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HETEROGENEITY OF OH GROUPS IN H-MORDENITES
TPD and IR studies of ammonia desorption

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Abstract

We have investigated the temperature-programmed desorption (TPD) of ammonia during the activation of NH_4Na-mordenites of different exchange degrees. Using a regularization method, desorption energy distribution functions have been calculated. The obtained results indicate the heterogeneity of the bridging Si–OH–Al groups in HNa-mordenites. This was concluded from the width of the distribution functions and from the presence of submaxima. For HNa-mordenites of exchange degrees below 50%, containing only hydroxyls in the broad channels, two distinct submaxima are present, thus suggesting the presence of at least two kinds of bridging hydroxyls of various acid strengths. In HNa-mordenites of exchange degrees above 50%, the hydroxyls appear in narrow channels and the distribution of ammonia desorption energy broadens on the side of higher energies. This may be related to a strong stabilization of ammonium ions inside narrow channels. The maximum concentrations of hydroxyls of desorption energies between 95 and 135 kJ mol^{-1} and between 135 and 165 kJ mol^{-1} calculated from TPD data were 3.9 and 3.3 OH per unit cell (u.c.). These values agree well with our previous IR results of concentrations of hydroxyls in broad and in narrow channels (3.7 and 2.8 OH per u.c.). The TPD data obtained for the heterogeneity of OH groups in HNa-mordenites are in accordance with the IR data concerning ammonia desorption. The IR band of OH groups restoring upon saturation of all the hydroxyls with ammonia and subsequent step by step desorption at increasing temperatures shifts to lower frequencies indicating that there are hydroxyls of various acid strengths and the less acidic hydroxyls restore first at lower desorption temperatures.

Keywords: desorption energy distribution functions, heterogeneity of Si–OH–Al groups in HNa-mordenites, infrared spectroscopic studies of ammonia desorption, temperature-programmed desorption (TPD) of ammonia

Introduction

Because of their strong acidity, H-mordenites are very active in hydrocarbon transformations. They also show interesting shape-selective properties. The commercial importance of mordenites explains why their acid properties were

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studied by numerous authors using IR spectroscopy [1–13], TPD [14–19], microcalorimetry [8, 20–28], adsorption isotherms [29], EPR studies of NO sorption [30], and also by ^{1}H MAS NMR [31, 32]. Recently we undertook a study to follow the acid properties of HNa-mordenites as a function of the degree of Na/H exchange [10, 13, 32], of the degree of dehydroxylation [11] and dealumination [12].

In HNa-mordenites hydroxyl groups may be localized both in large and in narrow channels. These hydroxyls exhibiting stretching frequencies at 3610 and 3585 cm^{-1} will be denoted in this paper as HF (high frequency) and LF (low frequency), respectively. According to our quantitative IR studies of ammonia sorption, in a series of HNa-mordenites of various exchange degree [10, 13] and in a series of dealuminated mordenites [12], the concentration of all the hydroxyls (both HF and LF) was close to the values calculated from the results of chemical analysis (amount of Al minus amount of Na). Quantitative IR studies of pyridine sorption showed that in H-mordenite of an exchange degree of 100%, about half of the protons were situated in large and half in narrow channels.

The acid strength of OH groups in HNa-mordenites was investigated by comparing the values of O–H stretching frequencies, absorption coefficients, ^{1}H MAS NMR chemical shifts and by ammonia thermodesorption experiments [11–13, 32]. It has been found that the mean acid strength increased with the degree of Na/H exchange and with the degree of dealumination (with increasing Si/Al) and decreased with dehydroxylation. One of the possible interpretations of these variations in the mean acid strength assumes the heterogeneity of bridging OH groups in H-mordenites. Some literature data, mostly obtained by microcalorimetric and IR studies [3, 8, 9, 21, 23], support the hypothesis on the heterogeneity of OH groups in H-mordenites. On the other hand, the results of Chen *et al.* [24, 25] suggested that OH groups in H-mordenites were homogeneous.

In order to obtain more data on the heterogeneity of OH groups in HNa-mordenites we started TPD and IR spectroscopic studies of ammonia desorption. TPD experiments provided detailed information about the distribution of the energies of ammonia desorption and IR studies on the acid strength of OH groups restoring upon a stepwise ammonia desorption. A series of HNa-mordenites of various exchange degrees was studied.

Experimental

The parent Na-mordenite composition $Na_{7.2}[(AlO_2)_{7.2}(SiO_2)_{40.8}]$ was synthesized by Chemie AG Bitterfeld-Wolfen (Germany). The ion exchange was carried out in NH_4NO_3 solutions at 80°C. The samples of various degrees of Na/NH_4 exchange were obtained by treatment in NH_4NO_3 solutions of various concentrations for various times. Chemical analysis (AAS) has shown that the exchange degrees of our $NaNH_4$-mordenites were: 15, 36, 47, 72 and 100%. They were denoted as HM-15, HM-36, HM-47, HM-72, HM-100, respectively.

The temperature-programmed desorption (TPD) of water and ammonia during the activation of NH4Na-mordenites was studied by using a simultaneous thermal analysis apparatus (TG-DTA-QMS, Netzsch, System STA-QMS 409/403). In all the experiments a helium flow of 6 l h^{-1}, and a heating rate of 10 K min^{-1} were used. Before thermoanalytical measurements, the zeolite samples (about 80 mg) were equilibrated over a saturated $Ca(NO_3)_2$ solution in a desiccator. The desorbed amounts of water and ammonia were recorded by means of the mass units 15 and 18 amu, respectively. At first the samples were flushed with helium at room temperature and then heated at 10 K min^{-1} to 373 K. After a period of 1 h at this temperature, the linear temperature program was started.

For IR studies, NaNH4-mordenites were pressed into thin wafers (3–5 mg cm^{-2}) and activated in situ in the IR cell in vacuum ($1\cdot10^{-6}$ Torr) at 770 K for 1 h. The IR spectra were recorded using a NICOLET MAGNA IR 550 spectrometer.

Results and discussion

TPD studies

The results concerning water and ammonia desorption from HM-100 are presented in Fig. 1A. Above 923 K, ammonia desorption was accompanied by a partial dehydroxylation of the zeolite (water desorption). Similar results have been obtained by other authors [17–19]. For HNa-mordenites of lower exchange degrees, dehydroxylation was not observed during ammonia desorption, as can be seen for HM-15 in Fig. 1B. The curves of ammonia desorption from all our HNa-mordenites are presented in Fig. 2. The increase in the exchange degree results in a widening of the desorption peak, and in its shift to higher temperatures.

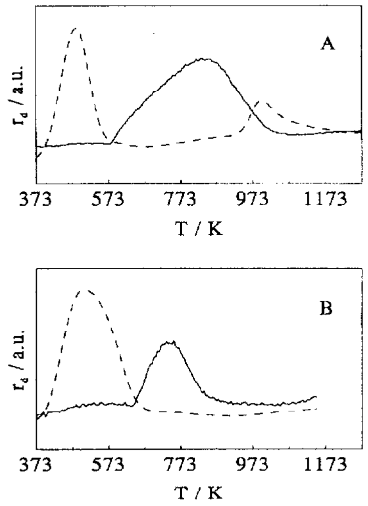

Fig. 1 TPD results for HM-100 (A) and HM-15 (B): --- water, — ammonia

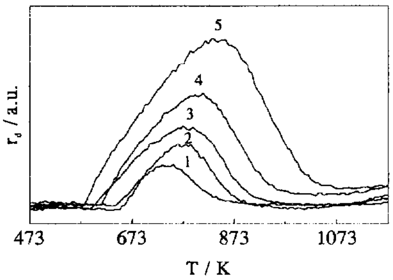

Fig. 2 TPD curves of ammonia desorption: 1– HM-15, 2 – HM-36, 3 – HM-47, 4 – HM-72, 5 – HM-100

In order to obtain detailed information about the interaction of ammonia with acidic sites a kinetic analysis of the desorption curves is necessary. It was not possible to evaluate the TPD data assuming a rate equation with constant values of pre-exponential factor and desorption energy. Therefore, a rate equation of first order with a distribution function $f(E)$ of the desorption energy E was considered [33].

$$r_d = -\frac{d\theta}{dt} = A\int_{E_{min}}^{E_{max}} \theta_l(E,T)\exp(-E/RT)f(E)dE \qquad (1)$$

where r_d is the overall desorption rate, θ is the overall degree of coverage, and A the pre-exponential factor. θ_l is the local coverage of sites characterized by a desorption energy E. E_{min} and E_{max} are limits of the range of desorption energy. The calculations were carried out by means of the program INTEG [34], which involves a regularization method for solving this integral equation. The pre-exponential factor A, required to solve Eq. (1), was taken from a previous paper (A=5·10^7 min^{-1}) [33]. The numerical solution of Eq. (1) by means of the INTEG program was carried out without any assumptions or constraints about the resulting distribution functions. Thus, negative parts in the distributions are possible. They have no physical meaning, but if the distribution is dominated by the negative parts, the local desorption model used will not describe appropriately the experimental data. The negative parts were neglected in the interpretation of the distribution functions.

The calculated distribution functions of the desorption energies are shown in Fig. 3. In case of HM-100 the desorption energy distribution (95–165 kJ mol^{-1}) agrees well with the ammonia adsorption heats determined microcalorimetrically [8, 26–28]. Furthermore, the position of the maximum for HM-47 at 129 kJ mol^{-1} corresponds to the maximum of the adsorption heat distribution at 130 kJ mol^{-1} calculated by Klyachko *et al.* [21] for NaH-mordenite with an exchange degree of 46%. Therefore, the distribution functions seem to be a useful measure to characterize the interaction strength of ammonia.

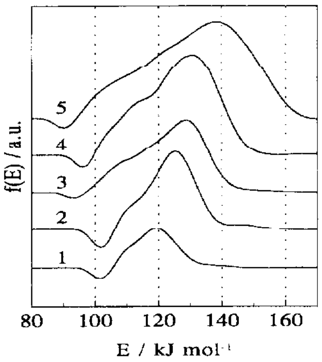

Fig. 3 Desorption energy distribution functions: 1 – HM-15, 2 – HM-36, 3 – HM-47, 4 – HM-72, 5 – HM-100

The data presented in Fig. 3 show a great heterogeneity of the acid strengths of OH groups in HNa-mordenites, which may be concluded from the width of the energy distribution and from the presence of submaxima. Two submaxima at 110 and 120 kJ mol^{-1} are present even for HM-15, the sample with the lowest exchange degree, in which all the hydroxyls are localized inside broad channels (HF) [13]. It means that two kinds of acidic HF hydroxyls exist. In HNa-mordenites with exchange degrees of 36 and 47% (Fig. 3, curves 2 and 3) and containing only HF hydroxyls [13], the same two submaxima are present, but the distribution of the desorption energies becomes increasingly wider and the maximum shifts to higher energies from 120 to 129 kJ mol^{-1} as the exchange degree increases. This suggests that the heterogeneity of the acidic hydroxyls increases.

According to our previous IR data [13], above 50% of ion exchange, the concentration of hydroxyls in large channels (HF) is constant and hydroxyls in narrow channels (LF) are formed. Our IR studies [11, 12] and also the IR results of Maache *et al.* [9] evidenced that the LF hydroxyls have a lower acid strength than those in large channels. It has also been found [12] that the ammonium ions (as well as other monovalent cations [35]) in narrow channels are very strongly stabilized by the negative charge of the oxygens in the channel walls and it explains why they decompose at higher temperatures than those in large channels. The data obtained in our TPD studies (Fig. 3) agree well with the considerations presented above. For HNa-mordenites of exchange degrees of 72 and 100% (Fig. 3, curves 4 and 5) containing also hydroxyls in narrow channels, the desorption energy distributions become increasingly wider on the side of higher desorption energies and the maximum shifts from 129 to 138 kJ mol^{-1}, indicating that the decomposition of ammonium ions inside narrow channels requires higher energy.

For a better comparison of TPD and IR data the desorption energy distributions were divided into two regions: 95–135 and 135–165 kJ mol^{-1}. The limit of 135 kJ mol^{-1} has been chosen from the width of the distribution function for HM-15.

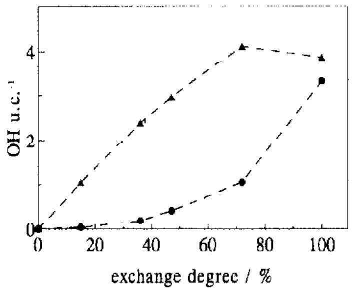

Fig. 4 Concentrations of OH groups for selected ranges of desorption energies: ▲ – 95–135 kJ mol^{-1}, ● – 135–165 kJ mol^{-1}

The concentrations of OH groups for which desorption energies are in these two regions are presented in Fig. 4 in dependence on the exchange degree. The obtained TPD results agree very well with those of our previous IR studies [13]. The maximum concentration of hydroxyls in large and narrow channels calculated from the TPD results (hydroxyls of desorption energy below 135 kJ mol^{-1} and of those above 135 kJ mol^{-1}, respectively) are 3.9 and 3.3 OH per u.c. Our IR studies of ammonia and pyridine adsorption [13] gave 3.7 and 2.8 OH per u.c., respectively. The very good agreement of TPD and IR results means that our assignment of hydroxyls of ammonia desorption energy below 135 kJ mol^{-1} to HF hydroxyls in large channels and those of desorption energy above 135 kJ mol^{-1} to LF hydroxyls in narrow channels was correct.

The main conclusion of our TPD studies of ammonia desorption concerns, however, the problem of heterogeneity of OH groups (and specially of HF OH in large channels) in HNa-mordenites. As stated above, this was evidenced by the presence of two submaxima of the distribution of desorption energy (Fig. 3) and by the broadening of the energy distribution as the exchange degree increased from 15 to 47% (HM-15: 29 kJ mol^{-1}, HM-47: 53 kJ mol^{-1}). This conclusion will be now supported by the IR studies of OH groups.

IR studies

Further information on the heterogeneity of OH groups in mordenites was obtained by comparing the frequencies of IR bands of hydroxyls restoring upon desorption of ammonia at increasing temperatures. If OH groups are heterogenous, ammonia desorbs from less acidic hydroxyls at lower temperatures and from more acidic ones at higher temperatures. It is accompanied by a shift of the OH band to lower frequencies. On the other hand, such a shift is unexpected in the case of homogenous hydroxyls. The spectra of OH groups restoring upon desorption of ammonia from HM-100 are presented in Fig. 5. According to our earlier IR results [12], and also our TPD results presented above, the HF hydroxyls (band 3610 cm^{-1}) restore first upon ammonia desorption at relatively low

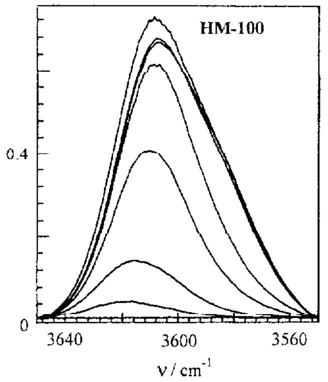

Fig. 5 IR spectra of OH groups in HM-100 restoring upon ammonia sorption and subsequent desorption: from bottom to top 320, 470, 520, 570, 620, 670 and 720 K, and activated mordenite

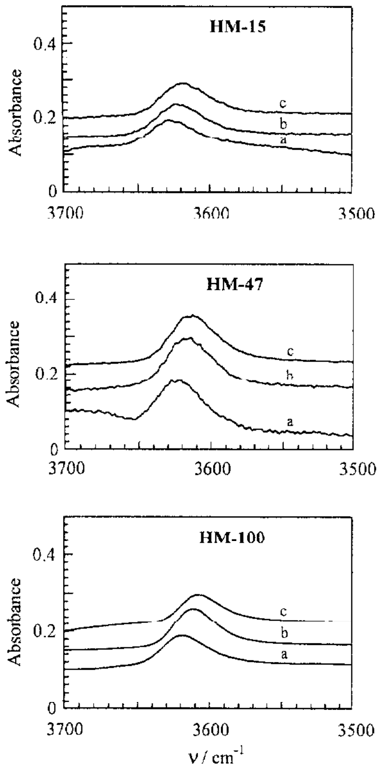

Fig. 6 OH groups in HM-15, HM-47 and HM-100 restoring at the desorption of ammonia: a: spectrum recorded upon desorption at 470 K minus spectrum recorded upon desorption at 320 K; b: spectrum recorded upon desorption at 520 K minus spectrum recorded upon desorption at 470 K; c: spectrum recorded upon desorption at 570 K minus spectrum recorded upon desorption at 520 K

temperatures (470–570 K), and LF ones (3585 cm^{-1}) at higher temperatures (above 570 K). The shift of the OH band of HF hydroxyls from 3620 to 3610 cm^{-1} suggests the heterogeneity of these OH groups. This shift is best seen in the difference spectra (Fig. 6) being the result of subtraction of spectra recorded after two subsequent desorption steps. The presented data concern only relatively low desorption temperatures: 470, 520 and 570 K at which ammonia desorbs practically only from HF hydroxyls. At 570 K almost all the HF hydroxyls are restored. The data for HM-15, HM-47 and HM-100 are presented: the sample of the lowest, and highest exchange degrees as well as for HM-47 containing the highest possible concentration of HF hydroxyls and no LF ones. According to the data presented in Fig. 6, the frequency differences (Δ_v) between hydroxyls restoring at the lowest temperature (470 K) and the highest temperature (570 K) were: 8, 10 and 13 cm^{-1} for HM-15, HM-47 and HM-100, respectively. These differences also indicate that the HF OH groups on HNa-mordenites are heterogeneous. It should be noted that in strongly dealuminated H-mordenite of Si/Al=120 in which OH groups were homogeneous, the Δ_v was only 2 cm^{-1} [12].

Our conclusion on the heterogeneity of OH groups in mordenites agrees well with the results of microcalorimetric studies [3, 8, 21, 23] as well as with the results of IR studies of CO adsorption [9]. It explains also the dependence of the mean acid strength of OH groups on the exchange degree [13, 32], dehydroxylation [11] and dealumination degree [12].

Most probably, the reason for the heterogeneity of OH groups in H-mordenites is the presence of Si–OH–Al groups of various numbers of Al atoms close to the bridge. Indeed, ^{29}Si MAS NMR showed [4, 36] the presence of three signals: Si(0Al), Si(1Al) and a weaker one, Si(2Al). Because Si(0Al) cannot create bridging hydroxyls, two kinds of hydroxyls are expected: $(SiO)_3Si–OH–Al(OSi)_3$ and a smaller amount of $(SiO)_2(AlO)Si–OH–Al(OSi)_3$. The latter are less acidic because of the lower electronegativity of Al in comparison with Si. Another reason for the heterogeneity of OH groups in HNa-mordenites may be the presence of Si–OH–Al groups of various bridge geometries. In mordenites there are four crystallographically nonequivalent *T* atom positions and ten O atom positions. Quantumchemical MNDO calculations evidenced that bridge geometry influences strongly the acid strength of bridging hydroxyls [36].

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