

THE STRENGTH OF OH GROUPS IN NaHZSM-5 ZEOLITES STUDIED BY IR SPECTROSCOPY

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ABSTRACT

The acid strength of OH groups in NaHZSM-5 zeolites increases with the cation exchange degree. It has been evidenced by the results of the studies of thermodesorption of pyridine and of the studies of extinction coefficient of OH groups. This effect is rather unexpected because in highly siliceous zeolites like ZSM-5, the concentration of Na⁺ and H⁺ is very low, the distances between them are long and influence of the exchange Na⁺ - H⁺ on the properties of OH groups should be negligible. Two explanations of this disagreement are proposed.

INTRODUCTION

Acidity is a very important parameter determining the catalytic properties of zeolites. There are numerous methods of modification of acidity of zeolites, such as the modification of cation exchange degree, change of Si/Al molar ratio, partial dehydroxylation, partial poisoning of acid sites etc. The effects of these modifications on the acid and catalytic properties of zeolites are reviewed in the Jacobs' monograph [1].

The present paper concerns the modification of the acid properties of NaHZSM-5 zeolites by the variation of cation exchange degree. In NaHY zeolites the increase of cation exchange degree increased the number of OH groups, their acid strength and also their catalytic activity (for example ref. 1-5).

In ZSM-5 zeolites, the situation is more complicated. T.p.d. studies of NH₃ desorption showed that ΔH_{des} values increase with cation exchange degree [6]. Similar situation was also observed in mordenites [7] in which the temperature of t.p.d. peak of NH₃ desorption does also increase with the cation exchange degree. All these results suggest that in ZSM-5 zeolites and also in mordenites the strength of acid sites increases with the exchange degree (similarly.

as in Y zeolites).

Contrary in ^{the 2nd} NaHY zeolites, in ZSM-5 the catalytic activity do not show the same trends as the acidity. In n-hexane cracking [6], o-xylene isomerization [8,9], and in dimethylether conversion [9] the rate constant increase linearly with the number of strong acid sites, but no correlation was found between the rate of n-hexane cracking and ΔH of NH_3 desorption [6]. Such lack of correlation between the strength of acid sites and their catalytic activity was interpreted assuming the existence of a threshold level for the acid strength [6]. Above this level the acid strength does not influence any more the catalytic activity of zeolites.

The aim of the present study was to follow the dependence the acid strength of OH groups in NaHZSM-5 zeolites on the cation exchange degree. In a previous study [10,11], it has been found that two kinds of Brønsted acid sites exist in NaHZSM-5 zeolites: 3609 cm^{-1} OH group being strong sites and another Brønsted sites of lower acidity.

The concentrations of both kinds of acid sites were determined. In the present study the efforts were made to obtain the information concerning the properties of 3609 cm^{-1} OH groups only. The acid strength of these OH groups was characterized by the i.r. spectroscopic studies of pyridine thermodesorption and by the comparison of extinction coefficients of OH bands.

Two series of NaHZSM-5 zeolites were studied. One of them was obtained by the ion exchange of parent Na form in the HCl solution (HZ series) and another one obtained by the exchange of Na form in NH_4NO_3 solution (NZ series).

EXPERIMENTAL

NaHZSM-5 zeolites were obtained from a parent sodium form ("Utrazet") sample prepared at the Institute of Industrial Chemistry (Warsaw), the composition of which was: $\text{Na}_{1.7}\text{H}_{0.3}[(\text{AlO}_2)_2(\text{SiO}_2)_{94}]$ (Si/Al ratio = 47, and Na/Al = 0.85).

Two series of hydrogen forms NaHZSM zeolites were prepared: one by the exchange of Na^+ into NH_4^+ ions in NH_4NO_3 solution and another one by the exchange in HCl solutions. Various exchange degrees were obtained by using various concentrations of NH_4NO_3 and HCl solutions. The highest concentrations of these solutions were 1 M and 0.5 M respectively. After the ionic exchange, the zeolites were washed and dried at 390 K.

In order to calculate the exchange degrees, the zeolites were dissolved in HF solution and sodium content determined by atomic

absorption. The zeolites obtained by the HCl treatment were denoted as : HZ-41, HZ-81, HZ-88 (exchange degree 41, 81, 88 % resp.), and the zeolites obtained by the NH_4NO_3 treatment and further decomposition of NH_4^+ ions as : NZ-43, NZ-83 (exchange degrees 43 and 83 resp.).

For the i.r. spectroscopic studies the zeolites were pressed into thin wafers ($3-10 \text{ mg/cm}^2$). The wafers inserted into i.r. cell were pretreated in vacuo at 450°C for 1 h.

At these conditions complete water desorption and decomposition of NH_4^+ ions took place without any appreciable dehydroxylation.

Pyridine (POCH Gliwice, analytical grade was dried over KOH. The i.r. spectra were recorded with a SPECORD 75 IR spectrometer. The accumulation and subtraction of spectra were done with a KSR 4100 minicomputer working on-line with the spectrometer.

RESULTS

Adsorption of pyridine on NaHZSM-5 zeolites. Two distinct OH bands are present in the i.r. spectrum of NaHZSM-5 zeolites : at 3609 and 3738 cm^{-1} . Adsorption of pyridine results in the formation of PyH^+ ions (1545 cm^{-1}), PyL and PyNa^+ complexes (1450 and 1444 cm^{-1} bands). First portions of pyridine sorbed in zeolite react with 3609 cm^{-1} OH groups forming PyH^+ ions. The intensity of 3609 cm^{-1} OH band decreases linearly and the intensity of 1545 cm^{-1} PyH^+ bands increases linearly with the amount of pyridine sorbed. After the consumption of all 3609 cm^{-1} OH groups the next introduced pyridine molecules react with weaker Brønsted acid sites forming additionally PyH^+ ions and 1545 cm^{-1} PyH^+ band continues to increase.

The desorption of pyridine removes the molecules bonded with weak sites at first, PyH^+ band diminishes, but 3609 cm^{-1} OH band is still absent. The pyridine molecules neutralizing 3609 cm^{-1} OH groups are removed at higher temperatures. The amount of PyH^+ ions decomposed by the desorption before the 3609 cm^{-1} OH band reappeared was taken as corresponding to the amount of weak Brønsted acid sites, and the remainder of PyH^+ ions as corresponding to the amount of 3609 cm^{-1} OH groups. The concentration of both kinds of Brønsted acid sites was determined in NaHZSM-5 zeolites of various exchange degrees [10,11].

i.r. studies of thermodesorption of pyridine. In order to study the acid strength of 3609 cm^{-1} OH groups the small portions of pyridine were sorbed at 440 K in the zeolite up to the disappearance of this OH band (the excess of pyridine was avoided). The spectrum was then recorded and next the cell was connected to the liquid nitrogen trap and heated to higher temperatures (in the range 620 - 820 K). After each desorption step the cell was cooled down to 440 K and the spectrum recorded. The intensities of 1545 cm^{-1} PyH^+ band were measured after the desorptions of two temperatures: at the temperature at which 3609 cm^{-1} OH band begins to reappear (A_0) and after the desorption at 790 K (A_{790}). The ratio A_{790}/A_0 represents the fraction of 3609 cm^{-1} OH groups which still hold pyridine after the desorption at 790 K. These values which were taken as the measure of the strength of 3609 cm^{-1} OH groups are presented at the Table. In both series of zeolites HZ and NZ the acid strength of 3609 cm^{-1} measured by the pyridine thermodesorption increase with the cation exchange degree.

The calculation of extinction coefficient of 3609 cm^{-1} OH band

In order to calculate the values of integrated extinction coefficient (IEC) at 3609 cm^{-1} OH band, the values of the integrated intensities of these bands were measured in the spectra of freshly activated zeolites. The concentrations of these OH groups were determined by the pyridine adsorption and desorption (as described above). The values of IEC of 3609 cm^{-1} OH bands calculated in such a way are presented in the Table. In both series of zeolites they increase with the exchange degree of zeolites.

Table
 A_{790}/A_0 values and integrated extinction coefficients of 3609 cm^{-1} OH groups

Zeolite ^x	A_{790}/A_0	integr. ext. coeff. cm mol ⁻¹
NZ - 43	0.22	1.8
NZ - 83	0.72	2.7
HZ - 41	0.17	2.3
HZ - 81	0.40	2.8
HZ - 88	0.45	2.7

^x the values of cation exchange degrees are given in the symbols of zeolites.

DISCUSSION

The information concerning the acid strength of 3609 cm^{-1} OH groups was obtained in the studies of pyridine thermodesorption and by the comparison of the values of extinction coefficients.

The results of the studies of pyridine thermodesorption (presented at the Table) show that the acid strength of 3609 cm^{-1} OH groups increases with the cation exchange degree of NaHZSM-5 zeolites. This statement is based on the increase of A_{790}/A_0 values, which represents the fraction of 3609 cm^{-1} OH groups which still hold pyridine after the desorption at 790 K.

The integrated extinction coefficient (IEC) of 3609 cm^{-1} OH band does also increase with the exchange degree, which can be interpreted as the increase of the acid strength of these OH groups. The values of IEC of OH i.r. bands can be successfully used as the measure of the strength of OH groups. Several authors [3,4,12-15] formulated the conclusions on the strength of OH groups by the comparison of the values of extinction coefficients and the results obtained in such a way were consistent with the result obtained by others methods. Recently the quantum-chemical calculations [16] showed that in the clusters $\text{H}_3\text{AlOHSiH}_3$, where the H atoms were successively substituted by fluorine, the values of dipole moment derivative $(\frac{\partial \mu}{\partial Q_{\text{OH}}})_0$ increase with the positive charge on hydrogen in OH groups and also with the ionicity of O - H bond.

The results of the studies of both thermodesorption of pyridine and extinction coefficients lead to the same conclusion that acid strength of 3609 cm^{-1} OH groups increase with the cation exchange degree.

Such effect was already observed in NaHY zeolites [2-4] and was interpreted as a consequence of an introduction of more electrophilic protons instead of less electrophilic Na^+ ions. It results in an increase of the polarization in neighbouring OH groups. The same phenomenon can be also explained in the terms of collective model of acidity of zeolites [17]. Hydrogen is more electronegative than sodium (electronegativity 3.55 and 0.70 in the Sanderson scale); the increase of cation exchange degree increases the average electronegativity of zeolite and the positive charge on hydrogen in OH groups.

In highly-siliceous zeolites as ZSM-5 the same trends but of much lower extent are expected. In ZSM-5 ($\text{Si}/\text{Al} = 47$) the average concentration of Al is much lower than in Y ($\text{Si}/\text{Al} = 2.5$). The concentration of Na^+ and of protons is also much lower, the distances

between them much longer, and therefore the exchange $\text{Na}^+ - \text{H}^+$ should have negligible effect on the properties of OH groups. The same conclusion can be drawn if considering the collective model of acidity of zeolites. In ZSM-5, the exchange of all Na^+ to protons results in much lower variation of average electronegativity ($\Delta S_{\text{av}} = 0.033$) than in Y zeolite ($\Delta S_{\text{av}} = 0.54$).

The results obtained at the present study are not in agreement with such previsions. The increase of the strength of OH groups in NaHZSM-5 zeolites is quite remarkable. Two explanations of this disagreement can be proposed at present :

1. in highly-siliceous zeolites like ZSM-5 the OH groups are stronger acid sites than in Y. The O-H bond is more polarized and is more sensitive to even very weak electrostatic influences.
2. in ZSM-5 zeolites the Al distribution is not homogeneous, there are domains of lower and of higher Al concentration. In the domains of higher Al concentration the inductive effects are stronger and the exchange $\text{Na}^+ - \text{H}^+$ influences the strength of neighbouring OH groups. It should be noticed that several authors reported non-homogeneous Al distribution inside the crystals [18,19] and among the ZSM-5 crystals of various shapes [19].

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