THE EFFECT OF DECATIONATION
OF HYDROXYLATED HNaY ZEOLITES ON THEIR INTERACTION
WITH ETHYLENE AND PROPYLENE. HYDROGEN COMPLEXES,
OLIGOMERATION AND ISOTOPE EXCHANGE

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The effect of decationation on the interaction of propylene and ethylene with the hydroxylated forms of HNaY zeolites has been studied. The compounds formed in the zeolite cavities were studied using their infrared spectra, the composition of the gaseous phase was followed by mass spectrometry. The results showed that among factors affecting the interaction with propylene properties of hydroxyl groups play the decisive role. With the increasing decationation of the zeolite the strength of the OH bond in the hydrogen complex of the large-cavity hydroxyls with propylene decreased and the rate of propylene oligomeration at 310 K as well as the isotope exchange rate of propylene-d_6 with the zeolite hydroxyls at 570 K increased. The propylene isotope exchange reaction proceeded by the multiple-step mechanism. In the case of ethylene only the physical sorption with a non-specific character was observed at 310 K. The adsorbed amount increased with the increasing content of Na$^+$ ions in the zeolite (with the decreasing decationation). A part of the adsorbed molecules formed hydrogen complexes with hydroxyls of large cavities. The observed lower weakening of the OH bond was in agreement with the lower basicity of ethylene if compared with propylene. The isotope exchange of ethylene-d_4 with the zeolite hydroxyls proceeded by a single-step mechanism, it had an autocatalytic character and its rate was 70 times lower than that of the isotope exchange of propylene-d_6 with OH.

The catalytic reactions of ethylene and propylene on various types of zeolites have been dealt with in a number of papers[1−6], However, in none of them a systematic study of the relations between the zeolite composition and its interaction with these two olefins has been presented. In the case of HY zeolites the interest was concentrated predominantly on propylene and on the mechanism of its transformation. From the composition of the gaseous phase it was deduced that carbonium ions are formed in the zeolite[7,8]. Liengme and Hall[9] observed oligomeration of propylene at the room temperature in cavities of H$_{45}$Na$_{55}$Y in the hydroxylated form while ethylene was only physically adsorbed; for both olefins they found the formation of hydrogen complexes with the zeolite hydroxyls. These authors explained the zeolite catalytic activity by the formation of the hydrogen complexes and by their transformation into the carbonium ions. They pointed out that the ethylene oligomeration is related to the presence of Lewis centers formed by the dehydroxylation of the zeolite. From our previous study[10] it follows that the catalytic activity of HY zeolite with respect to propylene depends on the degree of the decationation and dehydroxylation. With the increasing degree of dehydroxylation we have found also the effect of Lewis centers. The oligomeration of ethylene proceeded also on partially dehydroxylated samples and its rate also increased with the increasing decationation of zeolites.

The mechanism of the interaction of the reactant with the zeolite is demonstrated also in the studies of the isotope exchange in olefins. The comparison of the zeolite $H_{70}Na_{30}Y$ with $H_{60}Na_{40}X$ revealed the relation of the Si : Al ratio, of the acidity of hydroxyls, and of the activity in the oligomeration of propylene with the exchange $C_3D_6 + OH_{zeol}$[11,12]. The isotope exchange of C_2D_4 with OH groups has been studied in the paper[13] in which the changes in the isotopic composition of OH groups in the zeolite were determined using the IR spectra. Cant and Hall[13] concluded from their results that the transition state for the isotope exchange is not the same as the transition state for oligomeration.

In this paper we have studied systematically the effect of decationation on the inter- action of HY zeolites with ethylene and propylene at 310 K and 570 K. Along the adsorption measurements and the studies of catalytic transformations we have included also the isotope exchange of the above-mentioned perdeuterated olefins with the zeolitic hydroxyls. The data on the composition of the solid phase are obtained with IR spectroscopy, the gaseous phase was analyzed with a mass spectro- meter.

EXPERIMENTAL

Samples of various decationated zeolites of the Y type: $Na_{0.81}H_{0.19}Y$ (designated HY—20), $Na_{0.61}H_{0.39}Y$ (HY—40), and $Na_{0.30}H_{0.70}Y$ (HY—70) were prepared from the respective ammonium form of the zeolite by heating the samples for 14 hours at the temperature of 570 to 620 K in a vacuum apparatus under the pressure of 10^{-3} Pa. The zeolite NaY of the chemical composition $Na_{53}Ca(AlO_2)_{55}(SiO_2)_{137}$, from which the preceding zeolites were prepared using the ion exchange method[14], was dehydrated under the same conditions; the zeolites were supplied by the Research Institute of Oil and Hydrocarbon Gases (Czechoslovakia). The olefins were purified by repeated freezing in vacuum. According to the manufacturer specifications ethylene (Fluka) was of the 99·99% purity, ethylene-d_4 (USSR) with the deuterium content of 98·5% was of the 99% purity. Propylene (Slovnaft, Bratislava, Czechoslovakia) and propy- lene-d_6 (USSR) with the deuterium content of 97·2% were of the 99% purity.

The infrared spectra were measured with the spectrometer PE—621. Zeolites were pressed with the pressure of 700 kPa to form plates of the thickness of 7—9 mg/cm² and then placed into the IR cell[15], in the oven of which they were dehydrated and deammonated. The interaction with olefins was followed at the temperature of the IR beam when the spectrometer with the sample cell part was kept at 310 K. The adsorbate pressure did not change during the measure- ment and it was determined by a glass-membrane gauge[16]. The interaction with ethylene was followed in the pressure range from 1·5 to 47 kPa, with propylene only at the pressure of 1·7 kPa. The time dependence of the amount and composition of the adsorbed compounds in the zeolite cavities was determined by repeated scanning of the IR spectra in the wavenumber range 4000 to 1200 cm^{-1}. The use of another cell without any sample in the reference beam of the spectro- meter allowed to eliminate the gas-phase bands. The normalized absorbances A_v (g^{-1} cm²) $= d^{-1} \log (T_0/T)_v$, where d is the plate thickness, T and T_0 are the transmittancies of the sample and of the base line at the wavenumber v, respectively, were used for the comparison of the indi- vidual samples. For the determination of the hydrogen-deuterium exchange with various OH- -group types in the exchange $C_3D_6 + OH$ at 570 K the following procedure was adopted: *a*) the OH-group spectrum of the initial sample was recorded; *b*) the zeolite was heated to 570 K and C_3D_6 (0·4 kPa) was added for 5 min (in the repeated measurement for 10 min); *c*) propylene

was condensed in a cooled trap, the sample was rapidly cooled down and the spectrum of OH and OD groups was measured.

The isotope exchange in the gas phase was measured at 570 K in a static apparatus of the volume of 700 cm^3 with a continuous sampling directly into the mass spectrometer (a modified type MI 1305, USSR). The decrease of the initial pressure (0·1 kPa) did not exceed 5% during the measurement. The molecular peaks were measured at the electron energy 13·5 eV. The weight of the zeolite samples was chosen so that the ratio of the number of hydroxyl groups exceeded by an order of magnitude the initial number of D atoms in the respective olefin.

RESULTS

Interaction with Ethylene and Propylene at 310 K

The structural hydroxyls of the HY zeolites are characterized in the IR spectrum by bands at 3640 cm^{-1} (HF) and 3550 cm^{-1} (LF), *cf.* Fig. 1. From the height of these bands we have calculated the number of hydroxyls of the given type per unit cell of various decationated samples. The absorption coefficients were determined from the results of the chemical analysis and from the neutron diffraction of the

TABLE I

The Number of the HF Hydroxyls, the Shift of Their Bands Due to the Formation of Hydrogen Complexes with Ethylene and Propylene ($\Delta\nu_{HF,eth}$, $\Delta\nu_{HF,prop}$), the Intensity of the Absorption Band of Ethylene (A_{1446}), and the Rate of Propylene Oligomeration on the HY and NaY Zeolites at 310 K

Pressure kPa	Property	HY—70	HY—40	HY—20	NaY
		Ethylene			
6·6	$\Delta\nu_{HF,eth}$ (cm^{-1})	370	360	350	—
	A_{1446} (cm^2 g^{-1})	4·4	5·4	6·7	7·9
29·3	$\Delta\nu_{HF,eth}$ (cm^{-1})	360	345	335	—
	A_{1446} (cm^2 g^{-1})	13·4	15·0	17·3	18·3
		Propylene			
1·7	$\Delta\nu_{HF,prop}$ (cm^{-1})	460—450	440	420	—
	$k(CH_3)$ (cm^2 g^{-1} min^{-1})	5·8	2·9	0·35	0
	$k(CH_3)/(OH_{HF})$/unit cell (cm^2 g^{-1} min^{-1})	0·26	0·19	0·04	0
	OH_{HF}/unit cell	21[a]	15	8·5	0

[a] *Cf.* ref.[17].

HY−70 samples of the same production series[17]: $\varepsilon_{HF} = 10.4$ cm^2 g^{-1} (OH/u.c.)$^{-1}$, $\varepsilon_{LF} = 5.3$ cm^2 g^{-1} (OH/u.c.)$^{-1}$. From the point of view of the interaction with olefins the HF hydroxyls are important as they are located in the large cavities and are therefore easily accessible for the olefin molecules. Table I gives their number per unit cell in the samples under study. All zeolites including NaY contain also hydroxyls, designated SiOH, that are characterized by a weak band at 3 740 cm^{-1} (Fig. 1). These groups are situated on the surface of particles, on the amorphous impurities, or, eventually, on the structural defects in the zeolites. According to the results of the D$_2$ + OH exchange their number in our samples does not exceed 5% of the total number of hydroxyls.

In the zeolite cavities only the physically adsorbed ethylene has been found at 310 K. After adding C$_2$H$_4$ all changes in the IR spectrum of the sample cease within 2 min. The adsorption-induced changes in the spectrum are shown in Fig. 1. Due to the changes in symmetry and in the molecular dipole moment during adsorption there appear − along with the bands that are typical for the IR spectrum of ethylene − also weak bands of such vibrational transitions that are inactive in the IR spectra of gase-
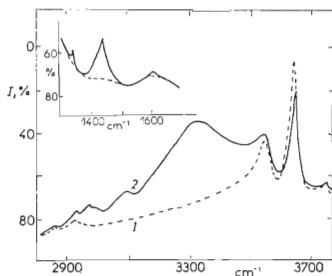

Fig. 1

The Effect of Adsorption of Ethylene on the IR Spectrum of HY-40

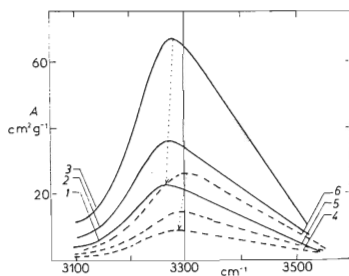*1* HY−40, *2* after the adsorption of ethylene at 310 K and at the pressure of 29.3 kPa.

Fig. 2

The IR Spectra of the Hydrogen Complexes of HY−70 and HY−20 with Ethylene, the Band of the Perturbed HF Hydroxyls

HY−70; *1 2 3* at the ethylene pressure 6.6, 12 and 35 kPa, respectively. HY−20: *4 5 6* at the ethylene pressure 6.6, 12 and 29.3 kPa, respectively.

ous molecules[18,19] but can be observed in the Raman spectra (Table II). At the given pressure the total adsorbed amount of ethylene depends on the sample composition: it increases with the increasing content of Na^+ ions, *i.e.* with the decreasing decationation of the zeolite. This is illustrated in Table I by the normalized intensities of the band at 1445 cm^{-1} of the adsorbed ethylene in various samples and at two values of the pressure. The above described trend is also corroborated by weighing[10].

The adsorption of ethylene is accompanied by the decrease of the intensity of the 3640 cm^{-1} band of free HF hydroxyls (*i.e.*, unaffected by the interaction with the adsorbate) and by the formation of a new broad band of OH groups at 3270 to 3310 cm^{-1}, the increase of which is proportional to the decrease of the 3640 cm^{-1} band. The maximum of the new band is shifted towards lower wavenumbers with the

TABLE II
The Spectral Bands of the Adsorbed Ethylene, Propylene, and Oligomers

Ethylene		Propylene		Oligomer	Assignment[18,a]
adsorbed cm^{-1}	gas[18] cm^{-1}	adsorbed cm^{-1}	gas[18] cm^{-1}	cm^{-1}	
3 086	3 105	3 065	3 090		} $=CH_2$ as.st.
	3 102[b]				
			3 013		$=CH$
2 996	3 026[b]				} $=CH_2$ s.st.
2 971	2 989	2 990	2 991		
		2 965			} CH_3 as.st.
		2 950	2 954	2 955	
				2 930	$-CH_2-$ as.st.
		2 925	2 932	2 865	CH_3 s.st.
		2 860	2 871	2 865	$-CH_2-$ s.st.
1 614	1 622·5[b]	1 634	1 650		$C=C$
				1 465	$-CH_2-$ def.
		1 455	1 470	1 465	}
		1 445	1 443		} CH_3 def.as.
		1 432			
1 446	1 443·5	1 418	1 420		$=CH_2$ def.
		1 378	1 378	1 395	}
				1 382	} CH_3 def.s.
				1 468	
1 340	1 342[b]				$=CH_2$ def. + $C=C$

[a] st. Stretch, def. deformation, s. symmetrical, as. asymmetrical vibration; [b] active only in the Raman spectrum.

increasing decatonation and towards higher wavenumbers with the increasing filling of the zeolite by ethylene, as it is demonstrated in Fig. 2 on some chosen spectra. (The respective bands were obtained by subtraction of the initial spectrum from that obtained after the adsorption of ethylene). The difference $\Delta\nu_{HF,eth.}$ in the position of the band at $3640\ cm^{-1}$ and of the new band characterizes the weakening of the OH bond in HF hydroxyls as caused by the adsorbate (Table I): the higher is this difference the weaker is the OH bond. The HF hydroxyls are directly affected only by a part from all adsorbed molecules of ethylene. The number of molecules interacting with these groups is proportional to the number of HF hydroxyls in the initial sample as it follows from Fig 3; in different decatonated samples with the same occupation of the zeolite by ethylene always the same fraction of HF groups from their total number is affected. At 310 K the desorption of ethylene in vacuum proceeds so that the resulting spectrum of the sample is identical with the initial one before the adsorption.

Propylene is physically adsorbed on the NaY zeolite at 310 K, as proved by the position of its bands in the IR spectrum (Table II) and by its easy desorption at this temperature. The same bands were found in the IR spectrum also after the interaction of the hydrogen form of the zeolite Y with propylene, but another broad band of perturbed HF hydroxyls at $3180-3220\ cm^{-1}$ was observed in this case. From the difference in the positions of bands of perturbed and free HF hydroxyls, $\Delta\nu_{HF,prop.}$ (Table I), it turns out that the OH bonds are more weakened than in the interaction with ethylene and the dependence on the zeolite composition follows the same trend, *i.e.*, it increases with the decatonation. Propylene at a given pressure affects a much higher number of HF hydroxyls of the same zeolite than ethylene: an estimation for catalytically low-active HY-20 gave a fourtimes higher value in favour of propylene (at the pressure of 6·6 kPa).

According to the spectral data the adsorption of ethylene and propylene gives rise to the formation of their hydrogen complexes with the HF hydroxyls of zeolites[9,10]. This is corroborated by the following results: *a*) relatively high values of $\Delta\nu_{HF,eth.}$ and $\Delta\nu_{HF,prop.}$, their dependence on the ionization potential of the respective olefin; *b*) the band shape of the perturbed hydroxyls and the increase of their integral intensity in comparison with the band of free HF hydroxyls; *c*) a small decrease in the C=C bond strength due to adsorption ($\Delta\nu_{gas-ads.} = 16\ cm^{-1}$ in the case of propylene). A similar character of changes in the IR spectra was also found for the hydrogen complexes of C_2—C_4 unsaturated hydrocarbons with HCl and HBr in the solid state[20]. In analogy to the paper[20] it may be reasoned that in zeolites there is a hydrogen bond between the olefin π electrons and the hydroxyls and that in the formation of the hydrogen complex along with the electrostatic forces an important role is played by the charge transfer between the olefin and the OH group. Weakening of the OH bond is proportional to the intensity of the interaction between the both components of the hydrogen complex. This intensity increases with the acidity of the

OH group and with the electron-donor ability (basicity) of the olefin, which is connected with its ionization potential.

The propylene bands in the IR spectrum of the decationated zeolites decreased with time and simultaneously the bands ascribed to the saturated CH_2 and CH_3 groups increased: the oligomeration took place. According to the spectra the formed saturated chains interact also the HF hydroxyls. The band at $3550\ cm^{-1}$ (ref.[9]), superimposed on the LF hydroxyl band, was ascribed to the perturbed HF...sat. group. A typical time dependence of the intensity of the vibrational bands $C=C$ ($1643\ cm^{-1}$), —CH_3 in oligomers ($2955\ cm^{-1}$ after the correction for the contribution due to the adsorbed propylene), free HF hydroxyls, HF hydroxyls perturbed by the olefin (HF...CC) and by the oligomer (HF...sat, superimposed on the LF band) is illustrated in Fig. 4 for the zeolite $HY-40$. The decrease of the unsaturated hydrogen complexes can be explained not only by their participation in the catalytic reaction but also by the decrease of the number of accessible HF groups due to their screening by the oligomer chains. During the oligomeration the sample
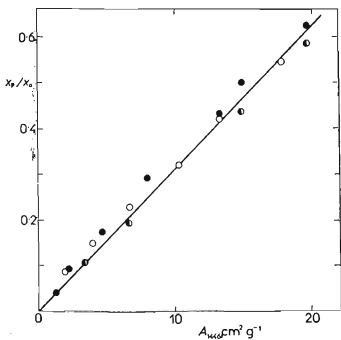

Fig. 3

The Dependence of the Ratio of the Number of HF Hydroxyl Groups Interacting with Ethylene to the Total Number of HF Hydroxyls (X_p/X_0) on the $1446\ cm^{-1}$ Band Intensity of the Adsorbed Athylene

○ HY−70, ● HY−40, ◑ HY−20.
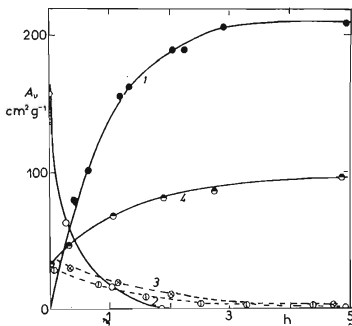
Fig. 4

The Time Dependence of the Band Intensities in the IR Spectrum of HY−40 During the Interaction with Propylene

Pressure 1·7 kPa, temperature 310 K. ○ free HF hydroxyls ($3640\ cm^{-1}$), 1: CH_3 ($2955\ cm^{-1}$), 2: $C=C$ ($1634\ cm^{-1}$) 3: HF···$C=C$ ($3200\ cm^{-1}$), 4: HF···sat. + LF ($3550\ cm^{-1}$)

weight increases[10] which indicates the participation of other propylene molecules from the gas phase on the chain growth. After the cavities are filled with oligomers also a part of the SiOH groups is covered — the band at $3740\ cm^{-1}$ decreases and another band at $3700\ cm^{-1}$ is formed which can be ascribed to the SiOH groups perturbed by the saturated chains.

In the oligomeration branched chains are formed as it is evident from the composition of bands corresponding to the deformation vibrations of CH_3 groups in the wavenumber range $1350-1400\ cm^{-1}$. The compounds contain the following groups: CH_3—R, R—$CH(CH_3)$—R, R—$C(CH_3)_2$—R, $(CH_3)_2CH$—R, and at low conversions also $(CH_3)_3C$—R (the band at $1395\ cm^{-1}$). The ratio of the CH_3 band intensity at $2955\ cm^{-1}$ to that of CH_2 at $2930\ cm^{-1}$ in the oligomers remained practically unchanged during the reaction (in the range $1\cdot2-1\cdot1$). The increase of the CH_3 band at the beginning of the reaction, $k(CH_3)$, could therefore be used for the comparison of the catalytic activities of individual zeolites. From Table II it follows that the total activity as well as the activity per one HF group per unit cell of the initial sample increase with the increasing decationation of the sample. The oligomers are not desorbed at 310 K, at higher temperature they decompose.

Isotope Exchange of Perdeuterated Propylene and Ethylene with the Zeolite Hydroxyls at 750 K

The composition of the gas phase in the isotope exchange reaction of propylene-d_6 with the OH groups of the zeolite HY−70, HY−40, and HY−20 is given in Figs $5a,b,c$. It is evident that the decrease of propylene-d_6 concentration diminishes in the series HY−70 > HY−40 > HY−20. With the decreasing decationation decreases also the yield of the most exchanged propylene-d_0, the formation of which is accompanied by an induction period in the case of HY−70 and HY−40. The exchange of other hydrogens of propylene proceeds *via* the so-called "multiple-step" mechanism: during one "visit" all five equivalently exchangeable hydrogens are exchanged. In the solid phase both types of the structural hydroxyls and the SiOH groups take part in the exchange. The results of the IR measurements show that the deuterium content in the HF and LF hydroxyls is the same while the hydrogens in the SiOH groups are exchanged more slowly (after 1 min by 60% less than in the structural hydroxyls, after 20 h still by 12% lower concentration of deuterium). As there are very few SiOH groups in the zeolite, the exchange rate in the gas phase is practically unaffected by their lower exchange rate. Table III presents the exchange rate (for the exchange measured in the gas phase so that it comprises all hydroxyl groups) expressed as the number of atoms exchanged per minute and the ratio propylene-d_0/ /propylene-d_1. With the decreasing decationation these values decrease.

In the time interval, in which the isotope exchange of propylene was followed, the amount of the catalytic reaction products released into the gas phase was negligible

(after 20 min ~5% relatively to the amount of propylene). These catalytic products (namely olefins and C_4 alkanes) were not enriched by deuterium at the beginning of the catalytic reaction so that they were formed only after the exchange of per-deuterated propylene with the zeolite OH groups.

In contrast to the propylene-d_6 exchange with the OH groups of HY zeolites the exchange of ethylene-d_4 proceeds *via* the so-called "single-step" mechanism. During one "visit" only one deuterium atom of ethylene is exchanged. The exchange reactions of both olefins were studied with a one-order-of-magnitude excess of hydrogen in the hydroxyl groups if compared with the hydrogen in the olefins; under these conditions

FIG. 5

The Isotope Exchange of Propylene-d_6 with the HY Zeolites at 570 K

a HY—70, *b* HY—40, *c* HY—20 at the ratio OH/D 9·7; 11·7 and 11·7, resp. and at the pressure of 0·15 kPa.

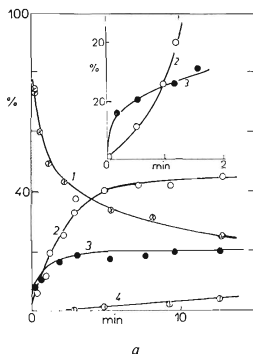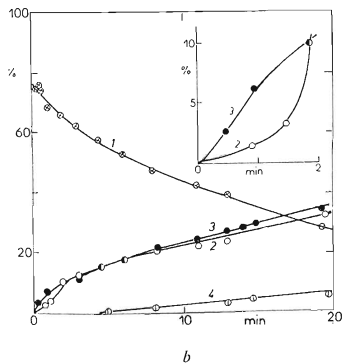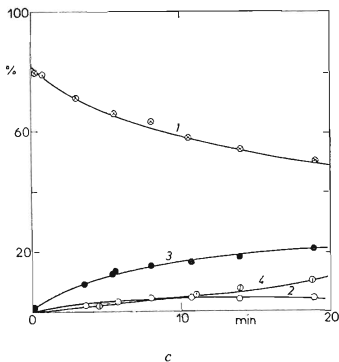*1* Propylene-d_6, *2* propylene-d_0, *3* propylene-d_1, *4* propylene-d_2.

TABLE III

The Isotope Exchange of Propylene-d_6 with the HNaY Zeolite Hydroxyls: the Rate R^a, the Ratio m of the Amount of Propylene-d_0 and Propylene-d_1 Formed after 5 min of the Exchange

Sample	$R \cdot 10^{-19}$ atom min^{-1}	m
HY—70	1·4	2·1
HY—40	0·9	1
HY—20	0·27	0·25

^{a} $R = \ln F \cdot [D] [OH]/([D]) + [OH])$; F cf. Fig. 3.
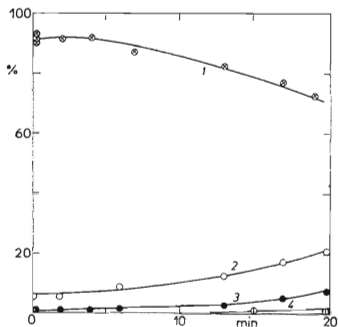
FIG. 6

The Isotope Exchange of Ethylene-d_4 with HY—70 at 570 K

Pressure 0·16 kPa, OH/D = 14. 1 Ethylene-d_4, 2 ethylene-d_3, 3 ethylene-d_2, 4 ethylene-d_1.
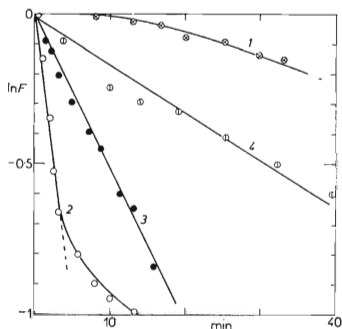
FIG. 7

The Time Dependence of ln F for the Isotope Exchange of Propylene and Ethylene with the HY Zeolites at 570 K

1 Ethylene-d_4 + HY-70, 2 propylene-d_6 + + HY-70, 3 propylene-d_6 + HY-40, 4 propylene-d_6 + HY—20. $F = (c - c_\infty)/(c_0 - - c_\infty)$, where c_0, c, and c_∞ are the atomic concentrations of deuterium at t_0, t, and t_∞.

both types of mechanism can be easily distinguished. From Fig. 6 it follows that during the decrease of ethylene-d_4 concentration ethylene-d_3 is formed primarily, while ethylene-d_2 and $-d_1$ are formed later. The exchange reaction starts with a rather long induction period and after 30 min it is 70 times slower than the exchange of propylene with the same $HY-70$ zeolite. Fig. 7 presents the kinetic dependence of the propylene and ethylene isotope exchange reactions. The exchange reactions of propylene-d_6 with $HY-70$ and ethylene-d_4 with HY-70 do not follow the logarithmic first-order relation (relatively to the deuterium concentration) that is characteristic for the isotope exchange reactions. In the former case the concave deviation is probably caused by the deactivation of the catalyst that slows down the exchange reaction. In the latter case the convex deviation, which means the acceleration of the reaction, is obviously related to the existence of the induction period. During the ethylene-d_4 exchange reaction no products of a catalytic transformation were observed.
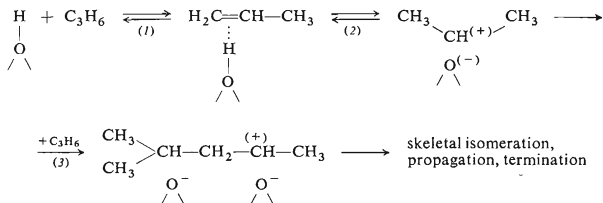
DISCUSSION

From the experimental results it follows that the decationation of the zeolite Y has a substantial effect on the interaction with both ethylene and propylene. With the increasing decationation the OH bond in the hydrogen complexes with both propylene and ethylene becomes weaker (i.e., the acidity of HF hydroxyls increases), the catalytic activity in the propylene oligomeration, the isotope exchange rate $C_3D_6 + OH$, and the extent of the exchange of the sixth hydrogen atom in propylene increase but the total amount of adsorbed ethylene decreases.

In connection with the replacement of Na^+ ions by protons during the decationation, when the protons are bound to the skeleton in the form of structural hydroxyls, the above mentioned relations can be explained by a combination of several factors, which include the different chemical nature and localization of Na^+ ions in comparison with the hydroxyl groups[17]. Decationation is therefore accompanied by a different charge distribution in the zeolite[21,22] and therefore also by the change of the electrostatic field within the cavities. From the sterical point of view the arrangement in large cavities (i.e., the effect of HF hydroxyls together with the occupation of S_{II} positions by the Na^+ ions) is the most important factor.

From the antiparallel dependence of the total amount of the adsorbed ethylene on the increasing decationation it can be assumed that in its physical adsorption the dominant role is played by the changes in the electrostatic field of the zeolite that accompany the decationation. The uniform distribution of ethylene between the HF hydroxyls and the remaining accessible parts of the zeolite corroborates this explanation. The mutual effect of the adsorbate on the zeolite and *vice versa*, that generally decreases the free energy of the system, is evident from the decreased lability of the OH bond in the hydrogen complexes during the gradual occupation of the cavities by ethylene in a given sample.

The dependence of the catalytic activity of the zeolites under study on their decationation shows that the HF hydroxyl groups are the most important factor from the catalytic point of view. The results obtained in this study are best explained by the carbonium-ion mechanism of the propylene oligomerization in the zeolite cavities, which assumes that the hydrogen complex is the precursor of the carbonium ion[9]:

$$
\begin{array}{c}
\text{H} + \text{C}_3\text{H}_6 \underset{(1)}{\rightleftharpoons} \text{H}_2\text{C}=\text{CH}-\text{CH}_3 \underset{(2)}{\rightleftharpoons} \text{CH}_3\diagdown\text{CH}^{(+)}\diagup\text{CH}_3 \longrightarrow \\
\underset{\diagup\,\diagdown}{\overset{\mid}{\text{O}}} \qquad\qquad \overset{\vdots}{\underset{\diagup\,\diagdown}{\overset{\mid}{\text{O}}}} \qquad\qquad \underset{\diagup\,\diagdown}{\text{O}^{(-)}}
\end{array}
$$

$$
\xrightarrow[(3)]{+\text{C}_3\text{H}_6}\;
\begin{array}{c}
\text{CH}_3 \\
\diagup \\
\diagdown \\
\text{CH}_3
\end{array}
\text{CH}-\text{CH}_2-\overset{(+)}{\text{CH}}-\text{CH}_3 \longrightarrow
\begin{array}{l}
\text{skeletal isomeration,} \\
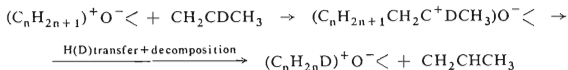\text{propagation, termination}
\end{array}
$$

Scheme 1

Propylene, with the ionization potential of 9·73 eV, is a stronger base than ethylene (I.P. 10·52 eV). This is why the weakening of the OH bond in the hydrogen complex with propylene is substantially stronger than in the complexes with ethylene. This is also the reason why the probability of the transfer of a zeolite hydrogen in step (2) is higher: the oligomerization takes place in the case of propylene, whereas no catalytic reaction has been found for ethylene. The validity of the carbonium-ion mechanism of oligomerization is supported not only by the relation between the increase of propylene oligomerization rate with the increase of the amount of HF groups and of their acidity strength on decationation but also by the formation of branched oligomer chains, indicating the skeletal isomerization. The increase of the HF hydroxyl acidity strength with the increasing decationation is obvious from the changes of the values $\Delta v_{\text{HF,prop.}}$ and $\Delta v_{\text{HF,eth.}}$ that accompany the formation of the respective hydrogen complexes.

The activation energy for the hydrogen transfer between the zeolite and the adsorbate in the step (2) has been estimated from the values of $\Delta v_{\text{HF,eth.}}$ and $\Delta v_{\text{HF,prop.}}$ according to the paper[23]. Depending on the decationation degree, the value of E_a should lie in the range 123·5 — 134 kJ/mol for ethylene and in the range 102·5 — 113 kJ/mol for propylene. The initial rate of oligomerization does not agree with these values — e.g., in HY—20 it should be higher than the experimental value. This disagreement is understandable because the oligomerization of propylene involves along with step (2) also other steps connected with the propagation and termination of the chain reaction. One can expect an effect of the lattice oxygen, of sodium ions, and therefore also of the electrostatic field. The lattice oxygen with the negative charge can affect the H- and CH$_3$-transfer in the chain and can have an influence on its growth; in this sense the oligomer adsorbate can probably play a role of the

proton transfer agent between the basic centers of the zeolite, which is in agreement with the NMR studies published for other zeolite–adsorbate systems. The dynamic character of the interaction of propylene with HY zeolites and the mobility of zeolitic hydrogens were proved by the isotope exchange $C_3D_6 + OH$ with HY[11,12], where the OD groups were uniformly distributed in the HF hydroxyls regardless whether they are free, interacting with propylene or saturated chains, or in the inaccessible LF hydroxyls. The reaction initiation is not directly connected with the Na^+ ions because the NaY zeolite is inactive in the propylene oligomerization. The increase of the chain length by Na^+ ions is also improbable due to their positive charge.

The decationation affects in the same sense both the propylene oligomerization rate and the propylene-d_6 exchange rate with various decationated HY zeolites. The increasing decationation increases the exchange rate and the fraction of the sixth exchanged hydrogen in propylene. From the present data it is impossible to determine directly the exchange mechanism. It is only possible to state that: *1*) the propylene molecule remains in the zeolite till it exchanges all five (obviously terminal) hydrogens of the zeolite; the exchange reaction proceeds therefore by the "multiple-step" mechanism and the five propylene hydrogens are equivalent in the exchange reaction; *2*) the exchange of five propylene hydrogens proceeds directly with the zeolite OH groups; the exchange reaction proceeds substantially faster than the catalytic reaction itself; *3*) the exchange of the sixth hydrogen in propylene (most probably the tertiary one) is proportional to the increasing decationation but it probably does not proceed directly with the zeolite OH, which is evidenced by the induction period observed in propylene-d_0. The autocatalytic character of the time evolution of the propylene-d_0 concentration can be explained by the interaction of the propylene molecule with the carbonium-type complex after the deuterium exchange with the formation of a new complex, in which the H(D) transfer proceeds along the chain with a subsequent decomposition:

$$(C_nH_{2n+1})^+O^-< \; + \; CH_2CDCH_3 \; \rightarrow \; (C_nH_{2n+1}CH_2C^+DCH_3)O^-< \; \rightarrow$$

$$\xrightarrow{\text{H(D)transfer + decomposition}} (C_nH_{2n}D)^+O^-< \; + \; CH_2CHCH_3$$

SCHEME 2

It seems worth mentioning that in course of the tertiraty hydrogen exchange in propylene on oxide systems Kemball[24] assumed the existence of H^- and proposed that the sixth hydrogen exchange in propylene and the ethylene exchange have a similar character.

The ethylene-d_4 exchange differs substantially from the isotope exchange of propylene with the OH groups of zeolites under study: *1*) it proceeds *via* the "single-step" mechanism, which may be in connection with the shorter residence time of the ethylene molecule in the zeolite (the extent of adsorption is in the case of ethylene

lower than in propylene) or it may be due to steric effects; *2*) the ethylene exchange does not proceed directly with the OH groups as witnessed by a rather long induction period. The exchange reaction probably starts only after the formation of a certain small amount of oligomers in the zeolite cavities that take an active part in the exchange reaction and mediate the transfer between ethylene and the hydroxyl group. This effect has been already pointed out in ref.[13]; *3*) the ethylene-d_4 exchange rate is 70 times lower than that of propylene-d_6 with the same type of zeolite HY−70.

We can conclude that in the adsorption of ethylene and propylene at 310 K on the hydroxylated forms of the HNaY zeolites the hydrogen complexes of these compounds with the structural HF hydroxyls are formed. The shift Δv of the hydroxyl band, caused by the formation of the hydrogen complexes, depends not only on the basicity of olefins (as it was already shown by Liengme and Hall[9]) but also on the acidity of hydroxyls. The values of Δv are closely connected with the catalytic activity: ethylene is only physically adsorbed while propylene enters into the oligomeration. The properties of OH groups play a dominant role in the propylene oligomeration on the hydroxylated forms of the HNaY zeolites. The difference in the isotope exchange rates of ethylene-d_4 and propylene-d_6 with the OH groups at 570 K corresponds qualitatively to the difference in the catalytic activity in oligomeration. In another paper concerning the dehydroxylated forms of HNaY zeolites it will be pointed out that the very large differences in the exchange rates of these olefins cannot be connected only with the fact that the HY zeolites in the hydroxylated forms are inactive in the ethylene oligomeration. The exchange of the five terminal D atoms of propylene proceeds probably *via* a direct interaction while the very slow exchange in ethylene indicates the participation of an intermediate. This can probably explain also the behaviour of the sixth D atom in propylene.

REFERENCES

1. Norton C. J.: Ind. Eng. Chem., Process Des. Develop *3*, 230 (1964).
2. Andreev V. M., Kazanskii V. B.: Izv. Akad. SSSR, Ser. Khim., *1974*, 1887.
3. Lafer L. I., Nabiev B. A., Yakerson V. I.: Izv. Akad. Nauk SSSR, Ser. Khim. *1975*, 1942.
4. Yashima T., Ushida Y., Ebisawa H., Hara N.: J. Catal. *36*, 320 (1975).
5. Yashima T., Nagata J. I., Shimazaki Y., Molecular Sieves II, ACS Symp. Ser. *40*, 626 (1977).
6. Karge H. G., Ladebeck J.: Proc. Symp. on Zeolites, Szeged; Acta Phys. Chem. (Szeged) *24*, 161 (1978).
7. Panchenkov G. M., Kuznetsov O. I., Shauki M. Kh.: Neftekhimiya *9*, 522 (1969).
8. Örhalmi O., Fejes P.: *Mechanism of Hydrocarbon Reactions*, Symposium (F. Márta, D. Kalló, Eds.), p. 457. Akadémiai Kiadó, Budapest 1975.
9. Liengme B. V., Hall W. K.: Trans. Faraday Soc. *62*, 3229 (1966).
10. Kubelková L., Nováková J., Bosáček V., Patzelová V., Tvarůžková Z.: Proc. Symp. on Zeolites, Szeged; Acta Phys. Chem. (Szeged) *24*, 189 (1978).
11. Nováková J., Kubelková L., Jírů P.: React. Kinet. Catal. Lett. *4*, 261 (1976).
12. Kubelková L., Nováková J., Jírů P.: React. Kinet. Catal. Lett. *4*, 151 (1976).

13. Cant N. W., Hall W. K.: J. Catal. *25*, 161 (1972).
14. Bosáček V., Patzelová V., Hýbl Č., Tvarůžková Z.: J. Catal. *36*, 371 (1975).
15. Schürer P., Kubelková L.: Chem. Listy *65*, 208 (1971).
16. Nováková J., Kubelková L.: Chem. Listy *68*, 186 (1974).
17. Jirák Z., Vratislav S., Zajíček J., Bosáček V.: J. Catal. *49*, 112 (1977).
18. Sverdlov L. M., Kovner M. A., Krainov E. P.: *Kolebatelnye Spektry Mnogoatomnykh Molekul.* Nauka, Moscow 1970.
19. Vinogradov S. N., Linnell R. H.: *Hydrogen Bonding.* Van Nostrand-Reinhold, New York, 1971.
20. Kimelfeld Ya. M., Lumer E. V., Shvedtchikov A. P.: Izv. Akąd. Nauk SSSR, Ser. Khim. *1974*, 1714.
21. Beran S., Dubský J.: J. Phys. Chem. *83*, 2538 (1979).
22. Dubský J., Beran S., Bosáček V.: J. Mol. Catal. *6*, 321 (1979).
23. Kazanskii V. B., Gritscov A. M., Andreev V. M., Zhidomirov G. M.: J. Mol. Catal. *4*, 135 (1978).
24. Kemball Ch.: Ann. N. Y. Acad. Sci. *213*, 90 (1973).