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Acid Site Strength Distribution in Mordenites by Differential Scanning Calorimetry

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Using differential scanning calorimetry (DSC), the acid site strength distribution in Na- and H-mordenites is investigated. Triethylamine (TEA) and ammonia are presorbed into the mordenites and then desorbed via a DSC programmed temperature increase from 50 to 600°C. Various presorbing contact periods are used to throw light on the rate of accessibility for the different types of acid sites in the mordenites by the two bases under study. A new DSC technique is used to nullify the zeolitic DSC effects such that the effects due to TEA and NH_3 desorption from the acid sites appear only in the thermograms. The ΔH values obtained may evaluate the relative proportions of the acid site types. © 1988 Academic Press, Inc.

INTRODUCTION

Recently, the author and co-workers have compared the acidity strength of metal-containing mordenite (zeolite) catalysts via the temperature programming of a differential thermal analysis (DTA) unit to desorb presorbed pyridine (*1*). Desorption of pyridine from the strongest acid sites takes place at the highest temperatures and vice versa. This idea has also been applied to differential scanning calorimetry (DSC) which gives, in addition to differences in desorption temperatures from acid site types, values of ΔH for desorption. The conventional procedure for DSC measurements has been successfully used to study the acidity strength distribution in materials such as alumina and silica–alumina (*2*). For these solids, the DSC effects obtained for desorbing a presorbed base are sufficiently separated from the effects obtained for desorbing the contained water. Nevertheless, in zeolites, water desorption DSC effects are largely endothermic and cover a broad temperature range such that they largely overlap the DSC effects due to the desorption of a presorbed base (*3*). Hence, the author adopted a modified "nullifying" technique that completely nullifies the water desorption DSC effects such that only the DSC effects due to the base desorption from the acid sites appear in a DSC thermogram (*4*). In the nullifying method, the reference cell (which is conventionally empty) contains a weight of the base-free zeolite exactly equal to the weight of the base-presorbing zeolite in the sample cell. However, this nullifying technique cannot be used in DTA measurements wherein the reference cell conventionally contains α-alumina.

Although the nullifying DSC method shares with the TPD method (temperature-programmed desorption) the general feature that the strongest acid sites desorb a presorbed base at the highest temperature (*5, 6*), the TPD method has yet certain disadvantages. Its ideal detector is a mass spectrometer that measures the composition of the effluent stream. Such a detector may not be available by many laboratories. However, catharometric detection can also be used but the high carrier flow rates employed to desorb the base are proportional

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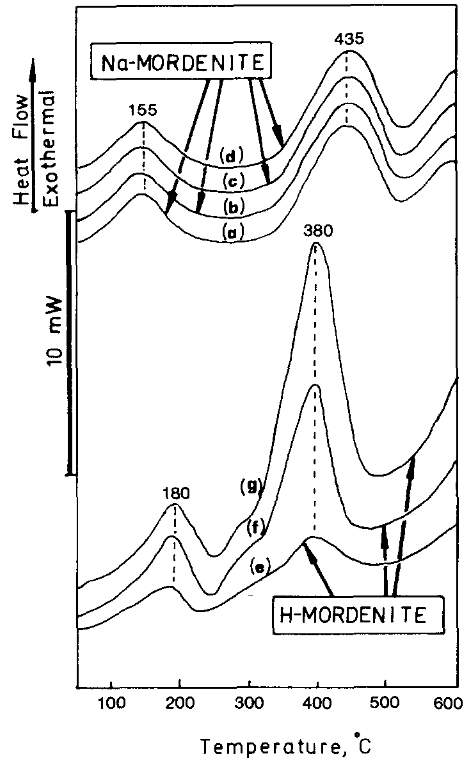

FIG. 1. DSC thermograms of TEA desorption from Na- and H-mordenites soaked for 2 h (a), 4 h (b), 6 h (c), and 48 h (d); 2 h (e), 4 h (f), and 48 h (g).

to the rate of desorption (*7*). Moreover, the TPD method uses a special reactor system for desorbing the base. On the other hand our DSC technique simply uses an ordinary DSC thermoanalytical unit. It easily differentiates between physically and chemically adsorbed phases which appear in a DSC thermogram as endothermal and exothermal peaks, respectively. Moreover, DSC can provide ΔH values for desorption which are proportional to the number of acid sites and activation energy (E) values which can be taken as a numerical criterion for comparing acidity strengths (*2–4*).

In the present work, two basic adsorbates with different strengths and critical diameters are used to probe acidity strength distribution in two catalytic materials, i.e., Na- and H-mordenites. Mordenites possess outstanding catalytic activities and selectivities (*8–10*).

EXPERIMENTAL

Materials. Na- and H-mordenites or zeolons 900-Na and 900-H, respectively, in the form of aggregates (Norton Co.) are used after grinding to powder. NH_3 and TEA were AR grade.

Preparation of zeolites for DSC measurements. The zeolites were calcined at 550°C for 4 h and then left to cool to room temperature. Presorption of TEA was carried out as described elsewhere (*4*), whereas ammonia presorption was carried out in the gas phase. Varying periods of contacting a zeolite with each base were examined as indicated in Figs. 1 and 2. Reference zeolites were also heated at 550°C for 4 h and then cooled to room temperature before the DSC measurements. Dry conditions are a must.

DSC measurements. The modified nullifying procedure adopted by the author and co-workers was employed (*4*). The sample cell contained 10 mg of a base-presorbing zeolite, whereas the reference cell contained an equal weight of the corresponding

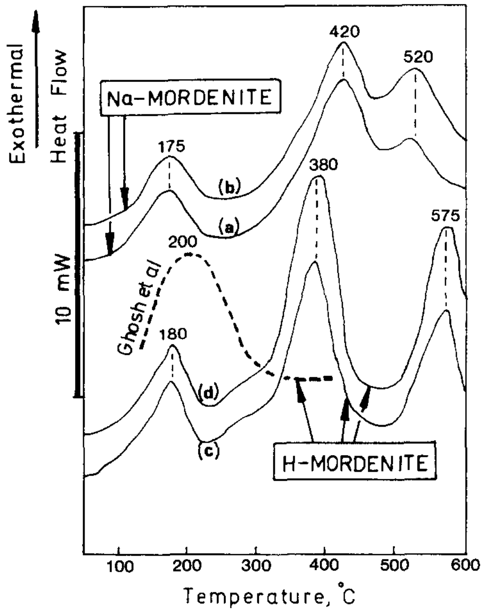

FIG. 2. DSC thermograms of NH_3 desorption from Na- and H-mordenites contacted for 4 h (a), 48 h (b), 6 h (c), 48 h (d).

base-free zeolite. The measurements were carried out at atmospheric pressure and no purge gas was used. A Mettler DSC-30 unit of the thermoanalytical system TA-3000 was used under the following conditions: initial temperature, 50°C; rate, 20°K min^{-1}; final temperature, 600°C; plot, 10 cm; full scale range, 25 mW.

RESULTS AND DISCUSSION

The present work is concerned with studing the acid strength distribution in Na- and H-mordenites through the presorption of two nitrogeneous bases with different basicities and molecular diameters on the mordenites followed by desorption of the bases in a DSC cell. The basic adsorbates employed are TEA and ammonia whose critical diameters (the minimum cross-sectional kinetic diameter, indicating the potential of adsorption through the effective pore size aperture of the adsorbent) are 7.8 and 2.6 Å, respectively, and their K_b in aqueous media are 5.6×10^{-4} and 1.8×10^{-5}, respectively. This may indicate that TEA is a significantly voluminous molecule with high basicity whereas NH_3 is a small molecule with low basicity. The base strength may control the rate of reaction with the different groups of acid sites in a zeolite, whereas the base critical diameter may reveal the extent of diffusion limitation encountered along the zeolitic channels before the base reaches and adsorbs on a group of acid sites. Thus, TEA is more reactive with weaker acid sites than ammonia as long as diffusion limitation along zeolitic channels is insignificant, and ammonia can react efficiently with the more hindered deeply located strong acid sites.

Figures 1 and 2 show that all peaks in the DSC thermograms obtained for desorbing the two presorbed bases under study are exothermal, indicating chemical adsorption only.

At the higher temperatures used for base desorption by DSC, decomposition of bases larger than ammonia occurs; for instance, TEA decomposes to give ethylene in the gas phase and a residual nitrogen-containing amine that will remain adsorbing on the same acid sites as those previously reacted with TEA. The hydrocarbon in the gas phase does not have any significant effect on the ΔH values obtained for desorbing the residual base and hence the DSC effect, cf. peak, obtained is insignificantly affected by the decomposition of presorbed bases. The highly exothermal heat flowing through the decomposing of the acid–base product (base desorption from certain acid sites) should be very high relative to the thermal effect due to removing a hydrocarbon portion not attached by itself to the acid sites.

In contradistinction to the DSC method used in the present work, decomposition of the presorbed base is a serious problem in TPD since measurement of the composition of the effluent stream is based on weight and mass spectrometry or catharometry is used for detection. So, ammonia is recommended to be the best presorbed base for acid site strength distribution (*11*) in the TPD method.

Desorption of Presorbed TEA via DSC

The DSC thermograms a–d in Fig. 1 indicate that the weakest acid sites in Na-mordenite (effect between 50 and 200°C) are easily accessible by the voluminous molecules of TEA (critical diameter 7.8 Å) since the magnitude of this DSC effect does not change by changing the soaking period of Na-mordenite in TEA (Table 1). Kung and Kung (*12*) attribute weak acid sites in zeolites to hydrogen bonding which can occur through the interaction of the nitrogen of the base with hydroxyl groups of the zeolite surface. However, Auroux *et al.* (*13*) assume that the acid sites that are first neutralized by a base are those close to the channel openings and that these sites are weaker in strength than the inner sites; such weaker sites are assumed to arise from a heterogeneous aluminum distribution along the channel.

The strongest acid sites in Na-mordenite,

TABLE 1

ΔH Values Obtained for DSC Effects via Base Desorption from Mordenites (J/g)

	ΔH for base desorption from Na-mordenite			ΔH for base desorption from H-mordenite		
Type of acid sites:	Weak	Lewis	Brønsted	Weak	Lewis	Brønsted
Temperature range (°C):	50–230	350–530	530	50–230	300–480	480
Peak maximum (°C):	155	435	?	180	380	?
Base contact time (h)						
Base: TEA 2	39	146	—	24	56	—
4	42	148	—	41	140	—
6	40	153	—			
24	42	151	—	43	199	—
48	41	152	—	42	206	—
Temperature range (°C):	50–230	300–475	475–600	50–230	330–450	500–600
Peak maximum (°C):	175	420[a]	520[a]	180	380	575[b]
Base contact time (h)						
Base: NH_3 2	44	—	—	40	38	22
4	39	—	—	42	110	68
6	41	—	—	43	135	87
24	43	—	—	41	178	106
48	44	—	—	44	182	110

[a] ΔH cannot be evaluated because of peak overlapping.

[b] ΔH corrected for peak completion.

i.e., Brønsted sites, which are bound to TEA through the transfer of a proton, appear in thermograms a–d in Fig. 1 to have reacted with TEA more slowly; the DSC effects appearing beyond 480°C and continuing to appear at temperatures considerably beyond 600°C (maximum apparatus temperature is 600°C) are becoming more and more exothermal as the period of Na-mordenite soaking in TEA is increased. Derouane *et al.* (*14*, *15*) show in their model for heterogeneous acid strength distribution along the zeolitic channels that the strongest acid sites are particularly those innermost. Since it can be assumed that a relatively strong base such as TEA will interact very soon with the strongest acid sites in Na-mordenite, it can be concluded that the slow reaction of TEA appearing in thermograms a–d in Fig. 1 should be attributed to diffusion limitation of voluminous TEA to reach those deeply situated Brønsted acid sites.

Again, in thermograms a–d in Fig. 1 another DSC effect appears, covering an intermediate temperature range with a maximum at 435°C, which, similar to the low temperature peak, is unaffected by increasing the period of soaking the Na-mordenite in TEA. This effect is thus the result of fast interaction of TEA with corresponding acid sites. This mode of interaction involves coordination of the base through the lone pair of electrons to the positively charged aluminum in the zeolite structure (Lewis acid sites (*2*)).

On the other hand, the DSC thermograms e, f, g in Fig. 1 are obtained for desorbing TEA from the acid sites present in the decationated mordenite (H form) after soaking in TEA for periods of 2, 4, and 48 h, respectively. The DSC effects due to desorption of TEA from the weakest acid sites appear between 50 and 230°C with a maximum at 180°C. Reaction of TEA with such acid sites appears somewhat slower than that with the respective sites in Na-mordenite (compare thermograms 1e and 1f). However, the reaction is complete after only 4 h (see also Table 1) since the ΔH values obtained for samples soaked for 4 and 48 h are almost equal. Nevertheless, those acid sites (weakest) may be relatively stronger in H-mordenite than in Na-mordenite since their maximum DSC effects appear at 180 and 155°C, respectively.

In H-mordenite, both Lewis and Brønsted acid sites do not seem to be easily accessible by the TEA molecules. The Lewis acid site effects with a maximum at 380° give widely different ΔH values for H-mordenite samples soaked for different periods (thermograms e–g in Fig. 1 and Table 1). Beyond 500°C in thermograms 1e–1g, the left side of a peak due to TEA desorption from Brønsted acid sites may indicate increasing DSC effects with increasing soaking period. However, as mentioned above, the Lewis site effects with maxima at 435°C obtained for TEA desorption from Na-mordenite are easily accessible by the TEA molecules (curves a–d in Fig. 1).

A significant difference between Na- and H-mordenite is that Lewis acid sites in the Na form are markedly stronger than in the H form (peak maximum 435 vs 380°C). Breck (*16*) shows that molecules having permanent dipole moments, e.g., the bases under study, interact very strongly with the electrostatic field of the cationic zeolite structure such that complete removal of the cations from the zeolite framework alters the local electric fields and field gradients and consequently reduces any interaction with a molecule having a permanent electric moment.

Desorption of Presorbed Ammonia via DSC (Fig. 2)

The desorption of ammonia via the DSC programmed heating gives the thermograms a and b in Fig. 2 for Na-mordenite and thermograms c and d for H-mordenite. These thermograms reveal the presence of three distinct exothermal peaks indicating three types of acid sites differing in strength in both zeolite forms. The low temperature peak is attributed to NH_3 desorbed from hydrogen-bonding acid sites, the second peak has the largest magnitude, covers an intermediate temperature range, and represents NH_3 desorbed from Lewis acid sites, and the last (highest temperature) peak has an intermediate magnitude and represents NH_3 desorption from Brønsted acid sites.

The weak acid sites peak in thermograms a–d in Fig. 2 almost have equal ΔH values (Table 1). This may indicate the following: (i) the strength of such weak acid sites may be high enough to react with ammonia which is a very weak base, (ii) the adsorption of ammonia on these sites is not controlled by the period of contacting the two zeolite forms with NH_3, i.e., these sites are easily accessible by NH_3 molecules indicating that they are located close to the opening of the zeolitic channels, and (iii) the numbers of such weak acid sites in Na- and H-mordenites are approximately equal.

Ammonia desorptions from Lewis acid sites in Na- and H-mordenites (Fig. 2) give exothermal peaks with maxima at 420 and 380°C, respectively; i.e., Lewis sites in the cationic form are significantly stronger than those present in the H form. This finding has also been recognized on TEA desorption from the two forms of mordenite and has been attributed to the larger electrostatic field of the cationic zeolite structure. The magnitude of the Lewis acid sites peak obtained for Na-mordenite does not appear to change through an increase in the period of contacting the zeolite with NH_3. This indicates easy accessibility of such Lewis acid sites by NH_3 molecules. On the contrary, the Lewis acid sites peak for H-mordenite (thermograms c and d in Fig. 2 increases in magnitude by increasing the contact period; i.e., Lewis acid sites in Na-mordenite are not as deeply located in the zeolitic channels as Lewis sites in H-mordenite. This finding has also been determined during TEA desorption from these mordenites (Fig. 1 and Table 1). Qualitatively, it can be assumed that the number of Lewis acid sites in H-mordenite may be larger than that in Na-mordenite. ΔH values for DSC effects obtained for Lewis sites in Na-mordenite cannot be evaluated because the respective peak is partially overlapping the Brønsted acid sites peak.

The peak representing ammonia desorption from the Brønsted acid sites present in Na- and H-mordenites fall within the temperature range available by the DSC unit employed (Fig. 2). This is attributed to the lower basicity of ammonia, and consequently the desorption of NH_3 from Brønsted acid sites is weaker than that with TEA (compare Figs. 1 and 2). Nevertheless, desorption of NH_3 from Brønsted sites in Na-mordenite gives a DSC peak with a maximum at 520°C, whereas such desorption in the case of H-mordenite gives a peak with a maximum at 575°C. This indicates that Brønsted acid sites in H-mordenite are significantly stronger than those in Na-mordenite. Moreover, slow interaction between NH_3 molecules and Brønsted acid sites in both Na- and H-mordenites is evident through a change in the magnitude of the corresponding peak with a change of the period of contacting these zeolites with NH_3 which is consequently indicative of the deep location of these acid sites in the zeolitic channels.

Ghosh *et al.* (*11*) in their TPD of presorbed ammonia from H- and dealuminated H-mordenites have shown that they obtained one broad peak between 100 and 300°C with a maximum at 200°C in their TPD chromatogram although temperatures up to 500°C were available. According to the present investigation using DSC, it may be assumed that such a peak is attributed to weak acid sites in H-mordenite (compare the dotted curve by Ghosh *et al.* with thermograms c and d in Fig. 2). The absence of other peaks in their chromatogram due to stronger acid sites may be, most probably, attributed to insufficient length of time for contacting the mordenites with ammonia. In addition, their recommendation to use ammonia but not other thermally decomposable amines for studying acid sites strength distribution via TPD does not apply to our use of the DSC desorption technique as has been discussed above; the DSC effects are insignificantly influenced by such decomposition.

Pyridine desorption via DSC from the mordenite acid sites is markedly different from the modes of NH_3 and TEA desorption (*17*). Pyridine desorption from Lewis acid sites is shifted to the highest temperature region and overlaps the Brønsted sites DSC effect; i.e., in the case of pyridine desorption, Lewis sites appear much stronger than those in the cases of NH_3 and TEA desorption. So dependence on data obtained for pyridine adsorption alone will lead to erroneous conclusions since the π electrons on the pyridine ring, adsorbed flat on the internal surface of the zeolite channels, will strongly interact with Al^+ of the zeolitic surface.

However, differences in the surface SiO_2/Al_2O_3 ratios in the Na- and H-mordenites may lead to chemisorption differences between NH_3 and TEA (Table 2).

CONCLUSIONS

Desorption of presorbed ammonia from Na- and H-mordenites gives three DSC effects that appear almost complete in the DSC thermograms. These are attributed to desorption from weak, Lewis, and Brønsted acid sites. Desorption of TEA from the mordenites shows weak and Lewis desorption effects only as almost complete peaks whereas Brønsted sites effects partially appear in the thermograms. In both mordenite forms, weak acid sites appear easily accessible by the two adsorbates. Lewis acid sites in Na-mordenite are easily accessible and rapidly react with the two bases, whereas in H-mordenite these sites react more slowly. Moreover, Lewis acid sites in the Na form are fewer in quantity but of greater strength than Lewis sites in H-mordenite. Brønsted acid sites appear to re-

TABLE 2

Some Characteristics of Na- and H-mordenites

	Molar $SiO_2:Al_2O_3$	Effective pore diameter (Å)	BET surface area (m^2/g)	Void volume (cc/cc)	Crystallinity (%)
Na-M	10 : 1	7.0	355	0.27	80
H-M	13 : 1	8.5	468	0.29	95

act more slowly with the two bases indicating their deep location in the zeolitic channels of both forms and that their accessibility is not controlled by the diameter of the adsorbate. These Brønsted sites are fewer in quantity than the Lewis sites in both forms. In contradistinction to Lewis acid sites, the Brønsted sites are much stronger in H-mordenite than in Na-mordenite.

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