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NOTES

The Strength of Brønsted Acid Centers in NaHY Synthetic Zeolites

It is generally assumed that the catalytic activity of decationated, synthetic zeolites is due to the presence of hydroxyl groups playing the role of Brønsted acid centers. The concentration of such centers may be varied in a given type of zeolite by changing the degree of cation exchange. In the case of NaHY zeolites the influence of the latter factor on their catalytic activity was studied by several authors. Turkevich *et al.* (*1*) investigated the cracking of cumene, Ward and Hansford (*2*) the isomerization of *o*-xylene and Beaumont *et al.* (*3*) the cracking of octane. In all these cases a linear or almost linear increase in catalytic activity was observed with increasing number of sodium cations exchanged in NaY as long as this number did not exceed about 35-38 Na^+ cations (out of 56) exchanged per unit cell of zeolite. In this Na concentration region the activity calculated per Brønsted acid site created by the substitution of one Na^+ cation was therefore approximately constant. On the other hand a distinct increase in the activity calculated per acid site was observed in all the above cases at a still higher degree of exchange.

This fact is rather surprising because the exchange of Na cations up to about 28 (*4*) to 34 (*2*) per unit cell creates only or predominantly OH groups with an infrared stretching frequency of 3660 cm^{-1} formed by the O_1 atoms (bridging oxygen atoms of the hexagonal prism) projecting into the large cavity and therefore easily accessible to the adsorbed molecules while the exchange of the remaining cations produces mainly OH groups with a stretching frequency of 3565 cm^{-1} formed by O_3 atoms (oxygen atom of the hexagonal prism six-ring which in contrast to the O_2 oxygen atom is not common to the supercage ring) projecting into the inside of the hexagonal prism and therefore not easily accessible (*5*).

Several explanations of this fact were proposed. Some authors (*1,2*) assume that under the conditions of a catalytic reaction occurring at elevated temperatures hydroxyl groups become delocalized and mobile. Such a delocalization was assumed, e.g., by Ward (*6*), in order to explain the reversible decrease in the OH 3650 cm^{-1} band absorbance observed in the case of NaHY zeolites in the temperature range 200-470°C. According to these authors (*1,2*), the increased mobility of protons under the conditions of catalytic reaction would also enable 3560 cm^{-1} OH groups to take part in the reactions as active centers.

Dempsey and Olson (*7*) on the other hand, suggest that the sodium ions in the zeolite supercages may act as a catalytic poison and their removal by substitution with protons explains the observed increase in the catalytic activity. Essentially the same interpretation is accepted by Beaumont *et al.* (*3*).

In the present note we present some facts suggeting that the increasing degree of cation exchange may also increase the acid strength of the 3660 cm^{-1} OH groups.

The increase in the strength of the Brønsted acid sites might be an alternative explanation for their enhanced catalytic activity at high cation exchange degrees. Our argument is based on the observations of the thermal desorption of pyridine adsorbed on NaHY zeolites and of the shifts of the OH bands.

The estimation of the strength of surface acid sites by measuring the desorption of adsorbed molecules in the course of heating the sample is based on the assumption that the molecules of a given base are adsorbed more strongly on strong acid sites than on the weak ones and being more difficult to desorb are given off by the sample at a higher temperature (*8*).

The measurements of the absorbance of the 1545 cm^{-1} band of pyridinium ion were applied by us to determine the relative amount of C_5H_5N adsorbed on 3650 cm^{-1} OH groups (pyridine does not react with 3560 cm^{-1} OH groups). The same technique of measurements and the same series of NaHY zeolites were used as in the previous papers (*4,9*). Figure 1 shows the results of the thermal desorption of pyridine as plots of B_T/B_0 against temperature. B_0 is the integrated absorbance at the 1545 cm^{-1} band registered after the adsorption of an excess of pyridine at 150°C and removal of the loosely bonded molecules by evacuating at 150–250°C. The B_0 value corresponds to the total saturation of 3660 cm^{-1} OH groups with pyridine molecules. B_T is the absorbance registered after subsequent heating of the sample to the temperature T, evacuating for 0.5 hr and cooling down to 150°C. The ratio B_T/B_0 represents therefore the fraction of pyridinium ions remaining on the zeolite surface after the desorption at temperature T.

Figure 1 shows that up to about 300°C there are not many pronounced differences in the behavior of particular samples. At higher temperatures and especially at about 500°C, however, the differences are distinct: the samples showing the lowest degree of cation exchange desorb pyridine most easily. With increasing cation exchange degree the molecules of pyridine are more and more strongly held which indicates an increase in the strength of Brønsted acid centers.

As the concentration of 3650 cm^{-1} OH groups increases with rising degree of cation exchange two other factors characterizing the properties of the 3650 cm^{-1} absorption band are also changing. There is a shift in the frequency of the band towards

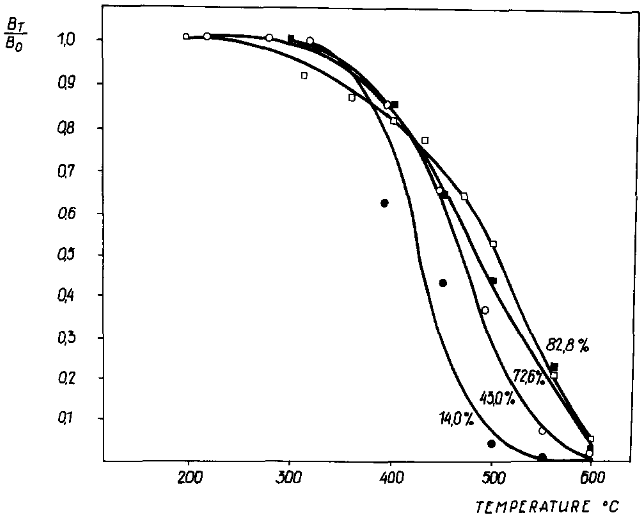

FIG. 1. Thermal desorption of pyridine: B_T/B_0 values as a function of temperature.

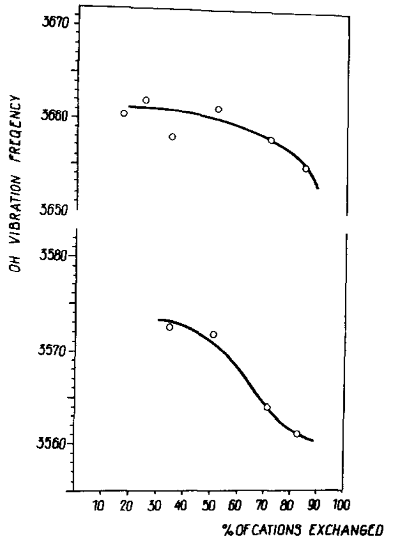

FIG. 2. Zeolitic OH group frequencies as a function of cation exchange degree.

lower values as well as a change of the integrated extinction coefficient towards higher values.

The shift in the frequency of the 3650 cm^{-1} band with increasing degree of cation exchange in NaHY zeolites was observed by Schoonheydt and Uytterhoeven (*10*). In our investigation, as Fig. 2 shows, a distinct shift in the frequency of 3560 cm^{-1} band occurred. The shift in the case of the 3650 cm^{-1} band was less distinct. However, the corelation coefficient between the frequency shift $\Delta\nu$ and the cation exchange degree was -0.76 and in another series of NaHY samples (SiO_2/Al_2O_3 ratio equal to 5.34) it reached the value of -0.83.

The change in the value of the integrated extinction coefficient of the 3650 cm^{-1} OH band was described by us elsewhere (*4*). Two levels of the latter value were observed, one of about 2.8 cm/μmole for the samples with 0–50% of Na^+ cations exchanged and another one of about 4.4 cm/μmole for the samples with 72.6 and 82.8% of Na^+ cations exchanged.

Both changes may be understood if an increased OH band polarization is assumed. Brown (*11*) pointed out that the increased value of $d\mu/dr$ (μ = dipole moment and the r = length of the bond) of OH groups in a series of compounds such as phenols or alcohols resulting in an increase of the extinction coefficient is most probably due to the increase of the ionicity of the bond. It is also connected with the increase in the bond length which in its course contributes to the decrease of the frequency of the OH stretching vibration.

The increase in the polarization and the length of the O–H bond must contribute in consequence to the increase in the OH acid strength. In fact such correlations are observed. Goulden (*12*) has shown that a linear correlation existed between the pK_a values of 49 carboxylic acids and the OH stretching frequency. A similar correlation was observed by him for a series of various phenols.

The correlation between the values of extinction coefficients of phenols and carboxylic acids and the values of pK_a may also be obtained. For example, by comparing the values of extinction coefficients of phenols taken from (*13*) and some carboxylic acids (*14,15*) with the corresponding pK_a values (*16*) we obtained plots showing that with decreasing pK_a value a distinct increase in extinction coefficient occurs.

Assuming that the behavior of OH groups in zeolites is similar to that in phenols and carboxylic acids the observed changes in the integrated extinction coefficient and frequency of OH group vibrations may be considered as an additional argument for the increase of Brønsted acid strength with increasing degree of exchange in NaHY zeolites.

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