

## DESORPTION OF PRESORBED AMMONIA, TRIETHYLAMINE AND PYRIDINE FROM THE ACID SITES OF MORDENITES VIA DIFFERENTIAL SCANNING CALORIMETRY

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### ABSTRACT

Differential scanning calorimetry (DSC) was used to desorb and detect presorbed bases having different strengths, i.e. ammonia, triethylamine (TEA) and pyridine, from the different acid sites of Na- and H-mordenites. A method recently adopted by the author was used to nullify the zeolitic water DSC effect such that base desorption effects only appear in the thermograms. The Lewis acid sites in Na-mordenite were found to be stronger than in H-mordenite, whereas the Brönsted acid sites in H-mordenite were stronger than in Na-mordenite. Ammonia desorption from the mordenites gave satisfactory information about the acid sites strength distribution. TEA desorption from the Brönsted acid sites takes place at higher temperatures than for ammonia. Pyridine desorption from most of the Lewis acid sites showed a shift to the high temperature region owing to the strengthening of their binding forces via interaction of the ring  $\pi$ -electrons with positively charged aluminium in the mordenite zeolitic structure.

### INTRODUCTION

Mordenites are active catalysts for a multitude of industrial processes [1,2] such as isomerization, cracking, hydrocracking, etc. Some reactions require Brönsted acid sites, whereas others require Lewis acid sites. Therefore, the acid sites strength distribution (ASSD) in catalysts should be precisely evaluated.

In the present work, ASSD in Na- and H-mordenites is evaluated by DSC using three basic adsorbates having different strengths and structures.

Recently, the author investigated acidity strength in a series of mordenite catalysts using pyridine as a presorbed base and differential thermal analysis (DTA) as a means for desorbing and detecting the base [3]. ASSD in alumina and silica-alumina [4] as well as in natural zeolites [5] is evaluated

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via desorption of presorbed TEA in a DSC unit, making use of its programmed temperature increase. Moreover, dehydration [6] and deammoniation [7] of zeolites have also been evaluated by the author using DSC.

## EXPERIMENTAL

### *Materials*

Na- and H-mordenites (zeolon 900-Na and zeolon 900-H, respectively) were obtained from Norton Co. in the form of aggregates.  $\text{NH}_3$ , TEA and pyridine were AR grade of at least 99.9% purity.

### *Preparation of mordenites for DSC measurements*

The Na- and H-mordenites were dried at  $120^\circ\text{C}$  overnight then calcined at  $550^\circ\text{C}$  in air for 4 h and left to cool to ambient temperature in a dry atmosphere. Presorption of TEA and pyridine was carried out as described elsewhere [5].  $\text{NH}_3$  presorption was carried out after evacuating the sample for 8 h at  $550^\circ\text{C}$ . The presorption period was 48 h in all cases. The mordenites used as reference samples were dried at  $120^\circ\text{C}$  overnight then calcined at  $550^\circ\text{C}$  for 4 h.

### *DSC measurements*

A Mettler DSC-30 unit of the thermoanalytical system TA-3000 was used under the following conditions: initial temperature,  $50^\circ\text{C}$ ; rate,  $20\text{ K min}^{-1}$ ; final temperature,  $600^\circ\text{C}$ ; plot, 10 cm; full scale range, 25 mW. The modified nullifying technique adopted by the author and coworkers was employed [5]. The sample cell (Al crucible) contained 10 mg of a base-presorbing mordenite, whereas the reference cell (Al crucible) contained 10 mg of the corresponding base-free mordenite. All measurements were carried out in air at atmospheric pressure without using a purging gas.

## RESULTS AND DISCUSSION

According to the Lowry–Brønsted definition, an acid is a substance that gives up a proton and a base is a substance that accepts a proton. In the Lewis definition an acid is a substance that can take up an electron pair to form a covalent bond (electron pair acceptor) and a base can furnish an electron pair to form a covalent bond (electron pair donor) [8]. In the zeolitic structure, a proton bound to a framework oxygen resulting in a surface hydroxyl is catalytically defined as a Brønsted acid site, whereas a

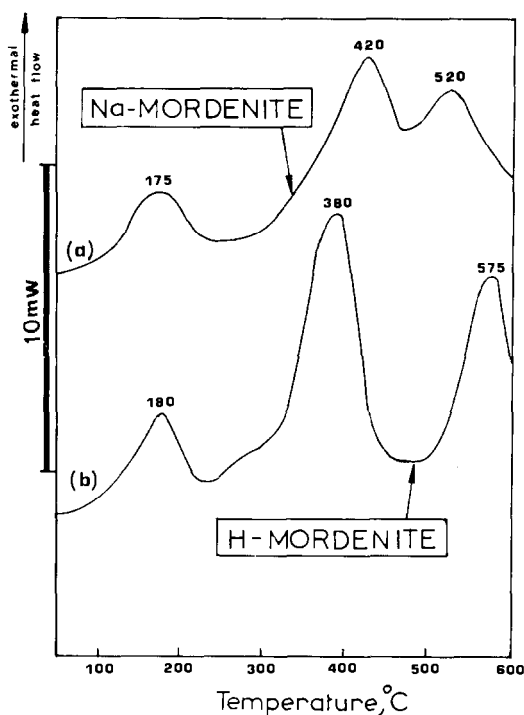


Fig. 1. DSC thermograms of ammonia desorption from Na-mordenite (a) and H-mordenite (b).

positively charged aluminium in the zeolitic structure is a Lewis acid site. Both Brönsted and Lewis acid sites are catalytically active sites for a multitude of industrial processes.

Besides being capable of reacting with Brönsted and Lewis acid sites, the three bases under study, i.e.  $\text{NH}_3$ , TEA and pyridine, can undergo hydrogen bonding (a strong kind of dipole-dipole interaction), where a hydrogen atom serves as a bridge between two electronegative nitrogens through holding one by a covalent bond and the other by purely electrostatic forces. However, this hydrogen-bonding attraction has a strength of about  $21 \text{ kJ mol}^{-1}$  only and thus is much weaker than a covalent bond. This type of attraction produces an exothermic base-desorption effect in the DSC thermograms in the low temperature region. Base desorption from the Lewis and Brönsted acid sites also gives exothermic effects (Figs. 1–3) in intermediate and high temperature regions of the DSC thermograms, respectively. In the DSC thermograms obtained on desorbing the presorbed bases under study from Na- and H-mordenites, all the DSC effects due to hydrogen bonding and Lewis acid sites appear, with the exception of those due to pyridine desorption from Lewis sites. However, the DSC effect due to the desorption of TEA and pyridine from the Brönsted acid sites (Figs. 2 and 3, respectively), does not appear completely in the thermograms because such desorp-

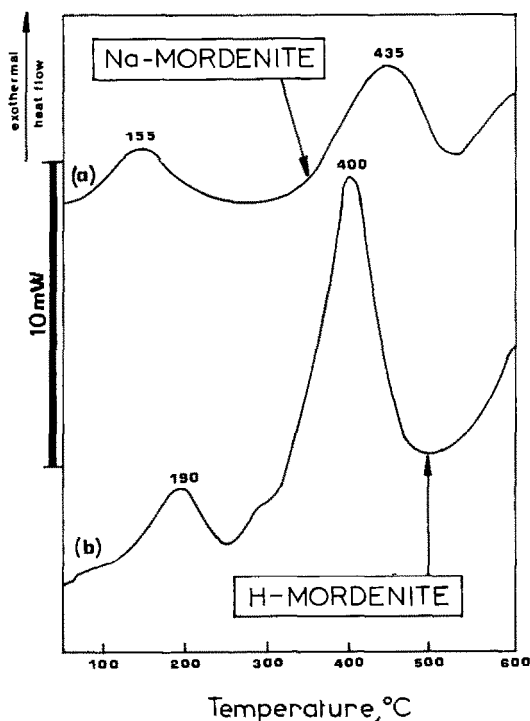


Fig. 2. DSC thermograms of triethylamine desorption from Na-mordenite (a) and H-mordenite (b).

tion requires higher temperatures beyond the maximum available with the DSC-30 unit employed. The base-desorption effect from the Brönsted acid sites only completely appears in the thermograms obtained for ammonia desorption from the mordenites (Fig. 1).

Another rather weaker attraction between the bases and the mordenites may appear in the low temperature region as an endothermic effect (physical adsorption effect). This very weak attraction is attributed to momentary (induced) dipoles and acts only between the surface of the molecules and the zeolitic surface via van der Waals' forces. This attraction has a strength below  $20 \text{ kJ mol}^{-1}$ . Nevertheless, such an effect does not appear in the thermograms obtained in this work (Figs. 1–3) since the base-presorbing mordenites are heated for 4 h at  $80^\circ\text{C}$  in an oven after contacting with the base [5].

#### *DSC desorption of presorbed $\text{NH}_3$ from the mordenites (Fig. 1)*

Since the basicity of  $\text{NH}_3$  in the gas phase is significantly lower than that of pyridine and TEA [9,10], the thermograms in Fig. 1 include almost all the DSC effects of hydrogen bonding, Lewis and Brönsted acid sites, i.e. the

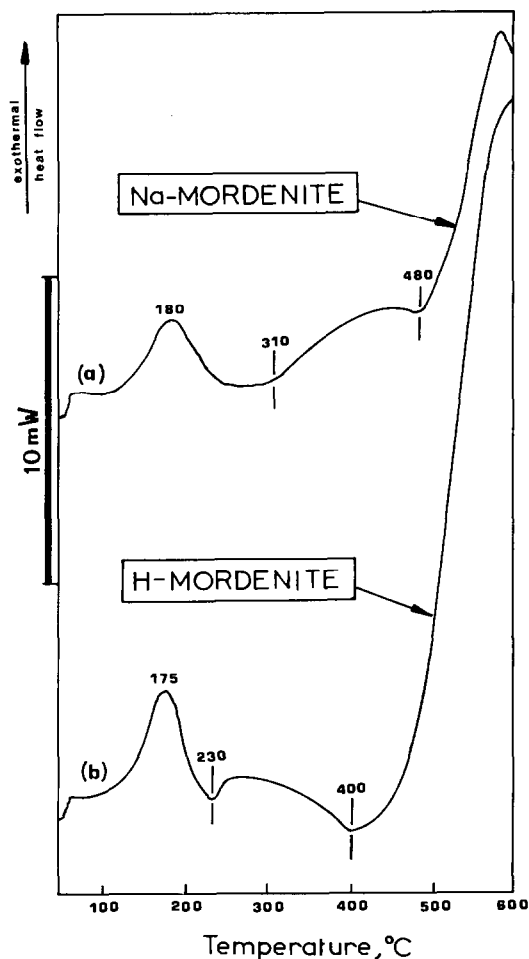


Fig. 3. DSC thermograms of pyridine desorption from Na-mordenite (a) and H-mordenite (b).

binding forces between  $\text{NH}_3$  and Brönsted acid sites in the mordenites are not so strong as in the case of presorbed TEA (Fig. 2) and pyridine (Fig. 3).

In the DSC thermograms obtained for  $\text{NH}_3$  desorption from the mordenites (Fig. 1), the weak acid sites effect appears to possess equal magnitude in the Na- and H-mordenites. These acid sites are easily accessible to  $\text{NH}_3$  molecules since they are assumed [11] to be located close to the opening of the zeolitic channels.

Desorption of  $\text{NH}_3$  from the Lewis acid sites in Na- and H-mordenites (Fig. 1) gives exothermic peaks with maxima at 420 and 380 °C, respectively. This indicates that the Lewis acid sites are considerably stronger in the cationic form (Na-mordenite) than in the decationic form (H-form). This may be attributed to the larger electrostatic field of the cationic structure.

Breck [12] showed that molecules with permanent dipole moments, e.g. the bases  $\text{NH}_3$ , TEA and pyridine, can interact strongly with the electrostatic field of the cationic zeolite, but on removing the cations and transforming the zeolite to its H-form, the interaction of these acid sites with the base is significantly weakened.

Desorption of presorbed ammonia from the Brønsted acid sites in Na- and H-mordenites gives DSC peaks with maxima at 520 and 575 °C, respectively (Fig. 1). This indicates that the Brønsted sites in H-mordenite are significantly stronger than in Na-mordenite.

It can thus be said that Na-mordenite has stronger Lewis acid sites and milder Brønsted acid sites than H-mordenite. Such findings may be of great interest to acid-catalysis investigators who may require milder acid sites of either type to avoid side reactions caused by stronger sites, or vice versa.

#### *DSC desorption of presorbed TEA from mordenites (Fig. 2)*

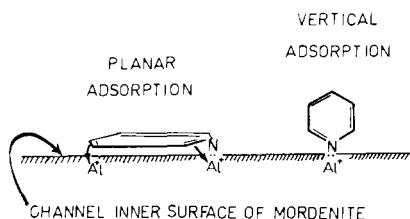
The magnitude of the peak of the weak acid sites obtained in the thermograms in Fig. 2 as a result of TEA desorption from the mordenites is not significantly different from that of the corresponding peak obtained through  $\text{NH}_3$  desorption (Fig. 1). TEA desorption from the strongest (Brønsted) acid sites in Na-mordenite gives a DSC effect that appears from 540 °C and continues upwards such that the end of this effect may occur considerably beyond 600 °C, i.e. the peak maximum does not appear in the thermogram up to 600 °C. This is attributed to the stronger basicity of TEA compared with  $\text{NH}_3$  and hence to stronger binding forces between TEA and the Brønsted acid sites. These acid sites appear to be deeply located in the zeolitic channels, since their rate of interaction with TEA, which is a strong base, is relatively low [13]. Derouane and coworkers [14,15] showed that the strongest acid sites are innermost in a model of the heterogeneous ASSD along the zeolitic channels.

TEA desorption from the Lewis acid sites in Na- and H-mordenites appears in the DSC thermograms (Fig. 2) as an exothermic effect covering the intermediate temperature region with maxima at 435 and 400 °C, respectively. Again, this is another indication that the Lewis acid sites in the cationic mordenite are significantly stronger than in the decationic form. As mentioned above, this is attributed to the stronger electrostatic field of Na-mordenite.

#### *DSC desorption of presorbed pyridine from mordenites (Fig. 3)*

Figure 3 shows that the mode of pyridine desorption from the acid sites of Na- and H-mordenites is markedly different from the modes of desorption of ammonia and TEA from the mordenites (Figs. 1 and 2). The DSC thermograms in Fig. 3 show a large shift of the effect of the pyridine

desorption from the Lewis acid sites from the intermediate temperature region to the high temperature region, i.e. desorption of pyridine from both Lewis and Brönsted acid sites appear together in the high temperature region. Although the combined Lewis–Brönsted effect partially appears in the high temperature region (the remaining part of this effect falls beyond  $600^{\circ}\text{C}$ ), its large magnitude, particularly in the case of H-mordenite (thermogram (b), Fig. 3) confirms that only the desorption of pyridine from the Lewis sites has been shifted to the high temperature region whereas the desorption of pyridine from the Brönsted sites does not encounter any shift. If the thermograms in Fig. 3 are investigated in isolation, one may erroneously presume that the mordenites possess a small number of Lewis acid sites (Fig. 3), or that both Lewis and Brönsted sites possess comparable strengths. The study of ASSD using  $\text{NH}_3$  and TEA in addition to pyridine should thus give a correct interpretation. Therefore, nothing can be assumed from the behaviour of pyridine desorption from Lewis sites, with the exception of the structure of the pyridine molecule and its mode of adsorption on these Lewis acid sites. The covalent bond formed using the lone pair of electrons on the nitrogen of the pyridine to fill the outer orbital of a positively charged aluminium should be much more stable than the bonds between the nitrogens of either  $\text{NH}_3$  or TEA and  $\text{Al}^+$ . Such high covalent bond stability can be attributed to a planar (flat) adsorption of the pyridine molecules on the internal surface of the zeolitic structural channels of the mordenites, whereby the  $\pi$ -electrons of the pyridine ring are involved in producing additional strengthening of adsorption. Furthermore, another  $\text{Al}^+$  may also interact with the ring  $\pi$ -electrons to produce additional pyridine–Lewis site attraction (Scheme 1).



Scheme 1. Adsorption modes of pyridine molecule on Lewis acid sites ( $\text{Al}^+$ ) in the mordenite channels.

Nevertheless, Fig. 3 also shows a broad band with a modest intensity in the intermediate temperature region. This may represent desorption of some pyridine molecules whose adsorption on the Lewis acid sites in both mordenites is vertically oriented (Scheme 1). The energy required to desorb these molecules is comparable with that required to desorb  $\text{NH}_3$  and TEA from the Lewis acid sites of the mordenites. Moreover, such a band appears in Na-mordenite (thermogram (a), Fig. 3) as a step at a higher temperature than that in which the corresponding H-mordenite band appears (thermo-

gram (b), Fig. 3). This finding appears to agree with the results obtained in the investigation of the desorption of  $\text{NH}_3$  (Fig. 1) and TEA (Fig. 2) from the Lewis sites of the two mordenites.

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