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Infrared Spectroscopic Study of High Temperature Behavior of the Brønsted Acidic Hydroxyl Groups on Zeolites

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Quantitative analysis of the high-temperature behavior of the Brønsted acidic hydroxyl groups on H-ZSM-5 and H-mordenite zeolites was conducted by in situ IR spectroscopy. The integrated intensity of the Brønsted acidic hydroxyl band on H-ZSM-5 was decreased to 67% at 873 K compared with that at room temperature. This was considered to reflect the deprotonation of hydroxyls at high temperature. Attributing the decreased OH groups at high temperature region to the conversion to IR inactive dissociated species, we estimated the energy difference between the nondissociated and dissociated hydroxyls as 24 kJ mol^{-1} on H-ZSM-5.

Infrared (IR) spectroscopy is a powerful method to investigate the properties of zeolites.[1) In general, in situ IR observation of probe molecules adsorbed on hydroxyl groups in zeolite pores is a representative method for the direct characterization of zeolites. Other groups and ours have employed IR for the characterization of the H-form of zeolites using N_2, CO, and other small probes in order to probe only the strong acid sites.[2—10) More practical investigations are, however, on the behavior of zeolites at high temperature, because the substantial catalytic reactions of zeolites occur above 673 K. For example, the hydrocarbon cracking and alkane conversion by H-ZSM-5 occur above 773 K.[11)

Although the characterizations of the properties of zeolites at high temperature are more desirable, there is an experimental problem for quantitative investigation in IR method. The emission from a sample becomes more intense at higher-temperatures and it tends to cause the saturation of the detector. Consequently, the detector response loses linearity. Without a solution to this problem, the quantitative analysis of IR spectra measured at high-temperatures is not possible.

In this paper, the high temperature behaviors of Brønsted acidic OH groups on H-ZSM-5 (MFI) and H-mordenite (MOR) were quantitatively studied, which was enabled by an improved experimental method.

Experimental

Materials. H-ZSM-5 (Si/Al = 50) and H-mordenite (Si/Al = 10) were provided by Sumitomo Chemical Industry Co., Ltd. and by The Catalysis Society of Japan, respectively.

Sample Preparation. For the sake of in situ IR investigations, each sample was pressed into a self-supporting disk, then placed in a quartz-made cell connected to a conventional closed-circulation system. All samples were pretreated at 773 or 873 K with exposure to 100 Torr of O_2 gas (1 Torr = 133.322 Pa) for 1 h, and then evacuated at the same temperature for 1 h. The temperature of the measurement never exceeded the pretreatment temperature of the sample.

FT-IR Measurements. IR investigations were carried out using a JASCO FT/IR-7000 spectrometer with an MCT detector. All spectra were collected with 4 cm^{-1} of resolution and 64 average scans. An IR spectrum of a vacant cell under vacuum measured at room temperature was used as a background spectrum.

In situ IR measurement was performed in the temperature range from room temperature to 773 or 873 K. The maximum intensity of the interferogram of FT-IR at the zero path difference ($I_{\max}$) was observed as being dependent on the sample temperature. The variation of $I_{\max}$ by temperature rising is shown in Fig. 1A (curve 1). Although $I_{\max}$ should be theoretically unaffected by the sample temperature, the result shows that $I_{\max}$ sharply decreases with increasing the sample temperature: The IR emission from the sample increases the total amount of the insident light to the detector and causes the aggravation of the linearity of the detector. For one to recover the linear responsibility, the excess light should be eliminated before an incident to the detector.

In this work, polymer-made meshes were installed in front of the detector to control the intensity of the light. In consequence, the aggravation of linear responsibility of the detector was recovered, where the temperature dependent of $I_{\max}$ was moderated (Fig. 1A, curve 2). However, it was still not constant. Therefore, a calibration curve was made by use of the OH-stretching band of silanol of amorphous silica to eliminate the temperature dependent factor on the integrated intensity of the hydroxyl bands on zeolites. While bands of the acidic OH groups of zeolites are detected in the region of 3800—3500 cm^{-1}, the silanol band (Si–OH) of amorphous silica was observed at 3748 cm^{-1}. Calibration curves were obtained by observation of the silanol band from room temperature to 873 K both over integrated intensity and peak top intensity of the band (Fig. 1B).

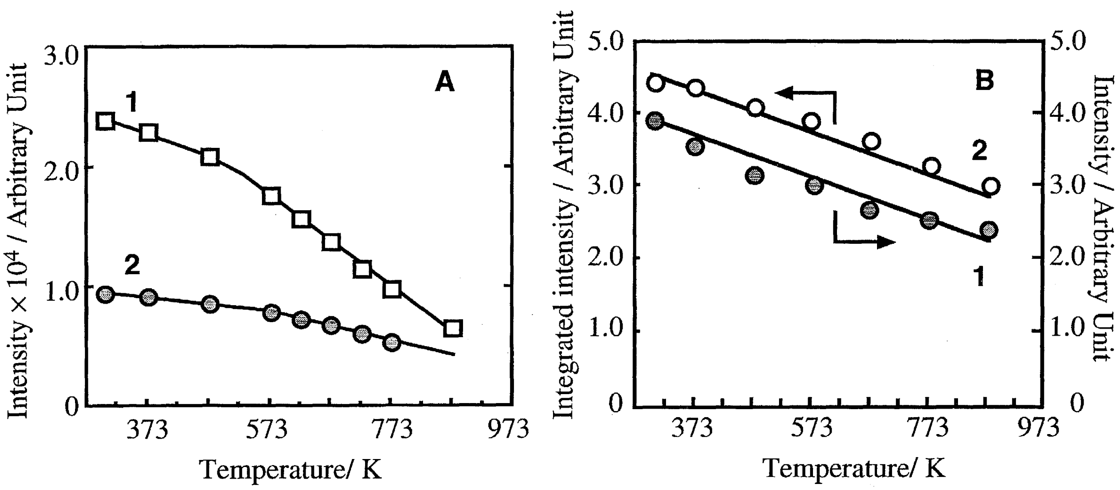


Fig. 1. A: change of the intensity I_{max} at the zero path difference peak of the interferometer; usual method (curve 1) and with meshes (curve 2). B: calibration curves of the change of integrated intensity (curve 1) and intensity (curve 2) of hydroxyl groups on amorphous silica at various temperatures (meshes equipped).

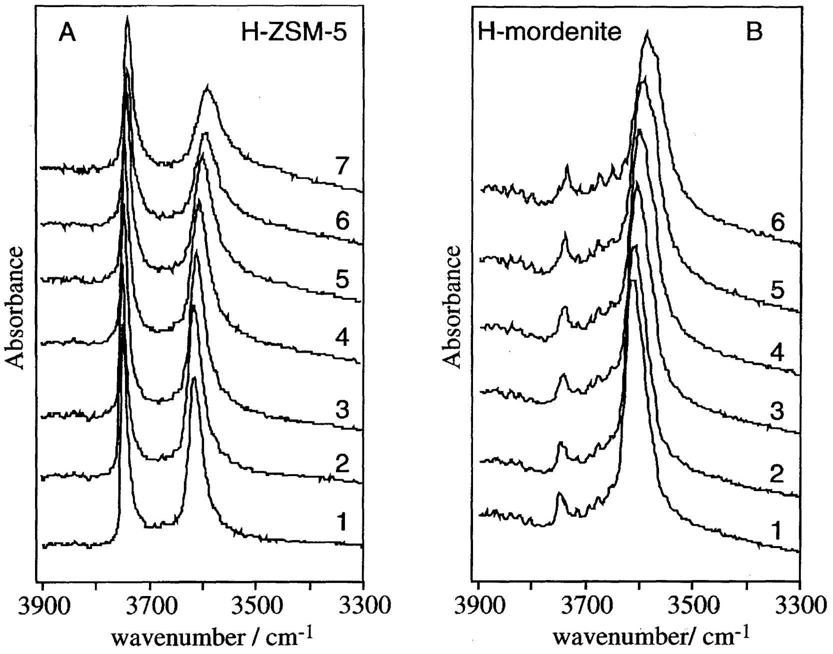


Fig. 2. Infrared spectra of H-ZSM-5 and H-mordenite at room temperature (1), 373 K (2), 473 K (3), 573 K (4), 673 K (5), 773 K (6), and 873 K (7).

Results and Discussion

The IR spectra in OH stretching region of the Brønsted acidic hydroxyl groups on H-ZSM-5 and H-mordenite at various temperatures are shown in Figs. 2A and 2B. The hydroxyl band at 3748 cm^{-1} which originated from silanol groups of zeolites was detected at the same position as that of amorphous silica. Likewise, the Brønsted acidic hydroxyl bands (Si(OH)Al) were observed at 3610 and 3616 cm^{-1} in H-mordenite and H-ZSM-5, respectively. It was clearly observed for both zeolites that the acidic OH bands were broadened with decreasing intensity and shifted as the temperature was elevated. For acidic OH bands of both H-ZSM-5 and H-mordenite as well as silanol band of H-ZSM-5, the same spectra were observed at each temperature during temperature increasing and decreasing (Fig. 3), indicating that the change is reversible and that no chemical reactions such as dehydroxylation occurred in Fig. 2. The non-acidic silanol bands were also varied by temperature change due to the incomplete elimination of the detector linearlity at high temperatures. For this reason, the variation curves of the Brønsted acidic hydroxyl bands were calibrated by using those of the silanol band below, as mentioned in the experimental section.

The changes of the peak top intensity and full width at half-maximum (FWHM) of the Brønsted acidic hydroxyls of H-ZSM-5 and H-mordenite zeolites after calibration by silanol band are illustrated in Fig. 4. Both the intensity and FWHM changes were slightly greater on H-mordenite than on H-ZSM-5. The integrated intensity is reduced in total by

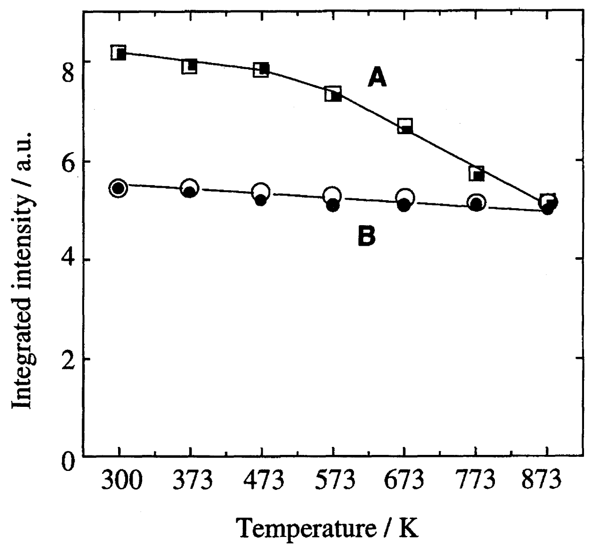


Fig. 3. Change of the integrated intensity of the acidic OH band (A) and silanol band (B) during temperature increasing (open symbols) and decreasing (closed symbols).

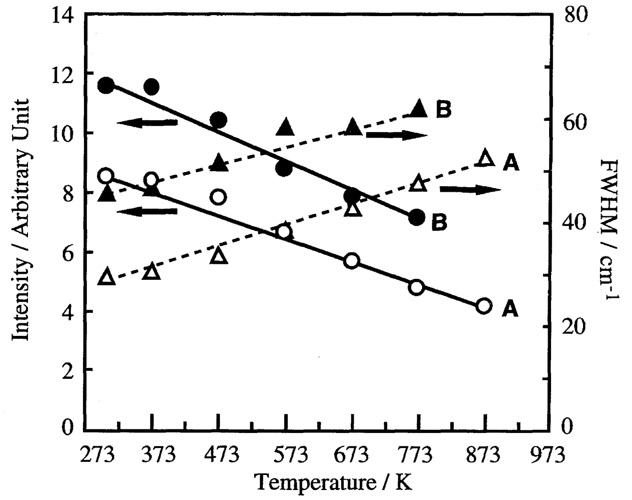


Fig. 4. Variation of intensity (——) and FWHH (- - -) of the Brønsted acidic hydroxyl bands in H-ZSM-5 (A) and H-mordenite (B).

the effect of both the decrease in intensity and the increase in FWHM.

In the case of mordenite, two bands of the Brønsted acidic hydroxyl bands appeared by the computer deconvolution. These are attributed to the small difference of two types of pore; the main channels (12-membered ring) and side pockets (8-membered ring).[12] On the other hand, in the case of H-ZSM-5, MFI type zeolite, there also exist two types of pore, the straight channel and the zigzag channel, with almost the same pore size (10-membered ring). The band shape of Brønsted acidic hydroxyl of H-ZSM-5 appears asymmetrically, which may be attributed to the convolution of two bands. For this reason, computer deconvolution was attempted to separately investigate the high-temperature behavior of two bands in H-ZSM-5, if exist. However, there was a problem on base line setting. The variation of the integrated intensity was greatly affected by baseline setting; by the temperature increase, the bands were extremely broadened, and a reasonable baseline setting at the high temperature region was not successful. Therefore, the total integrated intensity of the band of acidic OH group of H-ZSM-5 is quantitatively treated with a straight baseline between 3400 and 3650 cm^{-1}, hereafter.

Some researchers previously reported that the Brønsted acidic hydroxyls of zeolites were deprotonated at high temperatures.[13—15] Ward[13] reported that 29% of the band area of hydroxyl on H–Y zeolite decreased from 423 to 723 K, and that this was due to the proton delocalization on the Brønsted acidic hydroxyls. Uytterhoeven et al.[14] also reported that zeolite X and Y showed 20—30% decrease in band intensity from room temperature to 673 K. Hall et al.[15] indicated that the small intensity decrease was substantially observed for Y zeolite, and they also attributed it to the proton delocalization. Referring to these reports, the integrated intensity of the Brønsted acidic hydroxyl of H-ZSM-5 was plotted between 298 and 873 K. Here, the integrated intensity of the Brønsted acidic OH band was calibrated by the silanol band of H-ZSM-5 itself appearing in the same spectra, which was based on the assumption that the integrated intensity of silanol band showed temperature effects only and did not undergo dehydration (see above). Figure 5 shows decrease in the integrated intensity of the Brønsted acidic hydroxyl after calibration by the silanol curve. Since the silanol band of H-mordenite was too small to measure its integrated intensity, no reliable calibration curve was obtained. Therefore, H-ZSM-5 alone was studied.

Even after the correction, ca. 33% of the integrated intensity of the Brønsted acidic hydroxyl reduced from 298 to 873 K, and this was in good agreement with the previous works.[13—15] The decrease of the integrated intensity may elucidate the deprotonation of some of the Brønsted acidic hydroxyls at high temperatures (Scheme 1). Here, a part of Brønsted acidic hydroxyls are assumed to cleave the O–H

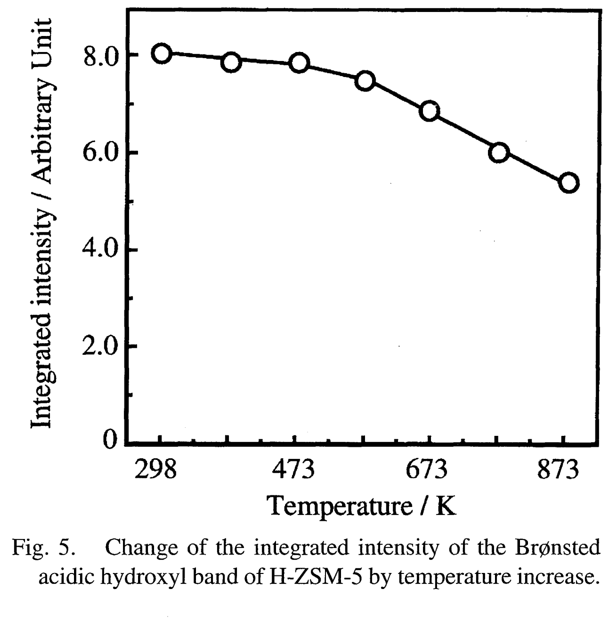
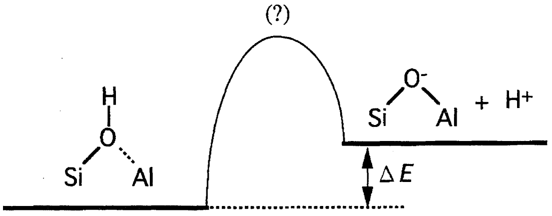


Fig. 5. Change of the integrated intensity of the Brønsted acidic hydroxyl band of H-ZSM-5 by temperature increase.



Scheme 1.

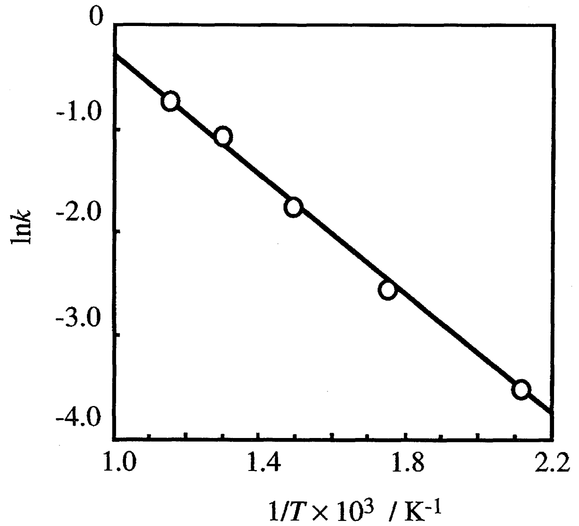


Fig. 6. Determination of energy differences of the nondissociated and dissociated Brønsted acidic hydroxyl groups in Scheme 1 (see text).

bond, becoming IR-inactive species, and to be trapped at adjacent sites which are not precisely defined. When the nondissociated and dissociated Brønsted acid sites are presumed to be in equilibrium state at high temperature range, the equilibrium constant, K, is expressed as follows:

$$K = \frac{N_\mathrm{d}}{N_\mathrm{n}} \cdot \frac{g_\mathrm{d}}{g_\mathrm{n}} \cdot \exp\left(-\frac{\Delta E}{kT}\right)$$

where N is the number of molecules, g is the degeneracy and k is the Boltzman constant. Subscripts d and n mean dissociated and nondissociated Brønsted acidic hydroxyl group, respectively. From this equation, quantitative analysis was performed on the assumption of the deprotonation, and the energy difference between the nondissociated and dissociated Brønsted acidic OH groups, ΔE, was evaluated to be ca. 24 kJ mol^{-1} by data above 473 K (Fig. 6).

Conclusions

By means of an improved method for in situ IR spectroscopy, a weakening of the integrated intensity of the Brønsted acidic hydroxyl bands was suggested to be a result of the deprotonation due to the temperature rising ($\Delta E \approx 24$ kJ mol^{-1}).

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