. The relative desorption of unconverted amines depends on the type of zeolite cations and not on the acid sites. Such a conclusion is supported by the observation of Ghosh and Curthoys [9] and Parker et al. [13] from their studies with other kinds of zeolites.

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