Description of a Characteristic Infrared Frequency for Acidic Hydroxy-groups in Zeolites

By Denise Barthomeuf

(*Laboratoire de Catalyse Organique, L.A. C.N.R.S. no.* 231, *Ecole Supérieure de Chimie Industrielle de Lyon, Boulevard du* 11 *novembre* 1918, 69621 *Villeurbanne, France*)

Summary A characteristic i.r. frequency range is defined for the 'high frequency' hydroxy-groups of several zeolites (A, X, Y, L, Ω, offretite, and mordenite).

Recently Poncelet *et al.*[1] have reported a linear correlation between the frequency of the high-frequency band (near 3650 cm^{-1}) in faujasite type zeolites and the ratio Si:Al. A protonated germanium zeolite similar to faujasite also fits the same relation. To investigate a more general correlation we have considered the frequency of the acidic bands in a larger variety of zeolites: zeolites X, Y, and L, offretite, and mordenite and to a lesser extent zeolites A and Ω. Many results have been published on X and Y samples; these have been reviewed recently.[2] Although the frequency depends on the nature and content of the cation, and pretreatment and experimental conditions, the various results obtained show that the frequency of the high-frequency band of X zeolites is 10—15 cm^{-1} higher than that of Y zeolites. For alkali-metal cationic forms the values reported by Poncelet *et al.*[1] fall in the average range obtained (*ca.* 3655 cm^{-1} for X, *ca.* 3640 cm^{-1} for Y). For the other zeolites the frequency for alkali-metal cationic forms (partially protonated) are close to 3630 cm^{-1} for HKL zeolites,[3] near 3620—3610 cm^{-1} for various HK offretites,[4] and *ca.* 3600 cm^{-1} for hydrogen mordenite.[5] Values of 3670 cm^{-1} (ref. 6) and 3620 cm^{-1} (ref. 7) have been reported for A and Ω zeolites, respectively.

A plot of these values as a function of the ratio Si:Al is shown in the Figure. For each zeolite a range of frequency (*ca.* 10 cm^{-1}) covers the shifts to high frequency observed at low cation contents. Such shifts have been related to an increase in the acid strength.[4,8] The results in the Figure indicate that there is a good linear relationship between the average hydroxy-frequency and the Si:Al composition independent of any structural influence. They also show that the differences in frequency due to the Al content from one type to the other (up to *ca.* 50 cm^{-1}) are higher than those arising from the cation content (*ca.* 10 cm^{-1}). The decrease in frequency as the Si:Al values increase might be related to an increase in the strength of the acid sites. Although no precise comparative study of all these zeolites has been performed it is well known that Y zeolites have acid sites stronger than X zeolites and weaker than offretite and mordenite. In any case the explanation is not consistent with the fact that the frequency for each zeolite

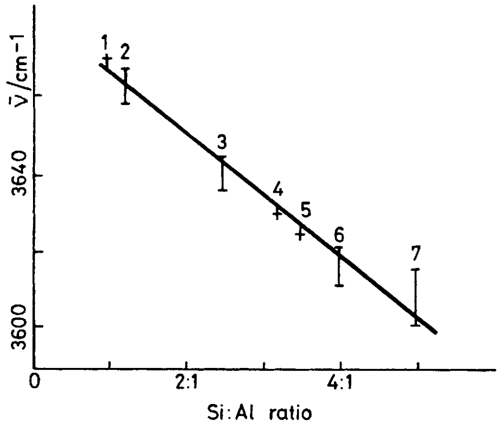

Figure. Frequencies of the acidic hydroxy-groups as a function of the Si:Al ratio for the following zeolites: 1, zeolite A; 2, X; 3, Y; 4, L; 5, Ω; 6, offretite; 7, mordenite.

type remains in a characteristic range for all cation levels, *i.e.* for all acid strengths, even when a rather high cation content precludes the presence of strong protonic sites. Hence zeolites with similar weak or medium acid strengths do not show the same frequency. Another parameter must then determine the characteristic hydroxy-frequency. It has already been reported that interactions between the charges in zeolites induce a higher field in Y than in X zeolites[9] which is related to higher acidic and catalytic efficiencies of sites.[10] We suggest that as the charge density increases (decrease in the Si:Al ratio), these interactions cause an increase in the force constant *k* of the hydroxy-group considered as a harmonic oscillator and hence shift the frequency to high values. The shape of the curve in the Figure would then reflect the influence of the charge density on the vibrational frequency.

In conclusion it is proposed that the acid 'high frequency' hydroxy-groups of each zeolite have a characteristic frequency determined by the charge density of the framework. The shifts to lower frequencies observed inside this characteristic range are related to an increase in the acid strength of the protons, upon cation exchange for example.

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