Distribution of Acid Sites in Mordenite

Katsuki Suzuki,[†] Naonobu Katada,[†,††] and Miki Niwa*[†]
[†]*Department of Materials Science, Faculty of Engineering, Tottori University,*
4-101, Koyama-minami, Tottori, 680-8552
[††]*PRESTO, Japan Science and Technology Agency, Kawaguchi 332-0012*

(Received November 25, 2004; CL-041427)

Brønsted acid sites of mordenite are preferentially located on the site of 8-member ring, and these are stronger than on the 12-member ring.

It has previously been known that mordenite has the very strong acid site. Its strength, 150 kJ mol^{-1}, which was measured by ammonia TPD (temperature-programmed desorption) as the heat of ammonia adsorption is the greatest among the studied zeolites.[1] It seems that mordenite has relatively homogeneous acid strength; however, the distribution of the acidity has been investigated. Mordenite has four kinds of T site, named T1 to T4, as shown in Figure 1; Alberti[2] studied the preference of Al location in these T sites and concluded the T3 site in the 8-member ring as the most preference site. Zholobenko et al.,[3] Wakabayashi et al.,[4] and Datka et al.[5] reported two kinds of Brønsted OH bands in mordenite, ascribable to those in 12- and 8-membered rings. In this paper, we study the acidic property of mordenite using IRMS-TPD of ammonia, a new technique for characterization, in which IR (infrared) and MS (mass spectroscopy) work together, and the site and strength of Brønsted OH bands are clearly revealed.

IR (Perkin-Elmer Spectrum-One) and MS (Pfeiffer QME200) were connected with a vacuum line kept at 25 Torr (1 Torr = 0.133 kPa), to which helium was flowed as the carrier

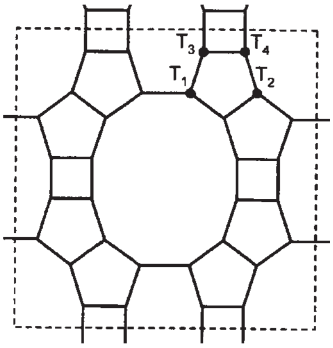

Figure 1. Structure of mordenite.

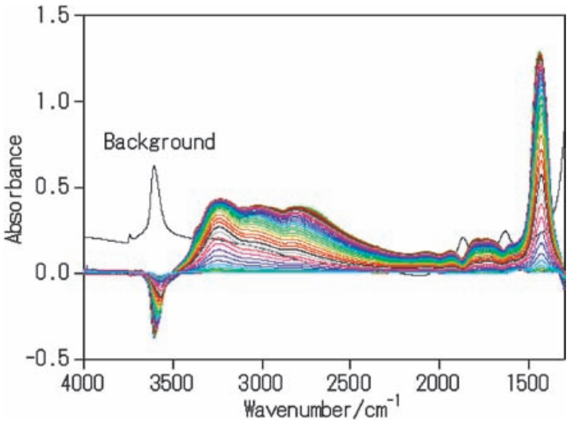

Figure 2. Difference spectra of ammonia on the in situ prepared HM-15 during the elevation of temperature from 373 to 773 K. Background spectrum was obtained at 373 K before the adsorption of ammonia.

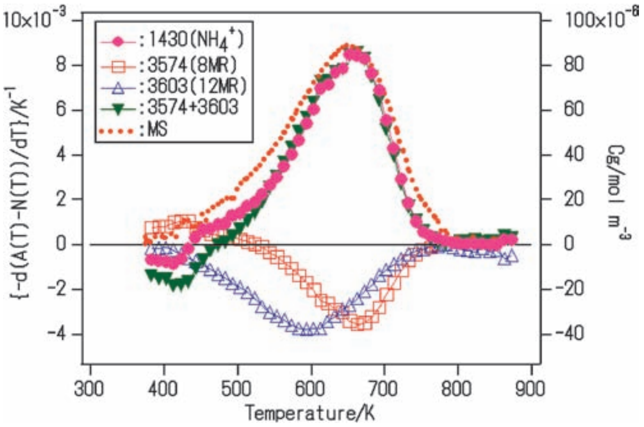

Figure 3. IR-TPD of ammonia on the in situ prepared HM-15 for the IR bands shown in the corner: MS-measured TPD (change of desorbed ammonia concentration, Cg) was shown for a comparison.

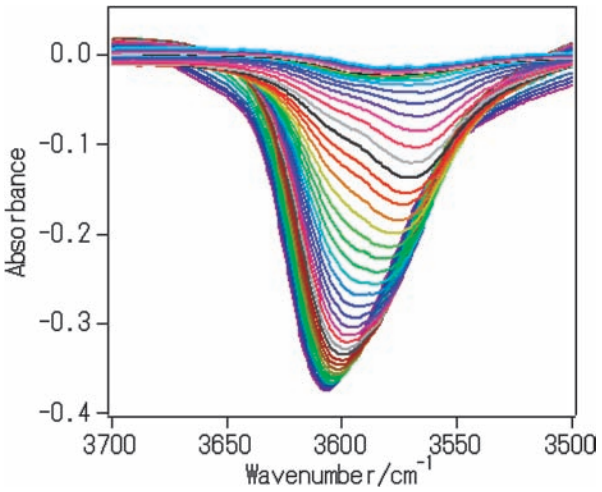

Figure 4. Enlarged portion of OH band in Figure 2.

(flow rate, 125 mL min^{-1}). IR beam was transmitted to the self-compressed disk (about 8 mg and 10 cm in diameter). After evacuation of the sample at 873 K, IR spectra were recorded before and after ammonia adsorption at 373 K during the elevation of temperature from 373 to 873 K in a ramp rate of 10 K min^{-1}, and the difference spectrum was calculated. In order to be compared with MS-measured TPD (m/e, 16), a differential change of the absorption intensity was calculated with respect to the measured temperature at the selected wave number (hereafter, called IR-TPD). Because the ammonium-type zeolite retains the solid acid site in the most unperturbed conditions,[6] in situ prepared HM-15 was used for the measurement; an Na-form mordenite with $\mathrm{Si/Al_2} = 15$ (Reference Catalyst, Catalyst Society of Japan, JRC-Z-M15) was ion-exchanged,[6] and evacuated in the IR cell at 873 K as above. The degree of exchange with $\mathrm{NH_4}^+$ was 99%.

Figure 2 shows the difference spectra of ammonia on the in situ prepared HM-15. A strong absorption ascribable to the bending vibration of $\mathrm{NH_4}^+$ cation was observed at 1430 cm^{-1}. On the other hand, a negative peak was observed in the OH region, because the $\mathrm{NH_4}^+$ cation was formed from the Brønsted OH and ammonia. IR-TPD was calculated for the $\mathrm{NH_4}^+$ band at 1430 cm^{-1}, as shown in Figure 3.[7] IR-TPD of the $\mathrm{NH_4}^+$ thus calculated was almost analogous to the MS-measured ammonia TPD, showing that the acid sites were predominantly Brønsted type.

On the other hand, the recovery behavior of the negative OH band during the elevation of temperature showed a shift of the band. As shown in Figure 4, the negative absorption was observed at 3603 cm^{-1} before the elevation (373 K), but the position shifted gradually to lower wave number, e.g., 3574 cm^{-1} at 773 K. The shift of the negative OH band shows that ammonia was bound to different types of OH with different strengths. Obviously, the weaker Brønsted acid site is located at the OH of the high wave number, and the stronger one at the low wave number. Therefore, IR-TPD was calculated for the two OH bands at 3603 and 3574 cm^{-1}, as shown in Figure 3. A linear combination of IR-TPD of these two bands[8] could be fitted to that of $\mathrm{NH_4}^+$. This shows that the Brønsted acid sites consisted of these two types of OH.

The OH bands of mordenite have been identified at 3612 and 3575 cm^{-1} as those located in the 12- and 8-member rings of the mordenite structure, respectively.[3,4] Therefore, on the basis of the finding above, it is concluded that the Brønsted acid site on the 8-member ring is stronger than that of 12-membered ring. The conclusion is consistent with the finding by Zholobenko et al.[3] who used ammonia probe. Furthermore, it is recognized that the Brønsted acid site is located at the 8-member ring preferentially, because the IR-TPD of the 8-member ring hydroxy more closely related to that of $\mathrm{NH_4}^+$. By the curve fitting as above, the simulated profile of IR-TPD resembled that of $\mathrm{NH_4}^+$, and relative population of two Brønsted acid sites was in proportion of 28:72 for 12-:8-member ring sites. Preference of the Brønsted acid on the 8-member ring is consistent with the previous study by Alberti,[2] claiming the preferential location of Al cation in the T3 site on the 8-member ring. On the basis of a study using ammonia and pyridine probes, Datka et al.[5] reported that 3.0 H^+ were situated inside the 12-ring channels among total 7.2 H^+ in H-mordenite. Kato et al. reported that the distribution of Al in the mordenite synthesized in the presence of fluoride ion was different from that prepared under the usual conditions.[9] Furthermore, it is found that $\mathrm{NH_4}^+$ is preferentially exchanged with Na^+ in the 12-member ring, and the distribution of the Brønsted acid site depends on the ion-exchange degree.[10] Thus, various conditions of mordenite species have to be taken into consideration.

Mordenite is known as a zeolite with a large pore channel of 12-member ring, and the presence of the strong acid site is remarkable as well. However, the strong Brønsted acid site is preferentially located on the 8-member ring. This conclusion strongly has an impact on the understanding of the catalysis in mordenite as well as the acidity of zeolite.

References and Notes

1 M. Niwa, N. Katada, M. Sawa, and Y. Murakami, *J. Phys. Chem.*, **99**, 8812 (1995).
2 A. Alberti, *Zeolites*, **19**, 411 (1997).
3 V. L. Zholobenko, M. A. Makarova, and J. Dwyer, *J. Phys. Chem.*, **97**, 5962 (1993).
4 F. Wakabayashi, J. Kondo, A. Wada, and K. Domen, *J. Phys. Chem.*, **97**, 10761 (1993).
5 J. Datka, B. Gil, and A. Kubacka, *Zeolites*, **17**, 428 (1996).
6 N. Katada, T. Kanai, and M. Niwa, *Microporous Mesoporous Mater.*, **75**, 61 (2004).
7 A (T) and N (T) in the ordinate are absorbance of the infrared band measured at temperature T before and after ammonia adsorption, respectively. Negative value of the differential change is used for a comparison with the MS-measured TPD.
8 Simulated TPD profile was calculated from the equation, $-2(I_{3574}) - 0.6(I_{3603})$, where I_x means the IR-TPD of the OH bands at the wave number $x\,\mathrm{cm}^{-1}$.
9 M. Kato, K. Itabashi, A. Matsumoto, and K. Tsutsumi, *J. Phys. Chem. B*, **107**, 1788 (2003).
10 K. Suzuki, M. Niwa, and N. Katada, unreported.