# An attempt to a semi-quantitative analysis of Lewis acid sites in H-ZSM-5 zeolite using water as an IR-spectroscopic titrant

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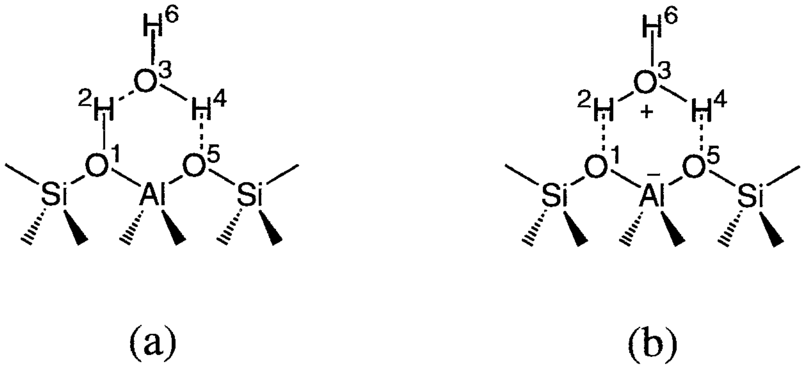
Water adsorption on H-ZSM-5 (with/without Lewis acid sites; LAS) at room temperature was studied by means of FT-IR spectroscopy. It has been clearly observed that water adsorbs preferentially on LAS. This result indicates that the IR bands at ca. 3550, 2900, 2400, 1600, and 1350 $cm^{-1}$, which are characteristic of water adsorbed on Brønsted acid sites (BAS), can be used as indicators of BAS; water can serve as an IR-spectroscopic titrant of LAS. Using this fact, an attempt was made to determine the absolute number of LAS in the H-form zeolites using water as a titrant. While this method has many restrictions in this stage, a relatively good result was obtained compared with that obtained previously for the same sample.

**Keywords:** FT-IR spectroscopy; H-ZSM-5; water adsorption; Lewis acid sites; Brønsted acid sites

## 1. Introduction

Adsorptions of water and methanol on H-form zeolites have attracted much attention from a catalytic point of view because they have a relation to the problem of proton transfer from zeolitic hydroxyl groups to adsorbates. In spite of the recent extensive experimental and theoretical studies, the adsorption states of water and methanol have remained controversial so far [1]. IR spectra of water/methanol adsorbed H-zeolites give characteristic absorption bands at ca. 2900, 2400 and 1600 $cm^{-1}$, which have been attributed to either strongly hydrogen-bonded water/methanol complexes [2,3] or protonated water/methanol complexes [4–6]. Their representative structure models are shown in scheme 1: the strongly H-bonded model (a) [2] and the protonated model (b) [5]. A band at ca. 3550 $cm^{-1}$ has also been observed for the water/methanol adsorption while its origin has not been properly discussed compared with the former three bands [1]. The very recent theoretical [7] and IR-spectroscopic studies [8] suggest that the strongly H-bonded state is the most probable structure for the water/methanol adsorption on H-zeolites. Although their assignment is under debate, it has been well recognized that these four bands are characteristic of the water/methanol species adsorbed on Brønsted acid sites (BAS) in H-zeolites. IR spectra of water adsorbed on Lewis acid sites (LAS) in zeolites have been, however, not reported so far.

On the other hand, the determination of the concentration of the BAS and LAS in zeolites is another important subject from a practical catalytic point of view [9].



Scheme 1. Structure models for the adsorption of water on Brønsted acid sites in the H-form zeolites: (a) hydrogen-bonded model; (b) protonated model.

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IR spectroscopy is widely used for this purpose because of the experimental facility owing to the recent development of Fourier-transform IR spectrometer [1,9]. However, it only leads to a relative concentration of the acid sites [10], and the ability of determination of the absolute concentration would make IR methods more powerful. Hence, it is quite interesting to develop an IR-spectroscopic method for the determination of the absolute concentration of the acid sites. In the course of IR studies on water adsorption on H-zeolites, we have found that water preferentially adsorbs on LAS in the zeolites. Using this phenomenon, one could determine the absolute number of the LAS: water serves as titrant of LAS of zeolites. Since the accuracy of determining the adsorbed amount of water is not sufficient now, the method remains semi-quantitative so far. However, an immediate proposal of the method would be useful and fruitful.

In the present letter, we report an IR study on the preferential adsorption of water on LAS in H-ZSM-5 as well as an attempt to determine the absolute number of LAS in the zeolites.

## 2. Experimental

H-ZSM-5 (Si/Al = 27) was provided by Asahi Chemical Industry Co., Ltd. The zeolite powder was pressed into a self-supporting disk (11.8 mg; $\rho = 3.6$ mg/cm$^2$) and was placed in a quartz-made IR cell. The cell was then connected to a conventional closed-circulation system (dead volume is ca. 150 cm$^3$). Gas pressure in the range between 0.13 and $1.3 \times 10^3$ Pa was measured using a capacitance absolute-pressure gauge (Baratron type 122A). The practical resolution of the gauge was 1.3 Pa. The base pressure of the closed-circulation system was less than $1.3 \times 10^{-3}$ Pa by pumping down using an oil diffusion pump. Even when the circulation system was isolated from the evacuation system, the pressure inside the system did not exceed 1.3 Pa for more than 1 h, which implies that the system can avoid contaminations during the experiment carried out here. The sample was pretreated in situ with a standard procedure that was described previously [11]. Through this procedure, the sample became IR-spectroscopically clean and a considerable amount of LAS was produced, which was evidenced by IR measurements of the $N_2$- and CO-adsorbed sample [11]. In order to obtain the sample without any LAS, the sample was subjected to a water-vapor treatment at 573 K for 30 min and a subsequent evacuation at 673 K for 30 min. LAS were re-produced by the evacuation at 873 K for 30 min and by the subsequent evacuation at 923 K for 15 min. Redistilled water was used after a degassing in vacuum. Water vapor was dosed to the IR cell at 303 K. Since a part of water adsorbs on the inner wall of the circulation system, the pressure of water decreases gradually at an early stage of the introduction of water vapor to the circulation system. Hence, water vapor was admitted into the IR cell after the pressure inside the circulation system reached its equilibrium state in order to minimize the effect of the water adsorption on the inner wall.

IR measurements were done with a Jasco FT/IR-7000 spectrometer using a TGS detector with a spectral resolution of 2 cm$^{-1}$ and by averaging 64 scans.

## 3. Results and discussion

Spectral change of H-ZSM-5 with the exposure to water vapor at 303 K is shown in fig. 1: fig. 1a shows the result for the sample without LAS; fig. 1b for the sample with LAS. For the bare sample (dose pressure = 0 Pa), two absorption bands were observed at 3750 and 3615 cm$^{-1}$. These bands have been assigned to the $\nu$(OH) band of the terminal silanol groups (–SiOH) and the bridging OH groups (≡Si–OH–Al≡) in H-ZSM-5, respectively [12]. The bridging OH groups are known to be the origin of the Brønsted acidity of the zeolite. For the sample without LAS (fig. 1a), five new bands grew at 3702, 3659, 3569, 2921 and 2470 cm$^{-1}$ accompanied by a coinciding decrease of the 3615 cm$^{-1}$ band. The corresponding bands were observed at 3702, 3660, 3553, 2923, and 2476 cm$^{-1}$ for the sample with LAS (fig. 1b). This slight difference in the peak position is not essential for the present study. Most of the exposed water adsorbs on the sample in the pressure range presented here, which was evidenced by the fact that the equilibrium pressure of water was almost zero.

The 3702 cm$^{-1}$ band has been attributed to the $\nu$(OH) band of free OH groups ($O^3H^6$ in either scheme 1a or 1b) of water species adsorbed on BAS [2,5]. The bands at 2921/2923 and 2470/2476 cm$^{-1}$ have been attributed to the A and B bands, respectively, of the (A, B, C) trio of the strongly H-bonded water complex from the H-bonded model [2], and to the antisymmetric and symmetric $\nu(H^2O^3H^4)$ bands of the protonated water species from the protonated model [5]. The 3569/3553 cm$^{-1}$ band has been reported in the literature although any clear explanation has not been presented. These bands are, however, characteristic to the water species adsorbed on BAS of H-form zeolites. A small band at 3659/3660 cm$^{-1}$ is not reported so far and its origin is unknown yet.

Comparing figs. 1a and 1b, it is clear that the growth of the IR bands that are characteristic to the water species adsorbed on BAS in the case of the sample with LAS (fig. 1b) lag behind that observed for the sample without LAS (fig. 1a). It seems that the spectrum for 40 Pa seen in fig. 1b is almost identical to that for 13 Pa in fig. 1a. Since the essential difference between the samples is the existence of LAS, this lag in the spectral growth is interpreted as the preferential adsorption of water on LAS.

In order to explore the spectral change in detail, the observed spectra are presented in difference-spectra

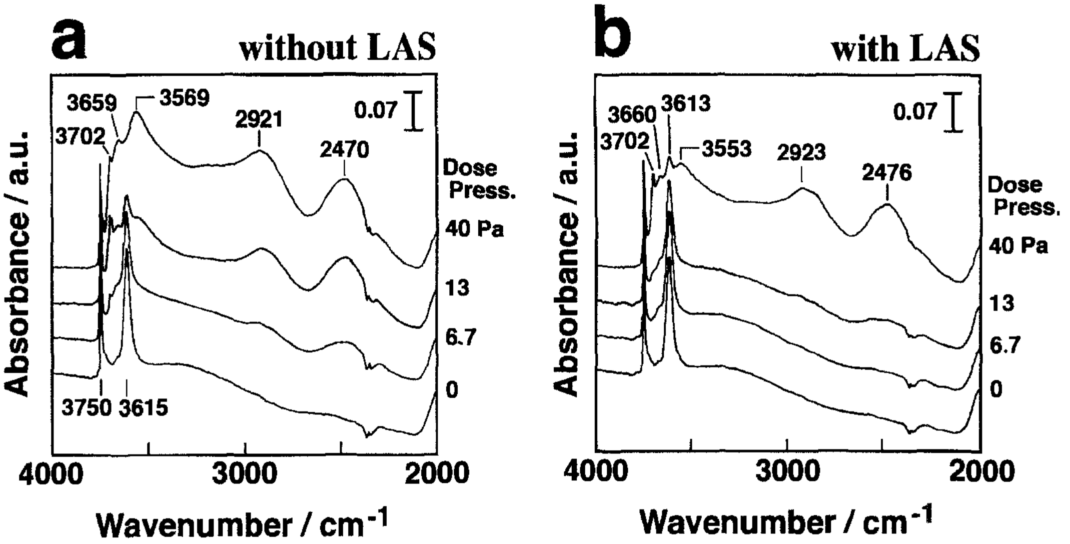

Fig. 1. FT-IR spectra of $H_2O$-adsorbed H-ZSM-5 at 303 K: (a) the sample without LAS; (b) the one with LAS. Dose amounts are indicated in the figure. See the text for the sample pretreatment procedure.

mode as shown in fig. 2. The spectrum of the bare sample is used as a background. The 3701, 3547/3543, 2898/2889, 2469/2465, 1630/1633, and 1356/1355 $cm^{-1}$ bands are characteristic to the water species adsorbed on BAS. The assignment of the former four bands is already discussed above. The 1630/1633 $cm^{-1}$ band has been attributed to the C band of the (A, B, C) trio of the strongly H-bonded water species from the H-bonded model [2], and to the $\delta(H^4O^3H^6\ /H^2O^3H^6)$ band of the protonated water species from the protonated model [5]. The 1356/1355 $cm^{-1}$ band has been attributed to the $\delta$(OH) band of the substrate Si–(OH)–Al groups perturbed by the water adsorption from the H-bonded model [2], and to the $\delta(H^2O^3H^4H)$ band of the protonated water from the protonated model [5]. The negative band seen at ca. 3615 $cm^{-1}$ indicates the perturbation of the bridging OH groups by the water adsorption. On the other hand, the 3750 $cm^{-1}$ band due to the silanol groups remained almost unchanged, which is evidenced by the fact that neither negative nor positive band is seen at the frequency. This fact indicates that the silanol groups are not perturbed by the water adsorption in the dose range. As seen from fig. 2a, these bands characteristic of the water on BAS were observed even at a small dose of 6.7 Pa for the sample without LAS. On the other hand, for the adsorption of 6.7 Pa of water on the sample with LAS (fig. 2b), a very broad feature between 3500 and 2200 $cm^{-1}$ was observed while the IR bands characteristic of the water on BAS were very weak. We assign this broad feature between 3500 and 2200 $cm^{-1}$ to the $\nu$(OH) band of the water species H-bonded to LAS. A band at ca. 1630 $cm^{-1}$ observed for the dose pressure of 6.7 Pa in fig. 2b would be the $\delta$(HOH) band of the water species on LAS. The fact that this band is relatively large compared with the 2889, 2465, and 1355 $cm^{-1}$ bands observed for the dose of 6.7 Pa supports the assignment.

Fig. 2 reveals that the spectrum of 40 Pa of water on

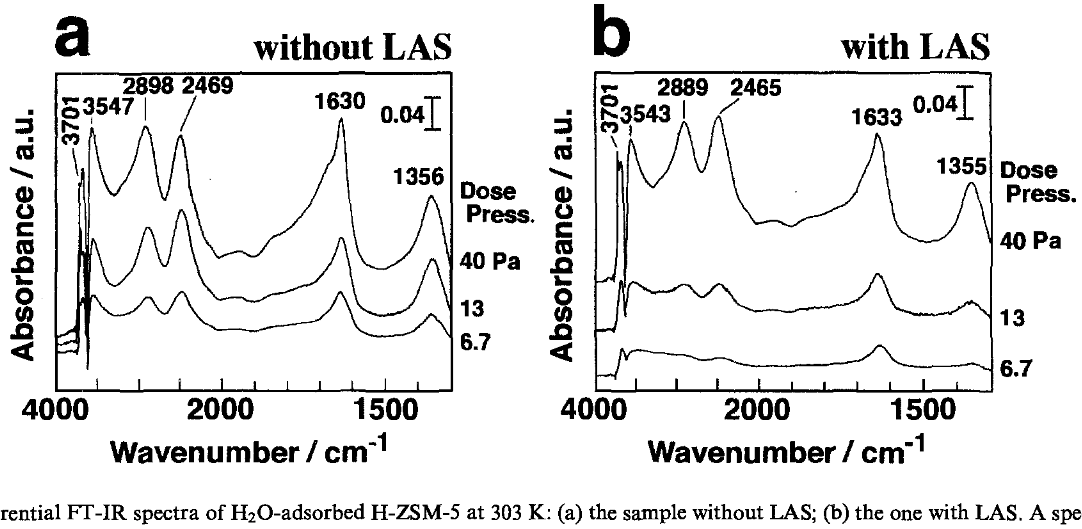

Fig. 2. Differential FT-IR spectra of $H_2O$-adsorbed H-ZSM-5 at 303 K: (a) the sample without LAS; (b) the one with LAS. A spectrum of the bare sample (see fig. 1: 0 Pa) is used as a background spectrum.

the sample with LAS (fig. 2b) does not exactly correspond to the spectrum of 13 Pa of water on that with LAS (fig. 2a) but is only intermediate between those of 13 and 40 Pa in fig. 2a. Then, in order to obtain the equivalent pressure, the peak height of the IR bands that are characteristic to the water on BAS was plotted against the dose pressure. Fig. 3 shows a result for the ca. 1335 $\mathrm{cm}^{-1}$ band. Fitted curves in the figure are the third-order spline curves for the plots. This figure suggests that the spectrum of 40 Pa in fig. 2b corresponds to that of 19.0 Pa in fig. 2a. A similar plot for the ca. 2900 and 2400 $\mathrm{cm}^{-1}$ bands gave the value as 20.1 Pa. Since the ca. 1630 $\mathrm{cm}^{-1}$ band is contributed to by both the water species on BAS and those on LAS, such an analysis was not made on the ca. 1630 $\mathrm{cm}^{-1}$ band. By averaging these values, we estimated that the spectrum of 19.5 Pa in fig. 2a would be equivalent to that of 40 Pa in fig. 2b; the IR bands characteristic of the water on BAS lag behind by 20.5 Pa for the sample with LAS compared with that without LAS.

If one assumes that water, that cannot be seen as the characteristic IR bands of water on BAS, adsorbs all on LAS, the amount of LAS can be determined quantitatively. Since the dead volume of the circulation system is ca. 150 $\mathrm{cm}^3$, the amount of $H_2O$ at a pressure of 20.5 Pa is calculated to be ca. $1.2 \times 10^{-6}$ mol. If one assumes that a $H_2O$ molecule adsorbs on a LAS, the absolute number of LAS, $N_{\mathrm{LAS}}$, is, then, estimated to be ca. $1.2 \times 10^{-6}$ mol. This value should be regarded as a *semi-quantitative* one because some assumptions were made and because the accuracy of the determining the amount of $H_2O$ adsorbed on LAS is insufficient yet. This method, however, would give a new perspective on the determination of the absolute number of LAS using IR spectroscopy.

Now, let us calculate the ratio of the number of BAS, $N_{\mathrm{BAS}}$, to $N_{\mathrm{LAS}}$ for the comparison with the previous study [11]. The Al content of the sample (11.8 mg, Si/Al = 27) is ca. $7.0 \times 10^{-6}$ mol. If all Al sites are responsible for a BAS in the case of the sample without LAS, $N_{\mathrm{BAS}}$ in the sample is estimated to be ca. $7.0 \times 10^{-6}$ mol. If two LAS are generated by an expense of two BAS as is the case of H-ZSM-5 [10,13], the ratio of $N_{\mathrm{BAS}}$ to $N_{\mathrm{LAS}}$ for the zeolite sample with LAS can, then, be calculated as follows:

$$N_{\mathrm{BAS}}/N_{\mathrm{LAS}} = (7.0\times10^{-6} - 1.2\times10^{-6})/1.2\times10^{-6} = 4.8\,.$$

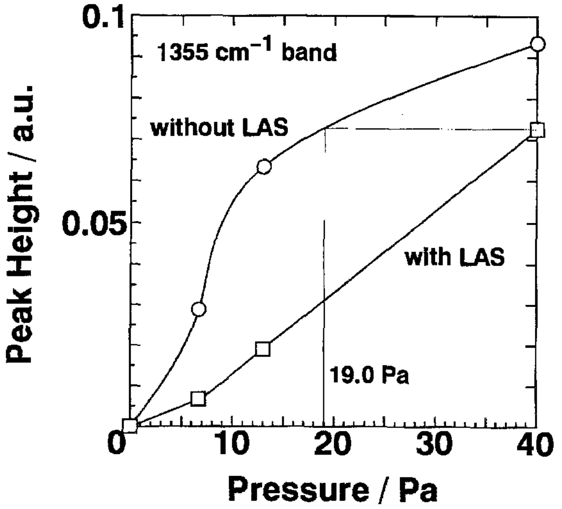

Fig. 3. Peak height of the ca. 1335 $\mathrm{cm}^{-1}$ band as a function of dose pressure of water: data were taken from fig. 2; fitted curves are third-order spline curves.

In the previous study, we have obtained the ratio as ca. 4.6 from the decrease in the integrated absorbance of the acidic-OH band at 3615 $\mathrm{cm}^{-1}$ accompanied by the formation of LAS for the same H-ZSM-5 sample treated in the same way [11]. The value is very close to that obtained here. However, this coincidence should not be overestimated because both estimations have been done under some assumptions so that they would have some errors. For an example, as described above, water adsorbs not only on the sample but also on the inner wall of both the IR-cell and the circulation system under the experimental conditions employed here. Such an excess adsorption would lead to a significant error in the determination of the adsorbed amount. Nevertheless, the adsorption amount of water on the inner wall could be kept constant if the experimental conditions except the condition of the sample treatment are kept constant, which minimize the effect of the water adsorption on the inner wall. In order to obtain a more precise result, the method is required to be refined further. Moreover, the method should be applied to other zeolites, such as H-Y, H-MOR and SAPO, in order to check its generality.

## 4. Conclusion

Water adsorption on H-ZSM-5 with/without LAS at room temperature was studied by means of FT-IR spectroscopy. It had been revealed that water adsorbs preferentially on LAS and that the IR bands at ca. 3550, 2900, 2400, 1600, and 1350 $\mathrm{cm}^{-1}$, which are characteristic of water adsorbed on BAS, can be used as indicators of BAS; water can serve as an IR-spectroscopic titrant of LAS in the zeolite. Considering this fact, an attempt was made to determine the absolute number of LAS semi-quantitatively using water as the titrant. A relatively good result was obtained while the method has some restrictions. Further refinement and experiment are required to establish the method for the quantitative analysis.

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