BUTENE-1 ISOMERIZATION ON ·ALUMINUM-DEFICIENT NaHY ZEOLITES

By

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A series of NaHY zeolites with SiO_2/Al_2O_3 molar ratio 5.34, 6.70 and 8.45 was prepared. The properties of zeolitic 3550 and 3650 cm^{-1} OH groups and especially their interactions with adsorbed pyridine and butene-1 molecules were investigated using qualitative and quantitative IR spectroscopy. It was also shown that their acid strength increased both with cation exchange degree and with increasing dealumination. 3650 cm^{-1} OH groups are active centres in the catalytic isomerisation of butene-1. Their activity (turnover number) changes parallel to their acid strength.

The aim of the present paper was to investigate the effect of dealumination of NaHY zeolites on their catalytic properties and to correlate it with the acidity of the zeolite which was studied by the infrared spectroscopy.

Experimental

The samples of aluminum deficient NaHY zeolites with SiO_2/Al_2O_3 molar ratio 6.70 and 8.45 were obtained from the Institute of Industrial Chemistry, Warsaw. The extraction of aluminum was carried out by treating normal NaY zeolite (SiO_2/Al_2O_3 ratio 5.34) with a boiling solution of EDTA. No distinct loss of crystallinity was observed. In the course of the present investigation sodium zeolites were transformed into ammonium form by treating them with NH_4NO_3 solution at 80 °C [1]. The conditions were chosen in such a way that 3 series of $NaNH_4Y$ zeolites were obtained showing different SiO_2/Al_2O_3 ratios but very much similar numbers of NH_4^+ ions in a unit cell (Table I).

The hydrogen form of zeolites was obtained by vacuum decomposition of $NaNH_4Y$ zeolites at 400 °C for several hours. Such a treatment was always applied "*in situ*" in the infrared cell or in the catalytic reactor.

The IR spectra of zeolites and molecules adsorbed on them were recorded with a UR—10 Zeiss Spectrophotometer. The detailed procedure of such measurements is given in previous papers [2, 3].

The catalytic measurements of butene-1 isomerisation were carried out in a pulse microreactor (sample of catalyst 0.02 g, hydrogen carrier gas) and the products

Table I

Chemical composition of zeolites

Sample*	Number of NH_4^+ ions per unit cell after cation exchange
NaHY (5.34) 22.4	12.2
NaHY (6.70) 25.6	12.1
NaHY (8.45) 31.0	11.2
NaHY (5.34) 47.5	26.2
NaHY (6.70) 48.8	23.4
NaHY (8.45) 72.7	26.4
NaHY (5.34) 72.5	40.4
NaHY (6.70) 81.5	39.8
NaHY (5.34) 93.6	51.2
NaHY (6.70) 96.0	46.1
NaHY (8.45) 94.5	34.3

     * The first figure after NaHY symbol is SiO_2/Al_2O_3 molar ratio, the second one the cation exchange degree (in %).

analysed gas-chromatographically. Further details of the method are given in [4, 5]. Rate constants k were calculated using first order kinetic equation

$$\ln \frac{1-x_0'}{x-x_0} = k \cdot \tau$$

where x and x_0 are molar fractions of butene-1 in the products and in the equilibrium state *resp*. τ is contact time.

Results and their discussion

OH groups in NaHY zeolites

     Only very weak OH band at 3760 cm^{-1} was present in the IR spectrum of not decationized NaY zeolites with normal SiO_2/Al_2O_3 ratio. The intensity of this band characteristic of silanol Si—OH groups increased somewhat with the increasing degree of dealumination. Such OH groups do not react with pyridine nor ammonia molecules and are inactive in the catalytic isomerisation of butene-1.

     In the IR spectra of NaOH zeolites two distinct OH bands at about 3550 cm^{-1} (LF OH groups) and 3650 cm^{-1} (HF OH groups) are present. It was stated that positions of both bands are not influenced by the dealumination of zeolites. Similar results for aluminum deficient zeolites were obtained by JACOBS AND UYTTERHOEVEN [6] who investigated the samples prepared — as in our case — by the dealumination of NaY zeolite. On the other hand BEAUMONT ET AL. [7] who dealuminated NH_4NaY zeolite observed the IR bands at 3555, 3630 cm^{-1} and a shoulder between 3670 and 3695 cm^{-1}. The procedure of dealumination seems therefore to influence the properties of OH groups in zeolites.

     The HF OH groups react with adsorbed pyridine molecules forming pyridinium ions. In the case of non-dealuminated NaHY zeolites LF OH groups do not protonate pyridine molecules (some diminishing of the corresponding IR band intensity is explained [8,9] as the result of hydrogen bond formation). The LF OH groups in aluminum deficient zeolites may protonate pyridine at 150 °C. The extent of this reaction increases with the

Fig. 1. The concentration of 3650 cm^{-1} OH groups as the function of the number of sodium cations substituted by protons (or NH_4^+ ions) in a unit cell. Particular curves represent the results obtained for the series of zeolites differing by the SiO_2/Al_2O_3 ratio

SiO$_2$/Al$_2$O$_3$ ratio [1]. These facts may be interpreted as indicating an increased accessibility of LF OH groups for pyridine molecules or increased mobility of protons bonded in these OH groups.

The intensity of 1545 cm^{-1} band of pyridinium ion increased linearly with the increasing amount of adsorbed pyridine. From the slope of such linear plot the integrated extinction coefficient of this band was calculated (0.82$\pm$0.08/μmole). The amount of pyridine molecules necessary to the neutralization of all HF OH groups was also determined and their concentration calculated [1, 3]. The results obtained for zeolites with SiO$_2$/Al$_2$O$_3$ ratio 5.34, 6.70 and 8.45 are given in Fig. 1. It is seen that irrespectively of the dealumination degree the curves are very much similar in their shape. They increase at first almost linearly with the cation exchange degree and then reach a constant value of about 15—16 HF OH groups per unit cell. An analogous result was obtained for NaHY zeolite with SiO$_2$/Al$_2$O$_3$ ratio equal to 5.22 [3]. It is interesting to notice that this highest concentration of HF OH groups observed by us is very close to the number of hexagonal prisms in the zeolite lattice (16 per unit cell). It means that the highest concentration of HF OH groups corresponds to the situation in which there is an average one such group per one hexagonal prism. Similar value was also obtained by JACOBS ET AL. [10] for a zeolite with 70% of cations exchanged.

The acid strength of HF OH groups was estimated by studying thermodesorption of pyridine. This method was based on the assumption that the molecules of pyridine adsorbed on the stronger acid sites are desorbed at higher temperature than those adsorbed on the weaker ones. The B$_{500}$/B$_{350}$ ratio was assumed as the measure of the acid strength (B$_{350}$ is the intensity of 1545 cm^{-1} pyridinium ion band after adsorption and evacuation at 350 °C, B$_{500}$ the same value measured after subsequent desorption at 500 °C. In both cases spectra were registered at 150 °C). B$_{500}$/B$_{350}$ ratio expresses the fraction of pyridinium ions remaining after desorption at 500 °C. The results given in Fig. 2a show that at the constant concentration of HF OH groups their acid strength increases with the SiO$_2$/Al$_2$O$_3$ ratio. On the other hand at the constant SiO$_2$/Al$_2$O$_3$ ratio the strength of HF OH groups increases with the cation exchange degree [11]. This latter conclusion was also reached by us in a previous study of a series of normal NaHY zeolites. The simultaneous increase in the acid strength of NaOH zeolites with increasing
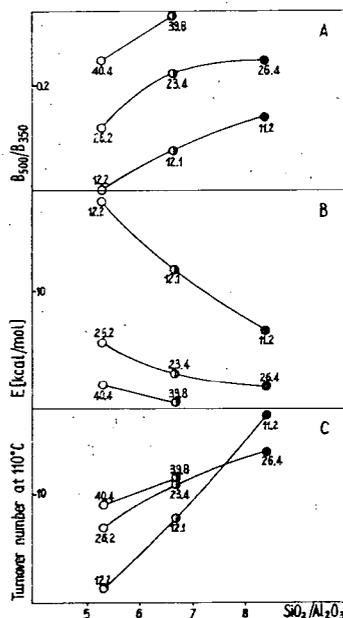
Fig. 2. a. The values of B$_{500}$/B$_{350}$ ratio characterizing the acid strength of HF OH groups
b. The activation energy of butene-1 catalytic isomerization
c. The turnover number of HF OH groups in the catalytic isomerization of butene-1 at 110 °C. All three values are presented as the function of SiO$_2$/Al$_2$O$_3$ ratio. The lines are joining the points corresponding to the different values of SiO$_2$/Al$_2$O$_3$ ratio but containing nearly the same number of protons introduced into a unit cell. The exact content of protons in unit cell is given by the numbers at each point.

dealumination and cation exchange degree was observed earlier by BEAUMONT AND BARTHOMEUF [12—14] who determined acidity using titrimetric methods.

Catalytic Properties of Aluminum Deficient NaHY Zeolites

In an earlier research [4] it has been shown by us that in the case of Y zeolites with SiO_2/Al_2O_3 ratio equal to 5.22 only the HF OH groups are catalytically active in the isomerisation of butene-1. Non-decationated NaY zeolites as well as dehydroxylated ones and containing only Lewis acid sites are non active. In addition IR studies have shown [9] that at the temperatures of the catalytic reaction only HF OH groups interacted with butene molecules which manifested by the decrease of the intensity of 3650 cm^{-1} band and simultaneous vanishing of unsaturated character of the olefine. The conclusion concerning the role of HF OH groups reached also by JACOBS ET AL. [10] was verified by us also in the case of dealuminated zeolites which are losing their catalytic activity in the measure as HF OH groups are poisoned by chemisorbed pyridine molecules.

The concentration of HF OH groups determined by quantitative IR spectroscopy was used for calculating the turnover numbers for butene-1 isomerisation. Their values together with the values of activation energies determined within the temperature range 90—125 °C are shown in Figs. 2b and c. It is clearly seen that if the samples contain approximately the same number of protons introduced into a unit cell (and also as Fig. 1 shows the same number of HF OH groups) the turnover number increases with increasing value of SiO_2/Al_2O_3 ratio. From the same figure one may conclude that at the constant value of SiO_2/Al_2O_3 ratio the activity is increasing with increasing degree of cation exchange. The increase in the catalytic activity is accompanied in all the cases by a decrease in the activation energy.

The catalytic properties of HF OH groups in NaHY zeolites correlate very well with their acid strength illustrated by the graphs in Fig. 2a. Increased acid strength of HF OH groups seems to be the most plausible explanation of the observed effects of decationization and dealumination.

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