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DIFFERENTIAL MOLAR HEATS OF ADSORPTION OF AMMONIA ON SILICIOUS MORDENITES AT HIGH TEMPERATURE

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ABSTRACT

The acidic properties of mordenite zeolites with various Si/Al ratios were analysed by calorimetric measurements of the heat of adsorption of ammonia and IR measurements. Two distinct adsorption sites were obtained on decationated mordenites. The adsorption of ammonia was irreversible on the more energetic sites even at 473 K and the number of these sites corresponded to the number of acid sites on the mordenites. Heats of adsorption on the less energetic sites were similar to those on sodium-type mordenites. Adsorption of ammonia on mordenites was significantly influenced by adsorption temperature; the adsorption was not selective below 373 K and averaged heats of adsorption were obtained between those on the more energetic (acidic) sites and those on the less energetic (non-acidic) sites. The adsorbed molecules on the latter migrated at higher temperature.

INTRODUCTION

The activity and selectivity of zeolite catalysts largely depend on the adsorption and diffusion characteristics of the reacting molecules and their acidic properties [1–4]. Of the zeolites, mordenites have attracted much attention because they exhibit interesting catalytic properties, e.g. shape-selective properties and great resistance to deactivation [5,6]. The mordenite structure is orthorhombic and possesses a peculiar channel system; the channel is one-dimensional along the *c* axis with an opening of 0.67 × 0.70 nm consisting of a twelve-membered oxygen ring. The interesting catalytic properties must originate from these structural characteristics as well as from the acidic properties [7]. The acidic properties of zeolites are affected by their type, their Si/Al ratio, the type and content of cations and so on. The Si/Al ratio plays a significant role since the aluminium atom is directly related to the acidic site and accounts for the formation of carbonium ions or cation radicals inside the zeolite [8,9]; this role has already been verified

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by measurements of heats of adsorption of several bases on faujasites [10], mordenites [11] and dealuminated faujasites [12].

The aim of this study is to analyse the acidic properties of highly silicious mordenites by calorimetric and IR measurements of ammonia adsorption. The effects of pretreatment conditions and Si/Al ratio are discussed. The influence of the temperature on the diffusion of adsorbed ammonia inside the channel is also examined.

EXPERIMENTAL

Mordenite zeolites (Na- and NH_4-type) were supplied by the Japan Reference Catalyst Committee and Toso Co. Ltd. Their chemical compositions are shown in Table 1. NH_4-type mordenites were assumed to become decationated (H-type) by thermal treatment. Prior to calorimetric and IR measurements, the samples were activated by calcination under 1 mPa pressure on increasing the temperature at a rate of 3 K min^{-1} and at the final temperature for 5 h. Ammonia gas was passed through a column containing dehydrated molecular sieve 4A and was then purified by freeze–pump–thaw cycles.

Heats of adsorption of ammonia were measured with a twin-conduction-type microcalorimeter equipped with a volumetric vacuum line. The details and procedures have been described previously [11,13]. About 1 g of the zeolite was placed in the sample cell and pretreated. The cell was then set in the calorimeter. After thermal equilibrium was established, a small amount of ammonia (< 50 μmol) was admitted. The thermal effect was detected by a thermopile and recorded. The amount adsorbed was calculated from the pressure change before and after adsorption using an MKS baratron pressure gauge. When the thermal equilibrium was re-established, another dose of gas was admitted.

IR spectra were obtained by the in situ method in the region 4000–1800 cm^{-1}. A thin wafer of the zeolite (< 10 mg cm^{-2}) mounted in a quartz

Table 1

Chemical compositions of mordenite zeolites

Sample	Chemical formula	Si/Al ratio
M-10	$Na_{8.14}(AlO_2)_{8.14}(SiO_2)_{39.86}$	4.90
M-15	$Na_{5.65}(AlO_2)_{5.65}(SiO_2)_{42.35}$	7.50
M-20	$Na_{4.35}(AlO_2)_{4.35}(SiO_2)_{43.65}$	10.03
HM-10	$(NH_4)_{7.97}Na_{0.07}(AlO_2)_{8.04}(SiO_2)_{39.96}$	4.95
HM-15	$(NH_4)_{5.64}Na_{0.03}(AlO_2)_{5.67}(SiO_2)_{42.33}$	7.45
HM-20	$(NH_4)_{4.51}Na_{0.04}(AlO_2)_{4.55}(SiO_2)_{43.45}$	9.95

sample holder was set into a quartz cell and pretreated at the desired condition. The spectrometer used was a JASCO IR-810 and the spectra were obtained by integration of 99 scans. The ^{27}Al magic angle spinning NMR spectra (^{27}Al-MAS-NMR) were taken using a JEOL GX-270.

RESULTS AND DISCUSSION

Effects of evacuation temperature

The acidic properties of zeolites are dependent on their evacuation/activation temperature, which is closely related to the mechanism of generation of acid sites [14,15]. The H-type zeolites are formed from the NH_4-type after removal of ammonia, which is easily ascertained by the appearance of hydroxyl groups in the IR spectra. The Bronsted acid sites are thus generated. A pair of Bronsted acid sites are converted to one Lewis acid site by further evacuation at higher temperature.

The IR spectra (recorded at 473 K) of HM-20 evacuated at various temperatures (573–773 K) are shown in Fig. 1. The sample treated at 573 K has sharp peaks at 3720 and 3610 cm^{-1}, and a broad band ranging from 2700 to 3400 cm^{-1}. The intensity of the latter band (which corresponds to the N–H stretching vibration) decreases with an increase in the evacuation temperature and disappears above 723 K; this suggests that the conversion of NH_4-type to decationated mordenites is complete. However, the band intensity at 3610 cm^{-1} increases with temperature and the maximum is obtained near 723 K. This band originates from the hydroxyl groups which are close to the aluminium atoms [16] and can be related to the Bronsted acid sites in the zeolite framework [14,15]. The band due to the hydroxyl groups on the external surface exhibits no significant change with variation in evacuation temperature.

The calorimetrically determined differential heats of adsorption of ammonia on HM-20 measured at 473 K are shown in Fig. 2. Adsorption isotherms are of type I (Langmuir type) according to Brunauer's classification. Drastic energy changes are observed between low coverage and high coverage with the exception of the sample evacuated at 1073 K; the energy gap corresponds to about 50 kJ mol^{-1}. Such distinct steps were not observed on faujasites [12,13,17], which suggests that at least two types of adsorption sites exist and their adsorption energies are more homogeneous in mordenites. The heat values of the second step are similar to those observed on Na-type mordenites as described later. The filled symbols in the figure represent heats of re-adsorption on the mordenite which was re-evacuated for 24 h at 473 K after the first adsorption run. The amount desorbed was calculated from the cumulative heats of desorption or from the amount trapped during desorption. Both values agree well with each other. The heat of re-adsorp-

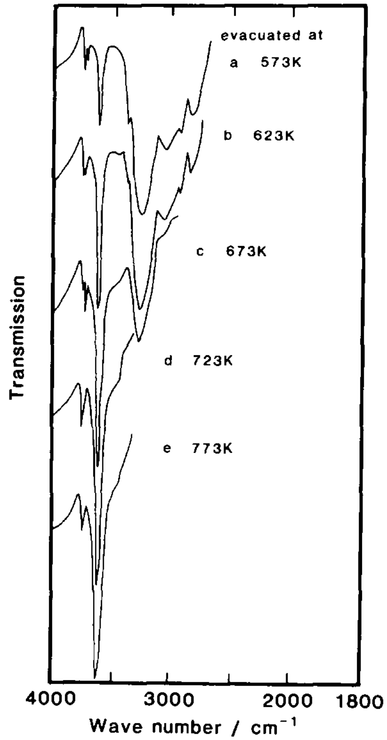

Fig. 1. IR absorption bands of HM-20 evacuated at various temperatures.

tion is consistent with the less energetic site energy in the first run and the amount of irreversibly adsorbed ammonia at 473 K corresponds to the total amount adsorbed on the more energetic sites. Such a strong interaction between the ammonia molecule and the more energetic site confirms the existence of strong acid sites which seem to originate from protonic sites in the mordenite. However, ammonia molecules adsorb rather weakly on the less energetic sites, which may be due to non-acidic interaction between ammonia molecules and the framework. The number of the more energetic sites and their energy increase with an increase in the evacuation temperature and attain a maximum at 773 K. Then a decline is observed. The heat curve of the sample evacuated at 1073 K does not exhibit a step and its initial value is much less than those of the other samples. Moreover, the amount adsorbed is half the value of the other samples, while the adsorption isotherm is of type I. This may be attributed to the breakdown of part of the mordenite structure and/or to the local formation of amorphous species.

In order to clarify the relationships between the generation of acid sites and the evacuation temperature, the energy distribution curve (acid spectrum) was deduced from a plot of differential heats of adsorption vs. amount adsorbed using graphical differentiation [13,18–20]; this is presented in Fig. 3. Two main peaks exist in the energy region 130–150 kJ

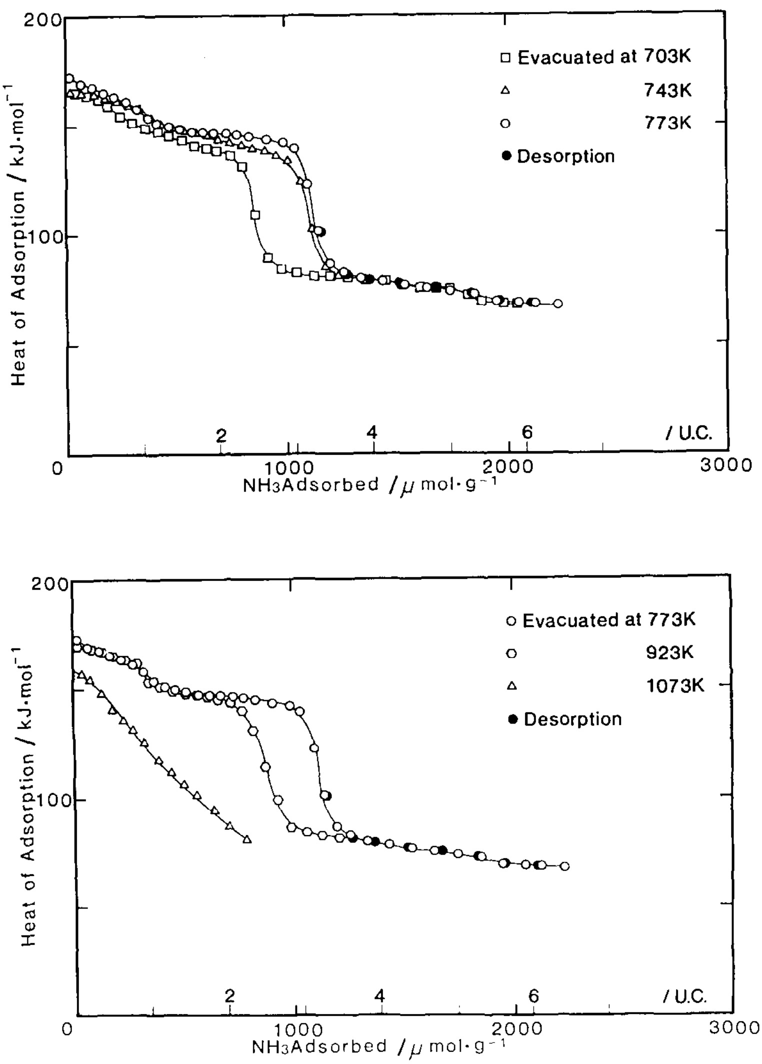

Fig. 2. Calorimetrically determined molar heats of adsorption of ammonia at 473 K on HM-20 evacuated at various temperatures. Filled symbols represent heats of re-adsorption on samples which were evacuated at 473 K after the first run of the adsorption measurement.

mol^{-1} and 160–170 kJ mol^{-1}. These peaks become sharper and their maxima shift slightly to the higher energy side with an increase in the evacuation temperature. The sample treated at 773 K exhibits the most distinct distribution and the greatest number of acid sites. This indicates that the acid properties of HM-20 become most homogeneous on evacuation at 773 K. For the sample treated at 1073 K, no peak maximum is observed, which suggests a broad energy distribution of acid sites.

In order to analyse the type of acid sites, IR spectra of adsorbed pyridine (Py) on HM-20 were measured. The number of Bronsted (B) and Lewis (L)

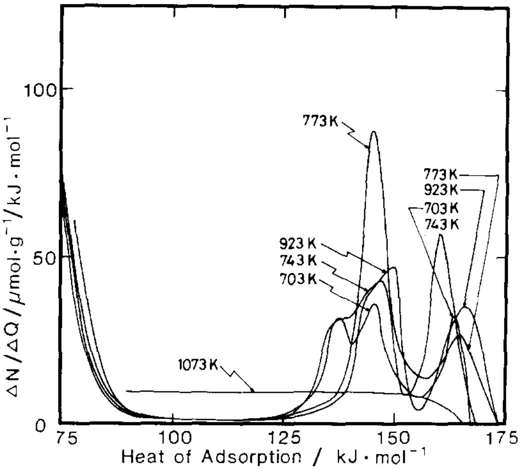

Fig. 3. Acid strength distribution of HM-20 evacuated at various temperatures.

acid sites were calculated from PyB (1542 cm^{-1}, molar extinction coefficient $= 1.3 \times 10^6$ cm mol^{-1} [21]) and PyL (1440 cm^{-1}, 1.5×10^6 cm mol^{-1}) bands, respectively. The value PyL/(PyL + PyB) is plotted against the evacuation temperature of HM-20 in Fig. 4. The conversion to Lewis acid starts to occur at 773 K but is accelerated above 873 K.

From IR and calorimetric measurements, it is observed that the generation of Bronsted acid sites is pronounced at 773 K and the conversion to Lewis acid is accelerated at higher temperature. However, the temperature range over which the conversion occurs is not distinct and should depend on the Si/Al ratio. Moreover, the displacement of aluminium atoms from the framework after thermal treatment is verified by the ^{27}Al-MAS-NMR spectra shown in Fig. 5. Only one peak is observed in the original NH_4-type

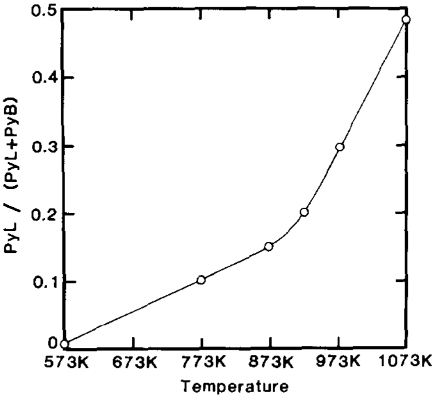

Fig. 4. Change in the ratio of Lewis acid to total acid as a function of evacuation temperatures.

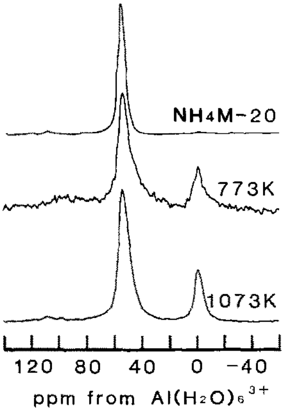

Fig. 5. ^{27}Al-MAS-NMR spectra of original HM-20 (NH_4M-20) and evacuated samples.

mordenite (NH_4-M-20), while the second peak is present in the thermally treated samples. The first peak is known to be due to tetrahedrally coordinated aluminium atoms and the second is due to octahedrally coordinated aluminium atoms [22]. Since each aluminium atom generally coordinates to four oxygens in the zeolite framework, the second peak should result from the aluminium atoms released from the framework. Such aluminium atoms may also be the origin of Lewis acid sites.

Effects of Si/Al ratio

The molar differential heats of adsorption of ammonia on mordenites with various Si/Al ratios (evacuated at 773 K) were measured at 473 K and are given in Fig. 6. Heat curves on Na-type mordenites (only one of which is shown in the figure) are homogeneous irrespective of their Si/Al ratio. However, distinct steps are observed in protonated mordenites and their initial heats of adsorption increase with an increase in Si/Al ratio and reach a maximum in HM-20. This increase can be attributed to the lowering of shield effects on the proton mobility by framework anions [23]. The value of approximately 175 kJ mol^{-1} for HM-20 is comparable with that observed on the solid super acid which was prepared by the reaction of SbF_5 vapour with dehydrated silica–alumina [19]. Heat values on less energetic sites, which reflect interactions of ammonia with the framework, are similar to those on Na-type mordenites. The interaction between the dipole of the ammonia molecule and the sodium cation should play a role in the case of Na-type mordenites, but this did not seem to be significant. Heats of readsorption (approximately 80 kJ mol^{-1}), which are indicated by filled symbols, are similar to the heats of adsorption on the less energetic sites. Therefore the number of ammonia molecules which adsorb with heats of adsorption above 80 kJ mol^{-1} can be considered to be the number of acid

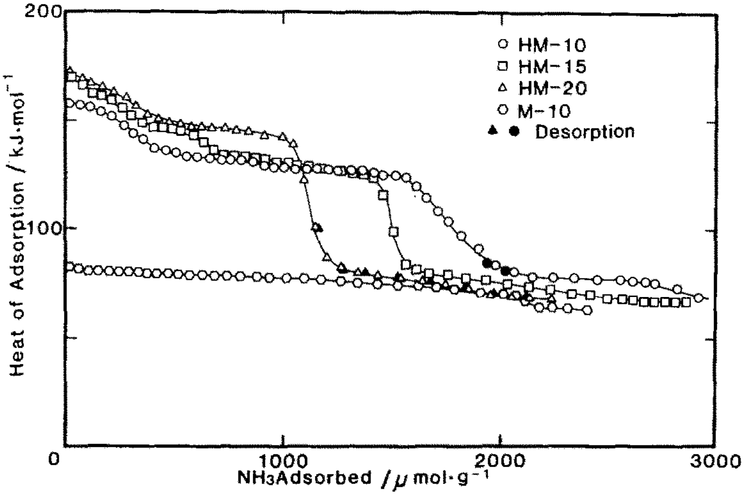

Fig. 6. Calorimetrically determined molar differential heats of adsorption at 473 K of various mordenites evacuated at 773 K. Filled symbols represent heats of re-adsorption on samples which were evacuated at 473 K after the first run of the adsorption measurement.

sites. The number calculated from the heat curves is plotted against the theoretical number of protons (aluminium atoms) per unit cell of mordenites in Fig. 7. Although they correlate well with each other, the slope deviates a little from unity. The deviation is less in HM-20 in which the separation between aluminium atoms becomes large. This result suggests that the framework aluminium atoms participate in the formation of acid sites and that some of the generated Bronsted acid sites are converted to Lewis acid sites. However, the displacement of aluminium atoms from the framework may also be responsible for the deviation.

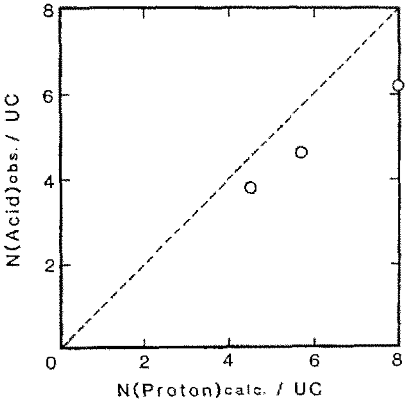

Fig. 7. Relationship between the number of acid sites calculated from calorimetric heat curves and the calculated number of protons.

Effects of adsorption temperature

Since zeolites have a regular pore structure with an opening close to the dimension of molecules, the diffusion of adsorbed molecules largely depends on the temperature. Several anomalies have been observed in heats of adsorption of certain adsorbates with kinetic diameters close to the pore diameter of zeolites [24–26]. It has been observed that pyridine or piperidine molecules cannot move freely in faujasites below 473 K [17,27]. Vedrine et al. [28] have reported the same behaviour in the ammonia–ZSM5 system. The effect of adsorption temperature on the calorimetrically determined heats of adsorption was analysed and is shown in Fig. 8. Two distinct steps are obtained on adsorption above 423 K and the heat curves are almost the same. Ammonia molecules are expected to adsorb first and selectively on the more energetic sites, which suggests that the movement of the molecules is not restricted in the pore before adsorption. However, a monotonic change is observed in the heat curve at 313 K. At this temperature, ammonia molecules are prevented from diffusing freely in mordenite channels even at relatively low amounts of adsorption. Some of them adsorb on the acid sites which are located close to the pore openings of the twelve-membered oxygen rings and others on the non-acidic sites. Therefore, it seems that averaged heats of adsorption are obtained between those on the acidic (more energetic) sites and those on the non-acidic (less energetic) sites. The cumulative heats of adsorption up to the final stage of adsorption are similar to those obtained at other temperatures. Diffusion of adsorbed molecules at 373 K is slightly limited.

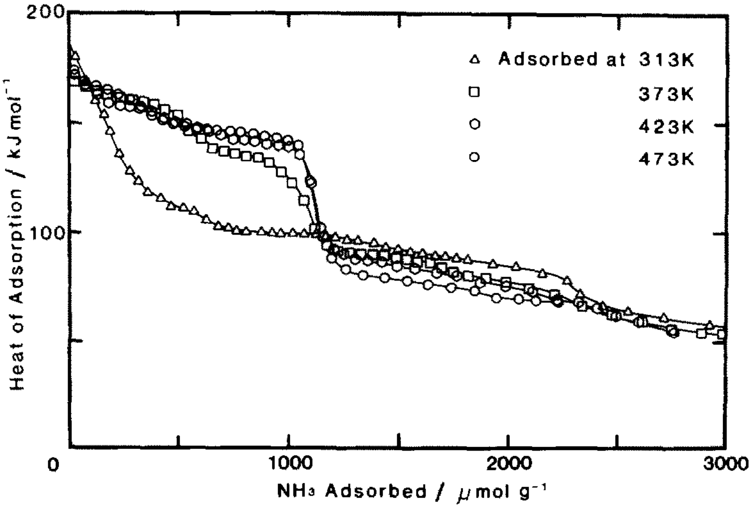

Fig. 8. Calorimetrically determined molar differential heats of adsorption on HM-20 evacuated at 773 K at various adsorption temperatures.

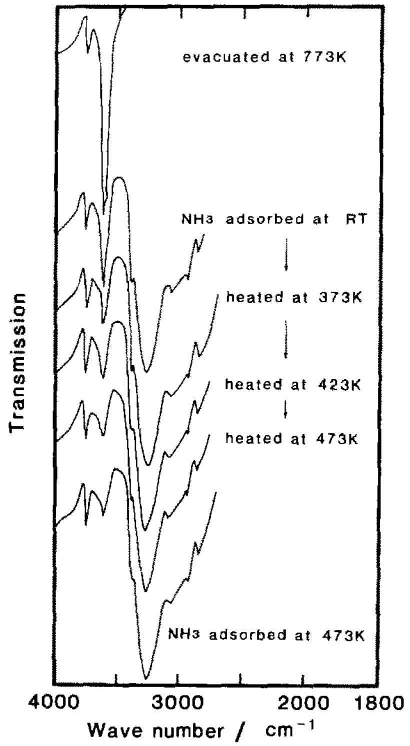

Fig. 9. IR absorption bands of HM-20 after adsorption of 1 mmol g^{-1} of ammonia.

Such diffusion limitation is also confirmed by IR measurements. The IR spectra of HM-20 before and after ammonia adsorption are shown in Fig. 9. The intensity of the hydroxyl stretching vibration at 3610 cm^{-1} is reduced by almost one-half and a broad band appears at 2700–3400 cm^{-1} after adsorption of ammonia at room temperature (1 mmol g^{-1}). The intensity of the band at 3610 cm^{-1} is lowered on heating in vacuo, which must be responsible for the migration of the adsorbed ammonia molecules from non-acidic to acidic sites. The other OH band at 3720 cm^{-1}, however, does not interact with ammonia molecules, which confirms that this band is related to the external silanol groups of the mordenites. The spectra obtained after adsorption of ammonia (1 mmol g^{-1}) at 473 K and after adsorption at room temperature followed by heating to 474 K are in excellent agreement.

Consequently, adsorption above 423 K is required to characterize the acidity of mordenites. Since no diffusion limitation was observed in the adsorption of ammonia on faujasites above room temperature [17] and on ZSM5 above 373 K [29], this phenomenon may result from the peculiar channel structure and the opening diameter of mordenites.

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