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A TPD and IR study of the surface species formed from ammonia on zeolite H-ZSM-5, H-mordenite and H-beta

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Abstract

Ammonia was found to react with the Brönsted acid sites of H-zeolites forming NH_4^+ ions, coordinate to Lewis acid sites and, at higher coverage, to NH_4^+ ions forming protonated ammonia associations, such as, $NH_4^+(NH_3)_n$. Besides the Lewis acid NH_4^+ ions, one kind of strong Lewis acid site was detected in zeolite H-ZSM-5 and H-mordenite, while strong and weak Lewis acid sites were substantiated to exist in zeolite H-beta. The strong acid Lewis sites were assigned to extra-framework alumina (EFAl) species generated by the partial dehydroxylation of the H-zeolites. The weak Lewis acid sites of H-beta were tentatively ascribed to framework Al atoms coordinatively unsaturated due to framework defects.

Keywords: Zeolite acidity; Acidity of H-beta; Adsorption of NH_3; TPD and IR spectra

1. Introduction

Acid sites of zeolites are often characterized by temperature-programmed desorption using ammonia as basic probe molecule (NH_3–TPD) [1–4]. On the NH_3–TPD curves of H-zeolites, such as, H-ZSM-5 and H-mordenite peaks appear usually well resolved in two temperature regions referred to as low-temperature (LT) and high-temperature (HT) peaks. For some zeolites, like H-beta, the LT and HT peaks may extensively overlap. In general, the HT peak is attributed to decomposition of NH_4^+ ions formed over strong acid Brönsted sites (B sites). Some Lewis sites (L sites), related to the presence of specific kinds of extra-framework Al-species [5], were found to have acid strength close to that of the protonic B sites. If both strong acid B and L sites are present, they release ammonia in the HT region [1–3].

Due to the catalytic significance of strong acid sites much attention was paid to the HT peaks, therefore, their assignment to sorption sites and species of adsorbed ammonia can be considered well established. In contrast, the LT peaks were usually neglected as unimportant or controversial ideas were forwarded about their origin. For instance, they were ascribed to desorption of ammonia bound to weak acid Brönsted [2], or Lewis sites [3] or to silanol groups [1]. Recently Lunsford et al. [6] presented MAS NMR evidence for the formation $NH_4^+(NH_3)_n$ ($n = 1-3$) associations from ammonia in zeolite H–Y. According to Niwa et al. [7] desorption of NH_3, hydrogen-bound to NH_4^+ cations may proceed at relatively low temperature and give rise to the LT TPD peak. Recently

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the adsorption of NH_3 in zeolite H-ZSM-5 was studied by infrared (IR), frequency response (FR) and TPD methods [4]. The results reported strongly support the last mentioned peak assignment.

While ammonia can undoubtedly form $NH_4^+(NH_3)_n$ associations in H-ZSM-5 and H-mordenite, present work suggests that ammonia weakly bound in zeolite H-beta must be ascribed to a different kind of species.

2. Experimental

2.1. Materials

The composition of zeolite H-ZSM-5 (T-3ZIPC, VEB Chem. Komb. Bitterfeld-Wolfen, Germany), H-mordenite (LZ-M6, UOP), and H-beta (Valfor CP, PQ Corp.), used in the present study, was $H_{0.995}Na_{0.005}(AlO_2)(SiO_2)_{15.6}$; $H_{0.963}Na_{0.037}(AlO_2)(SiO_2)_{6.8}$; and $H_{0.997}Na_{0.003}(AlO_2)(SiO_2)_{12.5}$, respectively. The tetrahedrally coordinated framework Al atom (Al_F) concentration of the samples is given in Table 1. It was assumed that each of the Al_F atoms could be associated with an ion exchange site. The NH_4^+-form of the zeolite was thermally decomposed and the ion-exchange capacity was determined by measuring the amount of ammonia evolved. The Al_F concentrations roughly corresponded to the total Al concentrations, except for H-beta where Al_F was much smaller (Table 1).

2.2. NH_3–TPD

The NH_3–TPD spectra were measured using a conventional flow-through reactor connected to a thermal conductivity detector (TCD). About 150 mg of sample was activated in flowing O_2 at 773 K for 1 h, then cooled to room temperature under continuous evacuation. The sample was equilibrated with NH_3 gas at 13.3 kPa pressure and then the weakly adsorbed NH_3 was removed by 30 min evacuation at 373, 423, or 523 K. The reactor temperature was ramped up at a rate of 10 K min^{-1} while a 20 cm^3 min^{-1} helium flow was passed through the reactor, a dry ice trap and the TCD. In order to separate the partially overlapping peaks the TPD spectra were resolved to component peaks, as suggested by Niwa et al. [8], using combinations of Gauss and Couchy peaks to find the best fit.

2.3. IR measurements

Self-supporting wafers of about 6–10 mg cm^{-2} thickness were pressed from the zeolite powders and placed into a conventional IR cell equipped with a built-on furnace. The wafer was pretreated, contacted with NH_3, and evacuated at different temperatures. The conditions corresponded to those applied before the TPD runs. The spectrum of adsorbed NH_3 was recorded at room temperature after each evacuation step using a Nicolet 5PC FTIR spectrometer.

The IR spectra of adsorbed pyridine (Py) was determined after contacting the pre-treated wafer with

Table 1
Characterization of the H-zeolites

Sample	Al^a and $(Al_F)^b$ (mmol/g)	B/L^c arbitrary units	HT $peak^d$		LT $peak^e$	
			B (mmol/g)	L (mmol/g)	L (mmol/g)	$B + 2L^f$ (mmol/g)
H-ZSM5	$0.99 (0.95)^b$	11.0/1.1	0.90	0.080	0.36	1.06
H-mordenite	2.06 (2.05)	9.9/0.3	2.08	0.023	0.21	2.12
H-beta	1.21 (0.77)	5.4/3.9	0.514	0.103	0.275	0.72

[a] From chemical analysis.

[b] Framework Al contents taken as equivalent to the ion exchange capacity for NH_4^+ ions.

[c] Brönsted (B) to Lewis (L) acid site concentrations given as the integrated intensities of the 1550 and 1450 cm^{-1} bands of adsorbed pyridine.

[d] Amounts of NH_3 desorbed above about 700 K, i.e. in the high-temperature (HT) TPD region. The TPD peaks in the HT region were assigned to desorption of NH_3 bound to strong Brönsted (B) and Lewis (L) acid sites. Before the TPD runs samples were pre-treated in O_2 flow at 773 K for 1 h, equilibrated with NH_3 at 298 K and 13.3 kPa pressure, and evacuated at 423 K for 30 min.

[e] The amount of ammonia desorbed below about 700 K, i.e. in the low-temperature (LT) TPD region.

[f] Calculated from the HT TPD data.

Py vapor of about 0.26 kPa pressure at 298 K and removing weakly bound Py by 30 min evacuation at 423 K.

3. Results

NH_3–TPD curves of zeolites are shown in Fig. 1. A HT peak appeared regardless of the temperature of evacuation prior to the TPD run. This peak seems to consist of at least two components: a dominating large peak and a smaller peak with maximum at somewhat higher temperature (see resolved curves in Fig. 1). For the samples pre-evacuated at 523 K peaks were detected only in the HT region. However, when ammonia was pumped off at lower temperatures, also weakly-bound ammonia remained in the zeolite that was giving rise to a LT TPD peak. The LT peak was comprising again of one or more component peaks (Fig. 1). The amount of NH_3 corresponding to each component peak was given in Table 1.

IR spectra obtained from adsorption of NH_3 on the H-zeolites are shown in Fig. 2. For NH_3 bound to zeolite H-ZSM-5 overlapping bands were observed in the region of the bending vibrations at 1398, 1452, and 1488 cm^{-1} (Fig. 2A). Similar bands were obtained from adsorption of NH_3 on H–Y and were assigned to the ν_4 modes of the $NH_4{}^+$ ion coordinated to the zeolite framework [6]. It should be noted that after the same treatment that was applied before the IR spectrum was recorded, i.e. NH_3 adsorption and evacuation at 523 K, only the HT peak appeared on the TPD curve. After evacuation at lower temperatures both the TPD and the IR results obtained were different. On the TPD curves a LT peak appeared, and the IR envelope could not be properly fitted by only three component peaks as before. The ν_4 bands shifted to higher wavenumber and, concomitantly, an additional component band appeared at the high frequency side of the envelope (Fig. 2A).

From NH_3 adsorption on H-mordenite a broad, featureless absorption band was obtained in the 1350–1550 cm^{-1} wavenumber region (Fig. 2B). If less ammonia was removed by applying lower evacuation temperature (<523 K) broader band appeared with center at higher frequencies. It should be noted again that the appearance of the higher frequency band corresponded to those pre-treatments, which resulted also in the appearance of the LT TPD peak (Fig. 1B).

Three ν_4 component bands of the $NH_4{}^+$ ion were resolved from the spectrum of ammonia bound to H-beta (Fig. 2C). However, for this sample, the appearance of the LT peak on the TPD curve was not paralleled by a significant broadening and shift of the ν_4 envelope (Figs. 1C and 2C).

The integrated intensities of the bands obtained at 1550 and 1450 cm^{-1} from adsorption of Py on the H-zeolites were determined. It is well known that the 1550 cm^{-1} band stems from Py protonated on B site, while the band at 1450 cm^{-1} is assigned to Py

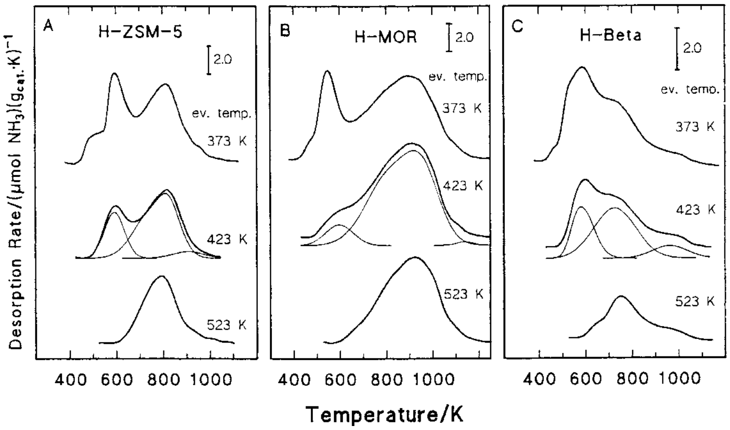

Fig. 1. NH_3–TPD spectra obtained on (A) H-ZSM-5, (B) H-mordenite, and (C) H-beta zeolite. Samples were pretreated in O_2 flow at 773 K, evacuated and cooled to 293 K. Ammonia was adsorbed at 13.3 kPa and 293 K. Prior to the TPD run the sample was evacuated at the indicated temperature for 30 min. Carrier gas: He at a flow rate of 20 cm^3 (NTP) min^{-1}. Heating rate: 10 K min^{-1}.

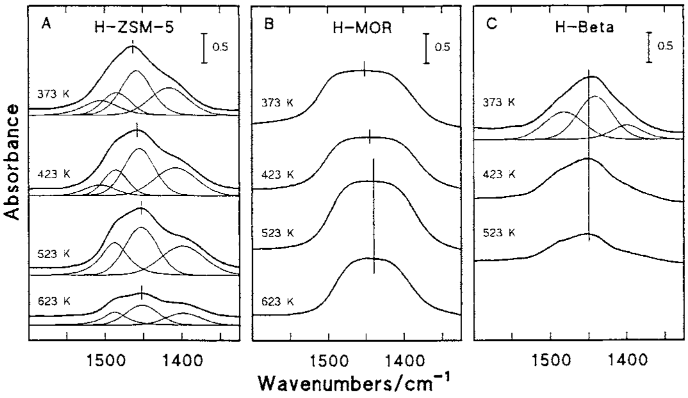

Fig. 2. Infrared spectra (thick lines) obtained from adsorption of ammonia in zeolite (A) H-ZSM-5, (B) H-mordenite, and (C) H-beta. The sample pretreatment was the same as given at Fig. 1. After adsorption of NH_3 at 293 K, samples were evacuated at the indicated temperatures for 30 min. A spectrum was taken after each evacuation at 293 K. Component bands obtained by computer band resolution are given under the spectra (thin lines).

molecules coordinated to L sites. The intensity ratio of these bands was determined to estimate the relative amount of the B and L type sorption sites (Table 1).

4. Discussion

In the process of zeolite dehydroxylation two B sites are annihilated and a positively charged EFAl species is formed that is a strong acid L site [9]. It follows from this stoichiometry that the original number of the framework Al atoms (Al_F) must correspond to the number of the B sites plus two times the number of the L sites (B + 2L). Earlier reports [1,3] suggested that the two components of the HT NH_3–TPD peak of H-zeolites stem from decomposition of the NH_4^+ ions and desorption from the strong acid L sites. For the H-ZSM-5 and the H-mordenite the ratio of the integrated intensities of the HT component peaks was found to be in reasonably good agreement with the intensity ratio of the bands assigned to B- and L-bound Py supporting above assignment of the HT peaks (Table 1). Thus, assuming that the amount of B and L sites was equivalent with the amount of NH_3 giving the larger and smaller HT component peaks the B + 2L values were calculated. For the H-ZSM-5 and H-mordenite samples the values obtained roughly agreed with the Al concentration ($Al \approx Al_F$) of these zeolites (Table 1).

The interaction of ammonia and the B sites results in the formation and stabilization of NH_4^+ ions. The stabilization of the ion takes place due to its coordination to the lattice oxygen atoms of zeolite. The three ν_4 modes of the bound NH_4^+ ion can give rise to two or three bands in the 1350–1550 cm^{-1} region [10]. Depending on the homogeneity and accessibility of lattice oxygen atoms, different band structures can be observed for different zeolites. The NH_4^+ cations, which are most probably in homogeneous environment in H-ZSM-5 and H-Beta, show three relatively well-defined ν_4 bands. In less homogeneous environment, such as, in H-mordenite the spectrum is obtained as an envelope containing numerous, slightly different, overlapping NH_4^+ bands. Interaction of the NH_4^+-ions and NH_3 via hydrogen bonds results in a shift of the ν_4 bands towards lower frequencies. The shift was most obvious in the case of the H-ZSM-5 sample, when an additional component band appeared at the low frequency side of the envelop where overlapping could not take place.

According to earlier suggestions the decomposition of $NH_4^+(NH_3)_n$ associations can account for the LT peak on the TPD spectra [4,7]. The relatively large LT peaks observed with zeolites H-ZSM-5 and H-mordenite indicate that significant amount of NH_3 was adsorbed in excess to that equivalent with the B and L sites [4,11]. An LT peak appeared on the TPD spectra of those samples that were characterized with a shifted NH_4^+ deformation band. This finding supports the assignment of the LT peak to desorption of NH_3 from NH_4^+ ions.

Above considerations, giving a consistent interpretation of the data obtained for H-ZSM-5 and H-mordenite, could not be applied directly for zeolite H-beta. The number of acid sites calculated from the HT peak as B + 2L corresponded to the number of Al_F ion exchange sites but the amount of ammonia released at HT was not enough to account for the total Al content of the sample (Table 1). It should be noticed that the Al_F concentration of the parent zeolite beta sample was smaller than the total Al concentration. The amount of NH_3, desorbed from the strong acid L sites was equivalent with about 14% of the Al_F and to about 8.5% of the total Al content (Table 1). In contrast the B/L ratio, determined by IR spectroscopy using Py as probe molecule, suggested that about 40% of the sorption sites were of L type. Obviously not all the L sites of H-beta can be associated with the strong acid L sites releasing NH_3 at HT. Moreover, in the case of H-beta the IR shift of the NH_4^+ bands was absent, although the LT peak on the TPD spectrum of the sample appeared. Thus, in the case of H-beta, the LT peak can not be due to decomposition of $NH_4^+(NH_3)_n$ associations. This infers that zeolite H-beta must carry weak acid L sites different from the L site NH_4^+ ions. These sites are also different from the strong acid L sites that were probably formed from B sites associated with Al_F atoms. These weak L sites, already present in the original H-beta sample, can be coordinatively unsaturated Al atoms in a defective zeolite framework [12]. However, neither the origin nor the structure of these weak acid L sites is exactly known yet.

5. Conclusions

The amount of Al atoms, equivalent to the ion-exchange capacity of the as-synthesized zeolites, such as, mordenite, ZSM-5, and beta, can account for the amount of strong acid sites in the partially dehydroxylated H-form of the zeolites taking the stoichiometry of the Lewis site formation from the Brönsted acid sites (2B → L) into consideration. In contrast to zeolites H-mordenite and H-ZSM-5, a significant fraction of the Al atoms does not represent ion-exchange site in zeolite H-beta. These sites show weak Lewis acid character.

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