INFLUENCE OF PREPARATION CONDITIONS
ON PHYSICOCHEMICAL PROPERTIES AND CATALYTIC ACTIVITY
OF STABILIZED ZEOLITES

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Highly decationized zeolite NH_4NaY, stabilized by water vapour under steaming conditions at 1030 K, was characterized by its lattice constant, sorption capacity, quantity of extralattice Al, number and character of OH groups present after dehydration in vacuum at 670 K. The catalytic activity and the effect of Lewis and Broensted type acid centers were tested by oligomeration of ethylene and propylene at 310 K and isotopic exchanges of ethylene-d_4 + OH and propylene-d_6 + OH at 570 K. The properties of this zeolite were compared with zeolites stabilized under selfsteaming conditions at 1040 and 820 K. Structural changes caused by the stabilization process are more pronounced with the steamed zeolite than with the selfsteamed one; in the latter case they diminish with stabilization temperature. Accordingly, the results of catalytic measurements reveal the effect of strong Broensted acid centers in the case of low-temperature selfsteamed zeolite; these centers apparently originate from remainders of the original decationized zeolite. The high-temperature self-steamed zeolite is essentially inactive, whereas the activity of the high-temperature steamed zeolite suggests the presence of catalytically active electron-acceptor centers.

The action of water vapour on NH_4NaY zeolites leads to a change of their properties. Thus, under certain conditions we can obtain a zeolite of a much higher thermal and hydrothermal stability than the HNaY zeolite prepared from the ammonium form by decomposition in vacuum. The preparation of stabilized zeolites was for the first time reported by McDaniel and Maher[1]. Since then, several methods of preparation have been described and the reactions stoichiometry and the physical properties of these substance have been studied by many authors[2], however an appreciable attention has not been paid to their catalytic behaviour.

The present work it devoted to the comparison of zeolites stabilized either under steaming conditions (during flow) or under selfsteaming (deep bed) conditions, especially with regard to the relations among the structural changes, acidity, and catalytic activity. As in the preceding work about nonstabilized HY zeolites[3-5], use was made of *a*) adsorption of ethylene and propylene and their oligomeration in zeolite cavities at 310 K, and *b*) isotopic exchange of ethylene-d_4 and propylene-d_6 with the zeolite hydroxyl groups at 570 K. The solid phase was studied by IR spectroscopy, the gaseous phase by mass spectrometry.

EXPERIMENTAL

Zeolite SHY was prepared from $(NH_4)_{95}Na_5Y$ zeolite (VURUP, Czechoslovakia, Si/Al = = 2·9) in a stream of 80% water vapour in oxygen atmosphere under atmospheric pressure at a temperature of 1030 K, at which the zeolite was kept for 3 h. After cooling, the zeolite was stored in a defined hydrated state above aqueous $MgCl_2$ solution. US-C and US-E zeolites were furnished by the authors[6,7] who prepared them from $(NH_4)_{70}Na_{30}Y$ (Si/Al = 2·5) under selfsteaming conditions in a static (deep bed) arrangement at 840 and 1040 K. The NH_4NaY forms and both types of the stabilized zeolites were dehydrated and deammonized in vacuum (10^{-3} Pa) at 570—890 K. In further text, the temperature of the treatment is given after the symbol of the sample, *e.g.*, SHY/670.

X-Ray spectra for the SHY zeolite in the hydrated form were measured on a Difractograph Chirana (Prague), which was calibrated with α-SiO$_2$. Aluminium was extracted with 0·1M-NaOH (200 ml per 1 g sample for 24 h) (ref.[7]) and determined by titration or AAS analysis on a Varian AA 775 spectrophotometer. The sorption capacity of zeolite for argon was measured on a quartz spiral balance at 77 K and 13·3 kPa pressure of argon; the samples were evacuated at 620 K. The total content of OH groups in the zeolites was calculated from the results of $D_2 + OH$ exchange measurements, obtained by analysis of the gaseous phase with MCH 1302 mass spectrometer (USSR).

Adsorption of ethylene and propylene and their eventual oligomeration in zeolite cavities were measured on an IR spectrophotometer Perkin–Elmer 621 at 310 K and 6·6 or 1·7 kPa pressure. The catalytic activity was characterized[3,4] by the initial increase of the 2955 cm^{-1} band of methyl groups in the oligomers per unit time, k_{CH_3}. The isotopic exchange of OH groups of zeolites with perdeuterated ethylene and propylene was measured at 570 K and 0·2 kPa pressure by mass spectrometric analysis of the gaseous phase.

The rate of exchange was measured far from the equilibrium according to

$$R = [(D) (OH)/t[(D) + (OH)]] \ln F,$$

where $F = (c - c_\infty)/(c_0 - c_\infty)$, (D) and (OH) denote the total number of D atoms in olefin molecules and OH groups in the zeolite, c_0, c, and c_∞ are isotopic concentrations of deuterium in the gaseous phase at times t_0, t, and t_∞, respectively. More details are given in our preceding communications[3,4].

RESULTS

Structure of zeolites. It is known from the literature[2] that the stabilization of NH_4NaY zeolites is accompanied by structural changes caused by transition of aluminum from the skeleton into the extralattice positions. As a result, there is a contraction of the lattice, lowering of the sorption capacity, and possibility of leaching out of some of the aluminium with the solution of NaOH. These changes become more pronounced in the order US-C, US-E, SHY (Table I). The decrease of the sorption capacity with respect to the parent decationized Y zeolites does not exceed 23%. The zeolites differ also by the number of OH groups and their character (Table I, Fig. 1). SHY/670 zeolite contains very little OH groups (comparably with $H_{70}Na_{30}Y/890$ zeolite, whose structural hydroxyls were removed

by dehydroxylation at 890 K; see Table I and Fig. 1). In its IR spectrum, the 3740 cm^{-1} band dominates, which is attributed to SiOH groups on the surface of the grains, on amorphous impurities, and on structural defects. This band is not characteristic for a certain zeolite type. Further a weak 3570 cm^{-1} band of hydroxyl groups is apparent which were formed as a result of the stabilization process. US-C and US-E zeolites contain a larger quantity of OH groups, which is substantially higher with the less stabilized US-C zeolite than with the US-E. Both selfsteamed zeolites have typical hydroxyls of the 3690 cm^{-1} band (eventually with a shoulder 3670 cm^{-1})

TABLE I

Characteristics of Stabilized and Decationized Zeolites

Values	Vacuum K	SHY^a	US-E^b	US-C^c	$(NH_4)_{70}Na_{30}Y$
Lattice constant (nm)	—	2·443	2·453^d	2·457^d	2·468^d
Extracted Al (atom/u.c.)	—	22·5^e	12·2^d	5·3^d	0^d
Sorption capacity decrease (%)	620	20·2	22·5^d	12·5^d	0
OH 10$^{-20\,f}$	670	3·0	10·1	28·4	19·1
	890	—	—	—	2·5

Stabilization ^{a} at 1030 K in steam, ^{b} at 1040 K under selfsteaming conditions, ^{c} at 820 K under selfsteaming conditions. ^{d} See ref.[6–8]; ^{e} extracted Al from $(NH_4)_{95}Na_5Y$: 2·5 atom/u.c. ^{f} per g of dry sample.
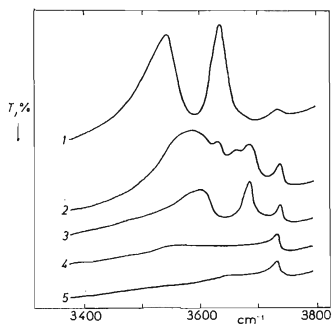
FIG. 1

IR Spectra of OH Groups of Zeolites
1 $H_{70}Na_{30}Y/670$; 2 US-C/670; 3 US-E/670; 4 SHY/670; 5 $H_{70}Na_{30}Y/890$.

and of the $3585-3600 \, cm^{-1}$ band; their occurrence was stated also with other stabilized zeolites[2]. US-C contains in addition OH groups of the to $3630 \, cm^{-1}$ band, which according to the band position, acidic properties, and behaviour during dehydration[8] are analogous to the structural HF hydroxyls of HNaY zeolites (HF band: $3640 \, cm^{-1}$, LF: $3550 \, cm^{-1}$ (Fig. 1); see Table I for the total number of OH groups in $H_{70}Na_{30}Y/670$).

Interaction with ethylene and propylene at 310 K. The values of k_{CH_3} given in Table II show that the studied stabilized zeolites have a very different activity for the oligomeration of ethylene: the reaction proceeds much more rapidly in SHY than in US-C, and in US-E only physically sorbed ethylene was found[6,8]. The interaction with propylene was for the reasons given earlier[3,4] followed on those zeolites which contained a considerable number of OH groups typical for the given substance, *i.e.*, on US-E and US-C. On the latter, the oligomeration of propylene proceeded very rapidly, whereas the former was practically inactive (Table II). Adsorption of unsaturated hydrocarbons and the formation of oligomeric chains were accompanied by decreasing intensities of the OH groups bands in the interval $3690-3630 \, cm^{-1}$ and by the appearance of new bands at lower wave numbers typical for H complexes[6,8]. When the zeolite was highly filled with oligomers, the SiOH groups were covered with them also. During reaction of propylene and ethylene on stabilized zeolites, branched saturated chains were formed, suggesting a skeletal isomerization and hence a cationic mechanism of the oligomeration. For comparison of the catalytic activity of stabilized zeolites with nonstabilized ones, the rates of the

TABLE II
Rate of Oligomerization at 310 K and of Isotopic Exchange of Ethylene and Propylene at 570 K

Zeolite	SHY	US-E	US-C	$H_{70}Na_{30}Y$	
Vacuum, K	670	670	670	$620-670$	890
Oligomerization, $k_{(CH_3)}$ ($cm^2 \, g^{-1} \, min^{-1}$)					
C_2H_4	1·5	0	0·15	$0-0·1$	0·5
C_3H_6	—	0·09	6·0	5·9	2·5
Exchange, $R . 10^{-18}$ ($atom \, min^{-1}$)					
$C_2D_4 + OH$	1·1	0·02		0·2	
$C_3D_6 + OH$	25·0	4·4	6·8	14·0	

reactions of propylene and ethylene on $H_{70}Na_{30}Y$ zeolite are given in Table II. This zeolite was prepared in two forms: a fully hydroxylated one with structural OH groups and a dehydroxylated one in which Lewis acid–base pairs were formed by removing the structural OH groups.

Isotopic exchanges C_2D_4 + OH *and* C_3D_6 + OH *at* 570 K. The exchange of D atoms in perdeuterated ethylene with the H atoms of the OH groups in stabilized zeolites proceeds by a single mechanism as with the HNaY zeolites studied earlier[6,7]. With the SHY zeolite, however, no induction period was found, which was always observed with zeolites stabilized under selfsteaming conditions, as well as with HNaY. The exchange of propylene-d_6 proceeded by a multiple mechanism as with all hitherto studied zeolites[3,4] and slowed down with time. The exchange rates in Table II were determined from kinetic dependences of the first order (with respect to the atomic concentration of deuterium), the data were measured far from the equilibrium (after 10 and 30 min for ethylene and propylene, resp.). The gaseous phase contained under these conditions in the case of the most active SHY zeolite less than 1% products of the catalytic reaction of ethylene and 7% those of propylene. Table II gives also the exchange rates found with the nonstabilized $H_{70}Na_{30}Y$ zeolite which was activated in vacuum at the same temperature (670 K) as the stabilized zeolites. The highest exchange rate for both ethylene and propylene was found with SHY zeolite, the lowest one with US-E. The exchange rate for ethylene-d_4 was by $1-2$ orders of magnitude slower than for propylene-d_6.

DISCUSSION

It follows from our results that the preparation conditions of the stabilized zeolites influence considerably the IR properties. The most profound changes as compared with the parent NH_4NaY zeolite were attained during preparation under steaming conditions (SHY zeolite). In this case much more aluminum ions passed into the extralattice positions than in the case of zeolites stabilized under selfsteaming conditions (US-C, US-E). The experimental data show that after evacuation of SHY zeolite at 670 K OH groups do not exist in significant amount in the co-ordination sphere of the extralattice Al as well as in the skeleton. US-C and US-E zeolites, on the contrary, contain a large number of OH groups, of which those characterized by bands in the interval $3690-3630 \text{ cm}^{-1}$ are accessible for ethylene and propylene.

The mentioned differences among the stabilized zeolites are reflected also in their catalytic activity during oligomeration of ethylene and propylene and during isotopic exchanges of these hydrocarbons with OH groups. These results can be discussed in terms of previous findings[3,4,9] on nonstabilized HNaY zeolites: It was shown that the strongly acidic structural HF hydroxyls of HNaY zeolites are decisive in the oligomeration of propylene, especially with samples that contain a negligible number

of Lewis acid–base pairs. The Lewis centers play an important role in the initiation of the oligomerization of ethylene (structural OH groups are inactive in this case). The exchange of five end atoms of D in propylene-d_6 involves a direct interaction of the molecule with structural HF groups of hydroxylated forms of HNaY zeolites[3,4], whereas the character of the exchange of D atoms in ethylene-d_4 and of the tertiary D atom in propylene-d_6 with OH groups is mediated and needs a small quantity of oligomers formed in the zeolite. As to the mechanism[3,4], the cationic oligomerization proceeds in HNaY at 310 K, the exchange between propylene-d_6 and OH at 570 K takes place *via* a multiple mechanism, and between ethylene-d_4 and OH *via* a single mechanism (*i.e.*, during one stay of a molecule in the zeolite all five end D atoms are exchanged in the first case and one D atom in the second). The same mechanisms were found with the stabilized zeolites. The oligomerization mechanism of ethylene and propylene suggests that the reaction is controlled by the same types of centers as with HNaY.

Accordingly, the differences in the activity of the stabilized zeolites can be elucidated as follows. *1)* The stabilization process under steaming conditions (and after dehydration at 670 K) results in the formation of electron acceptor centers which initiate the oligomerization of ethylene at 310 K. These centers apparently contribute to the high catalytic activity of SHY zeolite. These centers probably activate the ethylene molecules also in the exchange with hydroxyls at 570 K so that the formation of an oligomeric chain as with other stabilized zeolite types and HNaY form is not needed. A substantial increase of the exchange rate in comparison with other zeolites was found also in the exchange between propylene-d_6 and OH, besides the usual five D atoms also the tertiary D atom was to an appreciable extent exchanged. Since the strongly acidic structural OH groups were absent in SHY, this difference can be attributed again to the effect of the electron acceptor centers formed by stabilization during flow.

ESCA measurements on SHY and HNaY zeolites[10] showed that the surface layers of SHY were enriched with Al: its content in relation to Si was doubled in comparison with the decationized HNaY zeolite. It is probable that the formation of electron acceptor centers is connected with the formation of extralattice Al—O clusters and that the inhomogeneity of the distribution of aluminum and silicon in the zeolite has also a significant influence on the catalytic properties of SHY.

2) The properties of zeolites prepared under selfsteaming conditions depend on the temperature of stabilization. US-E zeolite was stabilized at 1 040 K, *i.e.* at the same temperature as SHY, however the structural changes were much smaller and no electron acceptor centers were formed which would be capable to initiate the oligomerization of ethylene. The very low rate of oligomerization of propylene suggests that the hydroxyls of US-E zeolite (considered typical for stabilized zeolites) have the properties of weak acids. Their low acidity was manifested in that the bond of OH groups of the 3690 cm^{-1} band was only little weakened after adsorption

of the hydrocarbons: the corresponding shift of the band was 200 and 250 cm^{-1} for the H complex of ethylene and propylene, respectively[6,8], whereas in the case of strong acidic structural HF hydroxyls (3640 cm^{-1} band) of $H_{70}Na_{30}Y$ zeolite[3,4,8] the shift was 370 and 460 cm^{-1}. The absence of Lewis centers and the low acidity of the hydroxyls elucidate the low rate of the isotopic exchange of both hydrocarbons with the hydroxyls of US-E zeolite.

US-C zeolite stabilized at 820 K is similar by its catalytic properties and isotopic exchange to the parent $H_{70}Na_{30}Y$ zeolite. In US-C zeolite, only a very little content of Al in the extralattice positions was found, however strongly acidic hydroxyls analogous to structural HF groups in parent $H_{70}Na_{30}Y$ zeolite were found instead. After the selfsteaming process at 820 K, certain features typical for the parent decationized zeolite remain apparently preserved, and these are likely decisive for the reactions of the unsaturated hydrocarbons and their isotopic exchange.

The comparison of the three types of stabilized zeolites shows the possibility of a broad variation of their acidic properties and thus their activity in carboniogenic reactions by varying their preparation conditions. The conditions of stabilization control the number of extralattice Al atoms, their distribution and coordination, the occupation of defects in the skeleton and the mode of compensation of the lattice charge together with the proton donor properties of the hydroxyls. The selfsteaming process at low temperatures (820 K) results in a zeolite in which the dominant role from the catalytic point of view play the Brönsted acid centers, probably relics from the original decationized zeolite. The high stabilization temperature (1040 K) and selfsteaming conditions cause a loss of the catalytic activity, while the stabilization during flow at the same temperature is accompanied by the formation of catalytically active electron acceptor centers.

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