TO THE NATURE OF THE CATALYTIC ACTIVITY OF DECATIONIZED AND STABILIZED FORMS OF Y-ZEOLITES

By

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The influence of decationization, stabilization and dehydroxylation of Y type zeolites on their catalytic activity was investigated. It was shown, that the active centres formed by these processes played a different role in the interaction with propylene, ethylene and deuterium.

The catalytic activity of HY zeolites is of common knowledge, while the nature of this activity has not been quite clear. We were interested therefore in the nature of active sites responsible for the catalytic interaction with propylene, ethylene and deuterium. The number and the type of the active centres was changed by the degree of decationization, by the stabilization of zeolites and by their dehydroxylation.

The decationization of the zeolites increased from NaY, $H_{20}Na_{80}Y$, $H_{40}Na_{60}Y$ to $H_{70}Na_{30}Y$ (shortly *e.g.* HY-70). The ratio Si/Al was in all cases 2.5, the sorption capacity of Ar was 10.4—11.2 mmol/g (all weights relate to a dried sample). The samples were prepared from the ammonium form *in vacuo:* the hydroxylated samples at 300, 350 or 400 °C (further denoted as Z_{300}, Z_{350}...), a partially dehydroxylated sample at 500 °C (Z_{500}). The HY-70 zeolite was stabilized under selfsteaming conditions at 570 and 770 °C [1], *resp.* The latter sample was denoted as St-E, the former St-C_1 and St-C_2. The preparation of these two last samples differed in the kinetic parameters of stabilization. The sorption capacity decreased with stabilization up to 9.4 mmol/g. The extra-lattice aluminium atoms per unit cell (removed by the extraction with 0.1N NaOH) increased from 2.9 to 6.6 from St-C to St-E. The stabilized zeolites were also treated in vacuo at 400 °C (Z_{400}) or 500 °C (Z_{500}). The zeolite-propene interaction was investigated at the pressure of 1.7 kNm^{-2} by setting the IR instrument (Perkin-Elmer 621) to scan repeatedly over the 3800—1200 cm^{-1} region [2]. The pyridine was adsorbed at 300 °C and after evacuation of the cell at the same temperature, the IR spectra at the temperature of the IR beam were recorded [1]. The interaction of propene and ethylene with individual zeolites was also studied at 80 °C by the gravimetric method at the pressure of 5.3 kNm^{-2} [3]. The exchange of deuterium at 400 °C with 0.075 g of zeolite was investigated at the pressure of 0.19 kNm^{-2} (Soviet mass spectrometer MCH 1302) [4].

Results

HY *zeolites-interaction with propene and ethylene*

The structural hydroxyls were present on all our samples of HY sieves, as resulted from IR spectra-bands at 3640 cm^{-1} (HF) and 3550 cm^{-1} (LF). In the interaction with unsaturated hydrocarbons only OH groups located in the large cavities were involved. Their number in the unit cell was calculated from the height of the HF band on the basis of the data from [5] (see Table I). Assuming that the removal of two hydroxyls gives rise to one Lewis acid-base pair, the number of the latter ones in a u. c. formed in dehydroxylated samples was determined.

The formation of hydrogen-bonded OH ... $\underset{C}{\overset{C}{\|}}$ complexes with HF hydroxyls was observed after the adsorption of C_3H_6 on HY sieves. An attenuation of the 3640 cm^{-1} band occurred and this was accompanied by a development of a broad band at positions given in Table I and by a band of propene. The intensity of these

Table I

HY-*zeolites, interaction with propene and ethylene*

	HF/u. c.	Propene k_{CH_3} [$cm^2 g^{-1} min^{-1}$]	Propene k_{CH_3}/HF [$cm^2 g^{-1} min^{-1}$]	Propene ν_{OH} [cm^{-1}] OH ... $\underset{C}{\overset{C}{\|}}$	Ethylene $k_{et.}$ [$mg\ g^{-1} min^{-1}$]	Ethylene $k_{et.}/Lw$ [$mg\ g^{-1} min^{-1}$]
HY-70 Z_{320}	22.1	5.8	0.26	3180—3190	<0.05	—
HY-70 Z_{400}	20.5	6.1	0.30	3180—3190	<0.05	—
HY-70 Z_{500}	4.8	5.9	1.22	*b*	5.5	0.64
HY-40 Z_{400}	15.3	2.9	0.19	3200	<0.05	—
HY-40 Z_{500}	6.3	1.8	0.28	3200	1.6	0.36
HY-20 Z_{400}	8.4	0.35	0.04	3230	<0.05	—
HY-20 Z_{500}	3.6	0.30	0.09	3230	0.38	0.16
NaY Z_{400}	0	0	0	0	<0.05	—

b the HF groups were so rapidly covered by saturated compounds that the position of this band could not be located.

bands decreased during oligomerization, when branched saturated hydrocarbons were formed. For the comparison of the catalytic activity the intensity A_{CH_3} (normalized on sample thickness) on the 2950 cm^{-1} band of CH_3 groups in a saturated chain was used. The activities order was confirmed by the intensity-time plots of the C=C band, the CH_2 band and the OH band in OH... $\underset{C}{\overset{C}{\|}}$ complex. The extent of spectral changes together with the measurement of the weight increase showed that gas molecules also participate in the building of chains. With regard to possible transport limitations, the rate of the CH_3 intensity changes k_{CH_3} given in Table I was determined

from the early stage of reaction. In the next column this value related to 1 HF group is shown.

From these data the following conclusions could be made: *i*) the activity of both hydroxylated and dehydroxylated samples in propene oligomerization drops with the decationization; *ii*) the position of the OH band in the OH...$\underset{\underset{C}{\|}}{}$ propene complex moves to a higher wavenumber with decreasing decationization; *iii*) the dehydroxylation usually decreases the total activity. However, the activity per HF group increases, particularly with the HY-70 sample.

Hydroxylated forms of HY zeolites were found to be inactive with respect to the ethylene oligomerization; this reaction proceeded on the dehydroxylated samples only. In the Table I, the rate of the weight increase $k_{et.}$ was used for the characterization of total activity. The rate related to one L. acid-base pair, formed by dehydroxylation, is shown in this table, too. From these data follows, that the effect of dehydroxylation on the catalytic activity in ethylene oligomerization is most remarkable with HY-70 sieve and lowers with decreasing decationization.

Stabilized zeolites-interaction with propene and ethylene

Bands of OH groups typical for stabilized forms were present in the infrared spectra of St-C and St-E samples — see Fig. 1. The zeolite St-C_1 contained in addition OH groups with a 3630 cm^{-1} band which was at similar positions as structural hydroxyls bands in HY samples.

Both ethylene and propene interacted with 3690 cm^{-1} hydroxyls of St-E zeolite giving rise to hydrogen bonded complexes (ν_{OH}=3440, 3490 cm^{-1} for adsorbed propene and ethylene, *resp.*). This zeolite was found to be inactive.

The activity of St-C samples in the oligomerization of ethylene was found to be still low and to be increased by dehydroxylation. The substantial differences were observed in the rate of propene oligomerization on the St-C_1 and St-C_2 samples together with the negative influence of dehydroxylation (Table II). The activity of St-C_1 zeolite pretreated *in vacuo* at 400 °C was similar to that one of parent HY-70 sieve. The catalytic reaction in the St-C samples was accompanied by the decrease of 3690 and 3670 cm^{-1} bands, in the case of the St-C_1 sample also by the disappearance of the 3630 cm^{-1} band.

From the interaction with pyridine it follows in respect to the propene and ethylene interaction: *i*) the amount of Brönsted centres which forms pyH^+ ions is by one order lower on St-E than on the parent HY-70 zeolite in its

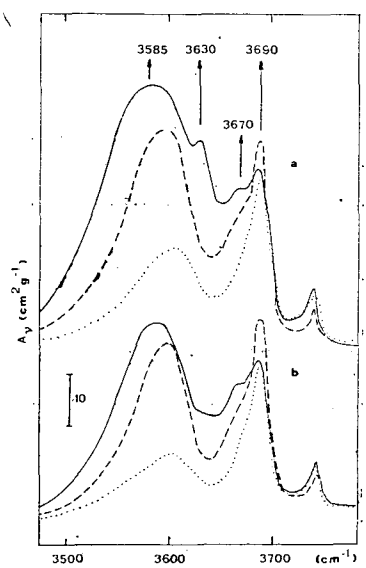

Fig. 1. IR spectra of stabilized zeolites. Full line: St-C_1; dashed line St-C_2, dotted line St-E; after 18 hrs evacuation at *a* 400° and *b* 500 °C.

Table II

Stabil. Zeolites — interaction with propene and ethylene

		propene k_{CH_3} [$cm^3 g^{-1} min^{-1}$]	*ethylene* $k_{et.}$ ($mg\ g^{-1} min^{-1}$]
St-C_1	Z_{400}	6.0	0.3
	Z_{500}	3.5	1.3
St-C_2	Z_{400}	1.7	0.2
	Z_{500}	0.6	0.8
St-E	Z_{400}	0.09	<0.05

hydroxylated form; *ii*) the number of these sites is 3—4 times higher on St-C than on St-E sieves and decreases with dehydroxylation, *iii*) the band of 3630 cm^{-1} hydroxyls of St-C sieve disappears.

Exchange with deuterium

Both types of D_2 exchange with zeolites were evaluated from one measurement using the initial non-equilibrated mixture of D_2 and H_2 [6]: the exchange of D_2 with zeolitic hydrogen groups (hetero-exchange) and the exchange of D_2+H_2 catalyzed by zeolite but not including the hydrogen of OH groups (homo-exchange).

Table III

Total number of the OH *groups and the rates of hetero- and homo-exchange*

		NaY	HY-20	HY-40	HY-70	St-C_1	St-C_2	St-E
$OH/g \times 10^{-20}$	Z_{400}	0.7	8.4	14.7	19.1	28.4	24.9	10.1
	Z_{500}	0.7	5.8	6.8	8.7	12.6	12.6	7.1
$R_{hetero} \times 10^3$	Z_{400}	—	3.5	2.7	1	4	2	3.5
[atom $min^{-1} g^{-1}$]	Z_{500}	—	12	7	5	9.5	8.8	5
$R_{homo} \times 10^{-18}$	Z_{400}	6.5	3.1	4.2	1.1	1	1	3.5
[atom min^{-1}] per OH	Z_{500}	6.5	9.3	9.3	69	6.4	4.5	3.5

In Table III, the rates for hetero-exchange and homo-exchange together with the total numbers of OH groups taking part in the hetero-exchange are shown.

The rates of hetero-exchange per OH group increased with decreased decationization and are also higher for stabilized zeolites than for the parent zeolite HY-70. The dehydroxylation always increased the hetero-exchange rate; an extraordinary high rate of homo-exchange was found for dehydroxylated HX-70 zeolite, but this effect was lowered with decreased decationization and increased stabilization.

Discussion

For the oligomerization of propene and ethylene on hydroxylated HY zeolites the carbonium ion mechanism is suggested. Proton transfer is supposed to involve tunneling *via* a strong hydrogen complex [7]. Our results support this opinion by the parallelism found between the activity of samples and the position of the OH band in the hydrogen bonded complex. The wavenumber shift related to unperturbed hydroxyls provides information about the OH bond weakening and in this way about their acidity strength. The diminishing of this shift with decreased decationization shows that both the acidity strength and the number of OH groups are responsible for the catalytic activity. The lack of ethylene oligomerization under our experimental conditions is probably caused by the lower basicity of ethylene in comparison with propylene and by the necessity of primary carbonium ion formation from ethylene as was already supposed by CANT [7]. The appearance of ethylene conversion with dehydroxylation evidently depends on the presence of Lewis acid- base pair centres. The maximum efficiency calculated per one pair of these centres was found with HY-70 and it decreased towards NaY. Propene conversion is catalyzed both with Brönsted and Lewis acid centres as can be seen from the comparison of propylene and ethylene interactions.

Homo- and hetero-exchange was found to be in antibatic dependence on the presence of Brönsted acid centres: it is of lowest value with HY-70 in hydroxylated form and increases with the increasing number of Na^+ ions. Na^+ ions could play an active role in deuterium exchange. The Lewis acid-base pair centres catalyze strongly the homo-exchange, especially on HY-70.

The properties of stabilized zeolites strongly depend on the stabilization conditions: the effect of dehydroxylation is of lesser importance. The zeolites stabilized at 770 °C were found to be practically inactive in hydrocarbon conversion probably due to the annihilation of the Lewis acid-base pair centres during the high temperature stabilization of the lattice. The shift of the OH band due to the formation of OH... $\underset{\underset{C}{\|}}{\overset{C}{\|}}$ complexes indicated a low acidity of the 3690 cm^{-1} hydroxyls located in the large cavities. This finding was in accordance with pyridine adsorption. This adsorption was higher with zeolites stabilized at 570 °C in a similar way as their activity in propene conversion. Hetero-exchange was found to proceed with a higher rate on stabilized zeolites than on HY-70, likely owing to some lattice deffects. The homo-exchange on slightly stabilized zeolites is similar to that on the parent HY-70 zeolite.

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