A High Resolution Infrared Study of HY and HZSM-20 in the Hydroxy Stretching Region

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Deconvolution of the high-frequency infrared hydroxy stretching band of NaHY shows that the band envelope is made up of five major components, and dealumination *via* Si substitution using $(NH_4)_2SiF_6$ leads to a decrease in the intensity of the high-frequency components; HZSM-20 is shown to possess hydroxy band properties similar to those observed in high-silica HY zeolites.

The industrial requirements of cracking catalysts are such that a catalyst with high acidity and high stability is needed.[1] Protonated Y zeolite and its dealuminated forms fulfill these roles to a large extent and hence are extensively utilized. Various methods have been used to obtain a high-silica Y zeolite. Activating $NaNH_4Y$ under so called 'deep bed' conditions[2] was found to give a product of high stability with a high Si : Al ratio. Extraction of aluminium with ethylenediaminetetra-acetic acid (EDTA)[3] has also been shown to generate a high-silica product having enhanced stability. Recently, direct substitution of Al by Si has been achieved using $SiCl_4$ or $(NH_4)_2SiF_6$.[4,5] Direct synthesis of a zeolite closely resembling Y in framework structure, but possessing a greater Si : Al ratio (ZSM-20), has also been reported.[6]

The Brönsted acid sites responsible for many catalytic conversions over NaHY zeolites are thought to be bridged hydroxy groups in accessible supercage positions. These bridged hydroxy groups give rise to a characteristic i.r. OH stretching band at 3640 cm^{-1}, often referred to as the high-frequency (h.f.) band.[7] The position of this band has been shown to vary with Si : Al ratio[8] and degree of exchange of residual Na^+ ions.[9]

In this report deconvolution of the h.f. band is performed for a series of HY zeolites having different Si : Al ratios. It is demonstrated that the h.f. envelope is composed of a number of sub-components. Framework dealumination *via* $(NH_4)_2SiF_6$ is shown to lead to a progressive decrease in the intensity of the higher frequency components. Direct detection of Brönsted acid sites of varying acidity is demonstrated with only the sites of lowest frequency, which are presumably the strongest acid sites, remaining after significant dealumination has occurred.

$NaNH_4Y$ zeolite (see Table 1) was obtained from Union Carbide. Dealumination with $(NH_4)_2SiF_6$ and activation for the i.r. measurements were as described previously.[5] The synthesis of ZSM-20 was similar to that described in ref. 6 and will be described in a later report. The i.r. spectra were recorded on a Mattson Cygnus 100 Fourier transform instrument. Deconvolution was performed following the guidelines described in refs. 10 and 11 using a software supplement

Table 1. Chemical composition of Y (I, II, III) and ZSM-20 (IV) zeolites obtained from chemical analysis.

Sample No.	Si : Al	Na : Al
I	2.8	0.2
II	4.3	0.0
III	7.4	0.0
IV	3.4	0.0

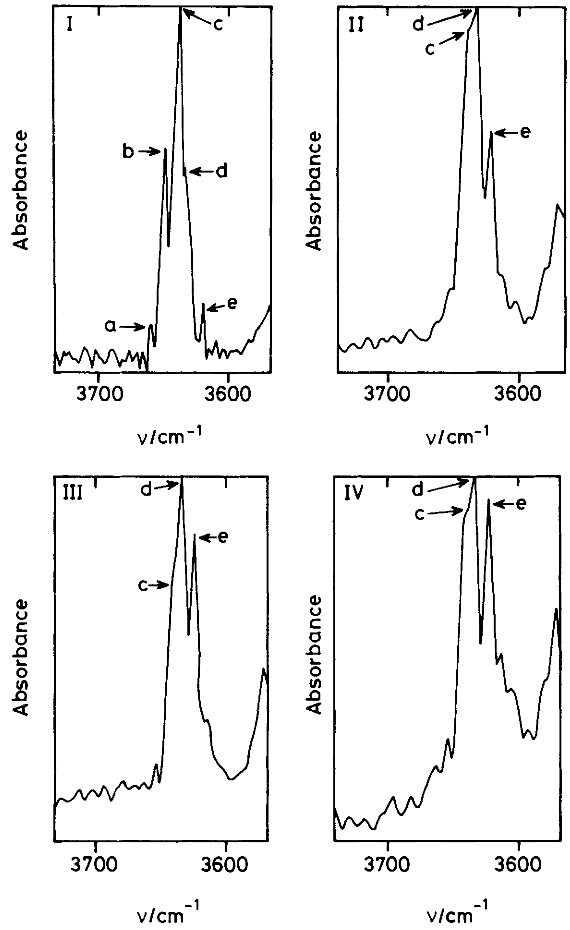

Figure 1. Deconvoluted h.f. bands I, II, III, and IV correspond to samples of Table 1; a = 3660, b = 3650, c = 3642, d = 3636, and e = 3622 cm^{-1}. All values are ±2 cm^{-1}. Pyridine sorption shows that all components are acidic.

supplied by Mattson Instruments. The chemical composition of the samples studied is given in Table 1.

In Figure 1 the deconvoluted h.f. band for the samples of Table 1 is illustrated. The increased resolution of the deconvoluted spectrum clearly indicates that more than one type of supercage OH group is present in the parent NaHY zeolite of Si : Al = 2.8. At least five bands are present having values of 3660, 3650, 3642, 3636, and 3622 cm^{-1}. A shoulder to the 3636 cm^{-1} band is also observed at 3630 cm^{-1}. Recent studies by Dombrowski *et al.*[12] using a curve analysis of the h.f. envelope are in good agreement with these results. The presence of distinct OH bands suggests that a corresponding range of Brönsted acidity should exist. Previous thermal analysis experiments[13] have indeed indicated such a situation. The environment giving rise to the different OH frequencies could presumably arise from the effect of nearest neighbour aluminiums. Kanzansky[14] has proposed a simple model based on neighbouring aluminiums which accounts for the presence of four different OH groups. The existence of five bands (see above) indicates that the situation may be more complex and other factors such as site geometry may need to be considered.

Dealumination (Figure 1) leads to a progressive decrease in the intensity of the high-frequency components (a,b,c in Figure 1). This is consistent with the proposal that removal of Al associated with the weaker acid sites occurs first.[8] Previous studies have suggested that the h.f. OH band shifts to lower frequency on dealumination.[8] The present results, however, indicate that there is no significant shift in the frequency of the different components, but that the shift in frequency observed previously for the band envelope is due principally to a decrease in the contribution of the higher frequency components to the intensity of the band envelope intensity. The h.f. bands for HZSM-20 (Figure 1) are similar in intensity and frequency to those observed for dealuminated Y having similar Si : Al, which is in line with the similar framework structures proposed for the two zeolites.[6]

In conclusion, the NaHY i.r. band commonly referred to as the h.f. band is shown to be made up of different components each presumably corresponding to a unique acidity range. High-silica analogues prepared *via* either Si substitution of Al by $(NH_4)_2SiF_6$ or *via* a direct synthesis route (ZSM-20) are characterised by a decrease in the intensity of the higher frequency components which are generally associated with weaker acidity.

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