

FT-IR study of behavior of acidic hydroxyl groups on zeolites at high temperatures

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Infrared (IR) spectroscopy has been used as one of the powerful methods for characterization for zeolites. While adsorption of probe molecules represented by CO [1] and pyridine [2] characterizes the acidity of zeolites, some disadvantages remain. For example, adsorption temperatures of probe molecules are lower than those operated in industrial processes. Therefore, results obtained by the conventional method are sometimes not directly related to the activity of catalytic reactions. Thus, a different method is proposed in this study for characterizing zeolite acidity at high temperatures; the thermal behavior of hydroxyl groups on zeolites. The dissociation enthalpy (ΔH) was estimated by assuming the equilibrium state between bonded hydroxyl groups and non-bonded proton form on zeolites. The former is observed by IR absorption, but it disappears for the later. Therefore, the quantification of OH stretching band leads to the estimation of dissociation enthalpy of acid site on zeolites. Moreover, effects of zeolite topologies, Si/Al ratios and temperatures on dissociation enthalpy are discussed.

For in situ IR investigations, ZSM-5 (JRC-Z5-90H, 10MR, Si/Al=45), mordenite (JRC-ZHM20, 12 and 8MR, Si/Al=10) and SSZ-13 with CHA type structure (8MR, Si/Al=39) were pressed into self-supporting disks, and placed in a quartz cell connected to a conventional closed circulation system. All sample disks were pretreated by evacuation at 773 K for 1 h.

IR spectra of ZSM-5 at various temperatures are shown in Fig. 1. The integrated intensity of the OH band of acid sites (3609 cm^{-1}) decreased by increasing the temperature, accompanied by the peak tops

shift to lower frequency side. The decrease of the band in intensity indicates that the number of OH bonds decreased by the temperature increase to form dissociated acid sites. Thus, the larger number of Brønsted acid sites were more dissociated at higher temperatures than the lower. It should be noted that the thermal conversion was completely reversible for temperature variation several times. Next, dissociation enthalpy was estimated by the quantification of bands of acidic OH groups on several zeolites. Table 1 compares dissociation enthalpy of several zeolites. Different values were obtained for different zeolite topologies as well as for different temperature ranges. These results imply that the topology of zeolites affects the dissociation enthalpy of acidic OH groups.

High temperature behavior of acidic hydroxyl groups on zeolites was observed by IR method. The dissociation enthalpy of hydroxyl groups on zeolites was affected by the zeolite topology.

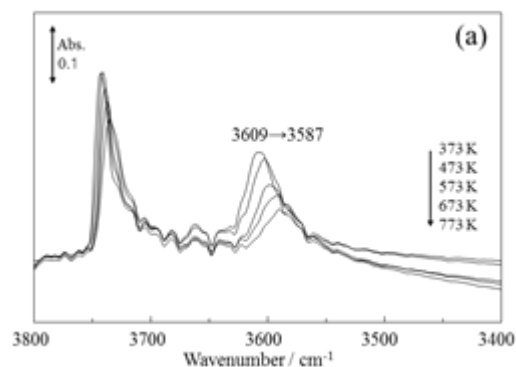


Fig. 1. IR spectra of ZSM-5 at different temperatures.

Table 1. Dissociation ΔH of various zeolites at different temperature ranges.

Zeolite topologies		HM20 (Si/Al = 10)	ZSM-5 (Si/Al = 45)	SSZ-13 (Si/Al = 48)
$\Delta H / \text{kJ mol}^{-1}$ (dissociation enthalpy)	398–548 K	22.8 ± 2	27.5 ± 3	22.9 ± 2
	573–773 K	23.7 ± 2	22.1 ± 2	17.5 ± 2

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