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IR SPECTROSCOPIC ANALYSIS OF THERMAL BEHAVIOR OF ADSORBED WATER ON Y-TYPE ZEOLITE[*]

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In this study, we measured the IR spectra of water adsorbed at a differential temperature under constant pressure. Our purpose is to present a simple estimation method for the recycled temperature condition of water adsorbents. For a NaY zeolite, the IR integrated intensity of the bending vibration band of adsorbed water was increased with a decrease of temperature. The IR spectra were measured from 230℃ to 30℃ for several ion-exchanged Y-type zeolites. On the other hand, the adsorption isotherms of water on these zeolites were measured at 30℃. The result of this work is that the best correlation between the IR integrated intensity and the amount of adsorbed water was found for some of the zeolites. We concluded that the obtained correlation equation could easily estimate the amount of water desorbed between arbitrary temperatures.

Keywords: IR Spectroscopic Analysis, Adsorbed Water, Y-type Zeolite.

1. Introduction

IR spectroscopic analysis of adsorbed water on zeolites was started being studied in 1963. Bertsch and Habgood discussed the correlation between the amount of adsorbed water and the maximum absorption of IR peak for adsorbed water on X-type zeolite.[1] In 2001, Rege and Yang studied about water and carbon dioxide being co-adsorbed on NaX zeolite.[2] In that study, the amount of adsorbed water, or carbon dioxide, was estimated by the IR integrated intensity of these gases. But in these studies, the IR spectrum of adsorbed water on zeolites was measured under the differential pressure at a constant temperature (only around room temperature).

In this study, we measured the IR spectra of water adsorbed at a wide range of temperatures from 230℃ to 30℃ under constant pressure. Our purpose is to present a simple estimation method for the recycled temperature condition of water adsorbents. For a NaY zeolite, the IR integrated intensity of the bending vibration band of adsorbed water was increased with a decrease of temperature. The IR spectra were measured from 230℃ to 30℃ on H_2O pressure of 0.67×10^3 Pa or 1.33×10^3 Pa for several ion-exchanged Y-type zeolites. The amount of adsorbed water on these zeolites was measured by the

Belsorp-max at 30℃. We studied the correlation between the IR integrated intensity and the amount of adsorbed water for these zeolites.

2. Experimental

The adsorbents used in this work are listed in Table 1. These were prepared by a conventional ion-exchange method[3,4] using a NaY (UOP) as a starting zeolite (Si/Al ratio of this zeolite was 2.6.). The ion-exchanged rate and BET surface area were measured by X-ray fluorescence analysis (JEOL JSX-3020M) and the conventional nitrogen adsorption method (Nippon BEL BELSORP-max). Water was distilled, degassed and used as an adsorbate.

The IR spectra of the water-zeolite adsorption systems were obtained with the cell reported in other papers.[3,5,6] A sample disc of 13 mm diameter, approximately 8.5 mg in weight and approximately 60 μm in thickness was degassed in the cell at 350℃ and 5.3 x 10^{-2} Pa for 2 h. The spectra were recorded on a Bio Rad FTX3000MX spectrometer at a resolution of 4 cm^{-1}. The spectra were recorded under a spontaneous decreasing temperature from 230℃ to 30℃ and under a water pressure of 0.67 $\times$ 10^3 Pa or 1.33 $\times$ 10^3 Pa. After the measurement, the disc was heated again to 200℃ and the spectra were recorded under the equilibrium condition at 200℃, 150℃, 100℃ and 50℃ under a water pressure of 0.67 $\times$ 10^3 Pa or 1.33 x 10^3 Pa.

Table 1. Y zeolites used as adsorbents.

Zeolite	Ion-exchanged rate (%)	Specific surface area m^{2}g^{-1}
NaY	original	850
LiY	86	850
MgY	82	800
CaY	87	850
MnY	77	840
CoY	60	810
NiY	50	810
CuY	54	780
ZnY	27	810

3. Results and Discussion

3.1. *IR spectra of adsorbed water*

The IR spectra of adsorbed water on NaY and MgY under a water pressure of 1.33 $\times$ 10^3 Pa at several temperatures (from 230℃ to 30℃) are shown in Fig. 1. The peak around 1650cm^{-1} was assigned to the bending vibration of adsorbed water.[1] The OH

stretching vibration band was also measured around 3500 cm^{-1}.[1] The OH stretching vibration band is originated from water and SiOH of zeolites.[2] So, we cannot discuss the peak area as only adsorbed water and choose the bending band to estimate the amount of the adsorbed water. The absorption intensity corresponding to amount of adsorbed water increased with a decrease of temperature. At a high temperature (over 200 °C), an additional peak around 1620 cm^{-1} was showed in spectra for MgY (in Fig. 1 (b)). A similar peak was showed for CaY, CoY and NiY (not shown in Fig. 1). The peak may be assigned to the differential adsorbed style of water on these zeolites.

The normalized integrated adsorption intensity was estimated as follows: (1) Integrated adsorption intensity from 1550 cm^{-1} to 1750 cm^{-1} was calculated. (2) The intensity was divided by the weight of the pellet per the area of pellet.
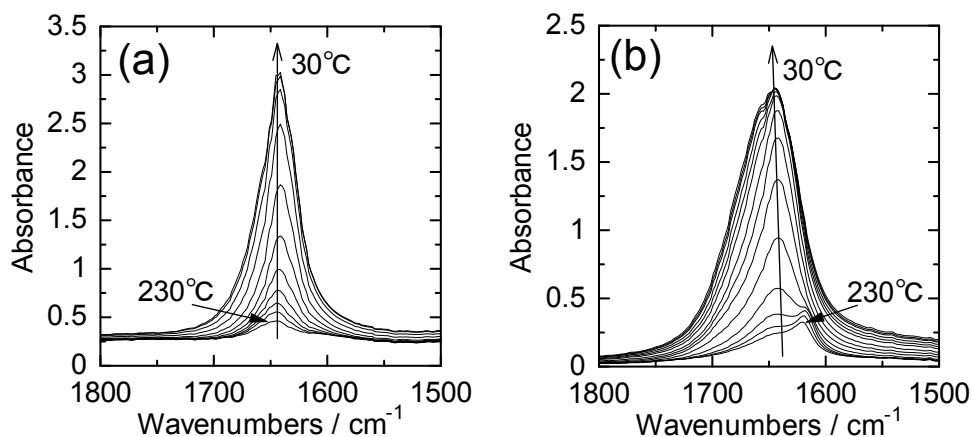

Fig. 1. IR spectra of adsorbed H$_2$O at 1.33×10^3 Pa on NaY (a) or MgY (b) zeolite.

3.2. *Temperature behavior of the normalized integrated intensity*

The normalized integrated intensity was plotted in Fig. 2 as a function of the temperature. In the figure, the data under equilibrium conditions were also showed as closed circle (2nd). Under spontaneous decreasing temperature, several integrated intensities for each temperature were measured as an open circle (1st), and the difference was easily calculated. These data from spontaneous decreasing temperature are in fair agreement with these data under equilibrium conditions. This result showed the equilibrium data was measured by decreasing the temperature spontaneously. The reason for this was that the pellet was so thin that the temperature was easily conducted to the pellet from the heater, and the adsorption equilibrium was easily attained at that temperature. An additional reason was that excess water existed around the pellet.
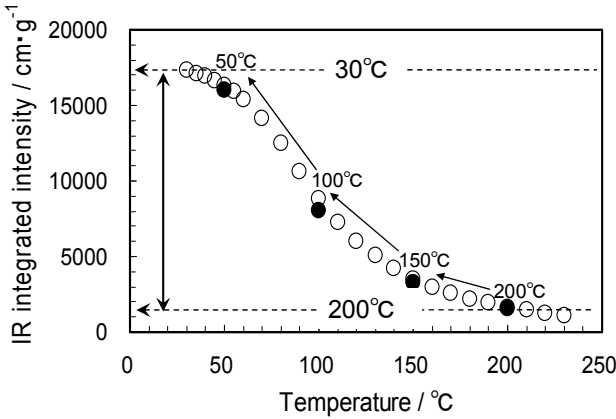
Fig. 2 Temperature dependence of IR integrated intensity of adsorbed H_2O at 1.33×10^3 Pa on NaY zeolite, ○: 1st, ●: 2nd.

3.3. *Amount of water adsorption isotherms*

In Fig. 3, water adsorption isotherms were showed. The sequence of the amount of water adsorbed around p/p0=1 was MgY>CoY>NiY>MnY>LiY>CaY>ZnY>CuY>NaY.
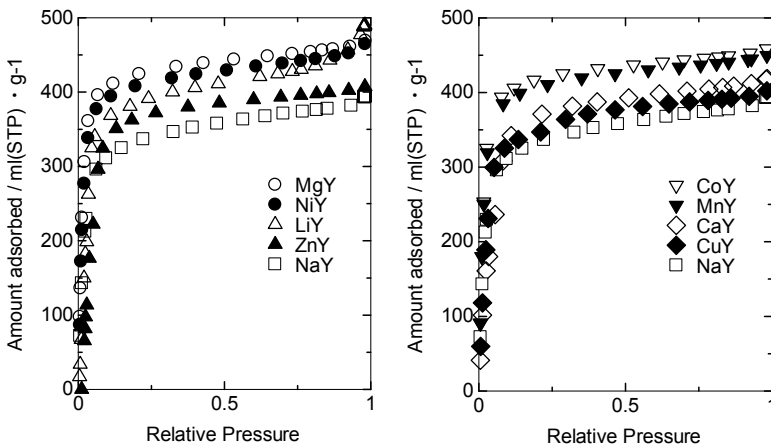

Fig. 3 Water adsorption of several zeolites at 30℃.

The relationship between the amount of adsorbed water from the isotherms and the integrated intensity from IR spectra is shown in Fig. 4 under two water adsorption equilibrium conditions at 30℃ under a water pressure of 0.67×10^3 Pa or 1.33×10^3 Pa. The data from the Y-type highly hydrophobic zeolite (Si/Al ratio = 32.4) is also included as closed circles in Fig. 4. The data for MgY, CaY, CoY and NiY behave differently to

the other samples and this may be due to the additional peaks seen in the spectra at the high temperature (Fig. 1). Although the additional peaks are not seen in IR spectra at the low temperature, the additional peaks must be included in the main peaks. If we hope to discuss about the additional peaks, we need to de-convolute these spectra to two peaks (main peaks and additional peaks) and think about the absorption coefficient for each peak. But we do not have information about the absorption coefficient for these peaks. We cannot discuss about the spectra of these zeolites. The data for LiY, MnY, ZnY, NaY and CuY, these data showed a good relationship and a correlation between the amount of water adsorbed (q / mL(STP)$\cdot$g^{-1}) and integrated intensity (I / cm$\cdot$g^{-1}) is described as;
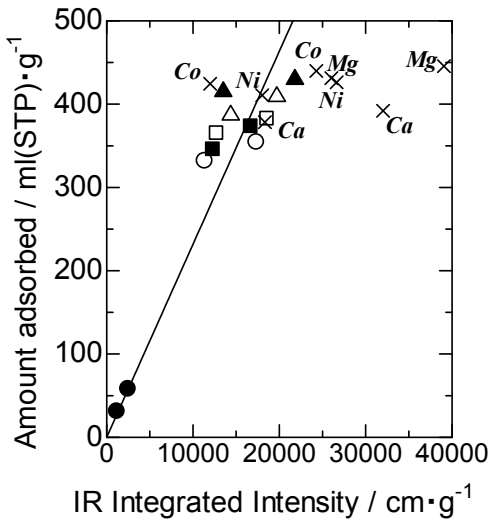
$$q = 0.0230 \times I. \tag{1}$$

Fig. 4 The relationship between the amount of adsorbed water from isotherms and the integrated intensity from IR water adsorption of several zeolites at 30℃; ○: NaY, ▲: LiY, △: MnY, ■: CuY, □: ZnY, ●: the Y-type zeolite (Si/Al ratio = 32.4）．

The amount of water desorbed between two temperatures (30℃ and 150℃ or 30℃ and 200℃) was estimated and showed in Table 2. We want to use the waste heat from the factory to recycle of adsorbents. We choose the temperatures 150℃ or 200℃ for the desorption temperatures. The sequence of the amount of water desorbed was LiY>MnY>ZnY>NaY>CuY. The ion-exchanged of zeolites enhanced the amount of water desorbed compared with the original zeolite (NaY).

Table 2. Estimated amount of desorbed water by equation (1).

Zeolite	Amount of desorbed water (ml(STP)g^{-1})	
	Between 30℃ and 150℃	Between 30℃ and 200℃
NaY	320	360
LiY	350	420
MnY	320	410
CuY	190	240
ZnY	330	390

4. Conclusions

Although the amount of desorbed water between two temperatures has been normally estimated by the adsorption isotherms at two temperatures, the measurement of water adsorption isotherms over 120℃ is difficult because the environmental temperature around sensors and all lines cannot be maintained over 120℃. But the amount of desorbed water between several differential temperatures was able to be estimated by continuous IR spectra measurement under a spontaneous decreasing temperature. We proposed a convenient method for the water desorption property for several Y-type zeolites. In the future, the IR spectra will be also measured for other zeolites types (A or ZSM-5 etc.) and the application area for this method will be determined.

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