

THE EFFECT OF DEHYDROXYLATION OF HNaY ZEOLITES ON THE INTERACTION WITH ETHYLENE AND PROPYLENE

Ludmila KUBELKOVÁ, Jana NOVÁKOVÁ, Blanka WICHTERLOVÁ and Pavel JÍRŮ

*J. Heyrovský Institute of Physical Chemistry and Electrochemistry,
Czechoslovak Academy of Sciences, 121 38 Prague 2*

Received March 22nd, 1979

The extent of dehydroxylation of HNaY zeolites of various degree of decationization was varied by the thermal treatment *in vacuo* over the temperature range 620–890 K. The solid phase was investigated by means of infrared spectroscopy, the gaseous phase by means of mass spectrometry. Lewis "acid-base pair" centers were formed by the dehydroxylation and these initiated at 310 K the oligomerization of ethylene in zeolite cavities. The reaction occurred *via* the cationic mechanism. A certain ratio of Lewis centers to OH groups was necessary in order to achieve the maximum oligomerization rate on given type of zeolite. It was showed up in a shift of the maximum to higher activation temperatures with less decationized zeolites, more stable with respect to the dehydroxylation. The zeolite activity increased with increasing decationization. The same trend was found also for the oligomerization related to one Lewis center. The presence of Lewis centers affected the oligomerization rate of propylene, too, though Broensted centers played the dominant role in this case. After the thermal decomposition of the oligomers aliphatic and cyclic hydrocarbons, mostly saturated compounds, were found in the gaseous phase. The isotopic exchange of propylene- d_6 at 570 K occurred *via* a multiple mechanism, the value of its rate being of the same order of magnitude as with the hydroxylated forms. In view of the varying amount of slowly exchanging SiOH groups in various decationized zeolites, the dependence of the exchange rate of structural zeolites on the decationization could not be established. The isotopic exchange of ethylene- d_4 occurred *via* a single mechanism with a slightly increased rate in comparison with the hydroxylated forms.

The question of Lewis centers and their catalytic effects in zeolites is still open. If we compare the number of papers devoted to properties of Broensted centers with those in which Lewis centers are treated, too, the result is strongly in favour of the former. The activity of the dehydroxylated $H_{45}Na_{55}Y$ zeolite in the ethylene oligomerization was ascribed to Lewis centers by Liengme and Hall¹. In our recent paper² we confirmed the connection between the HY zeolite dehydroxylation and its activity in the above mentioned reaction. Also, we showed that the oligomerization of ethylene depends on the zeolite decationization and that the dehydroxylation and decationization influence the oligomerization of propylene, too. This paper is a further extension of the previous study. It pays attention both to the effect of the dehydroxylation degree on the activity of HNaY zeolites of a different decationization during the oligomerization of ethylene and propylene at 310 K and to the

isotopic exchange of perdeuteroethylene and perdeuteropropylene at 570 K with hydroxyl groups of partially dehydroxylated samples. Infrared spectroscopy was used in investigating surface complexes and OH groups of the zeolites. In some cases, the zeolites were investigated by means of the EPR method. The gaseous phase was analyzed by means of mass spectrometry.

EXPERIMENTAL

Decationized zeolites $H_{0.19}Na_{0.81}Y$ (HY-20); $H_{0.39}Na_{0.61}Y$ (HY-40); $H_{0.70}Na_{0.30}Y$ (HY-70) of the ratio Si : Al = 2.5 and of the Fe content 400–600 ppm were supplied by the Research Institute of Petroleum and Hydrocarbon Gases, ČSSR. The samples were activated at 620–890 K for 16 hours at 10^{-3} Pa. The activation temperature is denoted as T with the temperature index (in Kelvin) written after the zeolite type designation, e.g., HY-70 T_{670} . The sorption capacity of the HY-70 samples T_{620} , T_{770} , and T_{870} was 11.34, 11.28, and 11.31 mmol Ar/g, respectively. The purity and deuterium content of the olefins used was reported earlier³.

Infrared spectra of zeolite plates 5–10 m/cm^2 thick were measured by a Perkin-Elmer-621 spectrometer. A detailed description of the experimental arrangement was given in the preceding paper³. The interaction with ethylene and propylene was followed at 310 K and 6.6 and 1.7 kPa, by repeated recording of the spectra over the interval 4000–1200 cm^{-1} . In order to compare band heights in the spectra of various samples values of the absorbance A were used, normalized to unit sample thickness. The catalytic activity of the zeolites was characterized by the initial rise of the 2955 cm^{-1} band of CH_3 groups in oligomers over a unit time interval (k_{CH_3}).

ESR Spectra of HY-70 and HY-40 zeolites activated *in vacuo* at various temperatures were recorded at 295 K by an ESR-220 spectrometer (Academy of Sciences of GDR, Berlin) over the magnetic field range 0–5000 G at $f = 3.2 cm^{-1}$.

Gaseous products resulting from the thermal decomposition of oligomers were led directly into a mass spectrometer (a modified MI 1302, USSR); the maximum pressure during the decomposition was $5 \cdot 10^{-4}$ Pa. The composition of the gaseous mixture was calculated both from the fragment peaks obtained at ionizing electron energy of 50 eV and from the molecular peaks obtained at a low energy of ionizing electrons. In some instances the composition was checked by the analysis of the sample on a GC-MS JMS-D 100 (JEOL, Japan). We are indebted to Dr V. Hanuš, for carrying out this latter analyses.

The isotopic exchange with ethylene- d_4 and propylene- d_6 was measured at 570 K using the MI 1302 mass spectrometer. A small amount of the gaseous phase was sampled from a static apparatus volume of 700 cm^3 so that the over-all pressure of 0.1 kPa practically did not change during the exchange. Molecular peaks of the particular isotopic species of the olefins were measured at 13 eV. The isotopic exchange rates were calculated from: $R = [D][OH](-\ln F) : t \cdot ([D] + [OH])$; $F = c - c_\infty / c_0 - c_\infty$, where c_0 , c , and c_∞ are deuterium concentrations in the gaseous phase at times t_0 , t , and t_∞ , respectively, OH the number of all hydroxyl groups and D the number of deuterium atoms in the particular isotopic species of the olefins. In the case of dehydroxylated zeolites, treated in this paper, the calculated rate may be up to twice in error, because in all cases the kinetic dependence deviates from the first order with respect to the deuterium concentration. These deviations are due both to a considerable fraction of SiOH groups which exchange more slowly than structural OH groups and to the deactivation of the surface. Because of experimental reasons it was not possible to follow the rate of exchange of the sixth hydrogen of propylene in any of the samples; these measurements require a con-

siderable excess of OH groups over the number of deuterium atoms in propylene. However, the zeolites T_{770} contain only a small number of OH groups so that carrying out the above mentioned experiment would require too large sample weights. Similarly as in ref.³, a very small amount of products of the catalytic reaction appeared in the gaseous phase during the isotopic exchange measurements. This amount did not exceed 5%.

RESULTS

It is known that the decomposition of ammonium forms of zeolites *in vacuo* at 620 K leads to H-forms of the zeolites whose infrared spectra exhibit three bands of OH groups: 3640 cm^{-1} (HF), $3540-50\text{ cm}^{-1}$ (LF), and 3740 cm^{-1} (SiOH). The former two bands have been ascribed to the structural hydroxyls of the zeolite lattice; of these, HF are oriented into the zeolite large cavities and thus they are accessible both to ethylene and propylene. The latter band, 3740 cm^{-1} , has been ascribed to hydroxyls on the particle surface, in structural defects, and on amorphous impurities; results of the $D_2 + OH$ exchange show that their amount does not exceed 5% of all OH groups. Starting with the activation temperature 670 K, dehydroxylation of the zeolite begins to take place in which Lewis acid-base centers are formed on the expenses of two structural OH groups⁴. Fig. 1 exhibits the dependence of the HF band height on the activation temperature; the height of LF bands changes in an analogous manner. It is evident from this figure that the zeolite stability with respect to dehydroxylation increases with the increasing Na^+ content. The intensity of SiOH

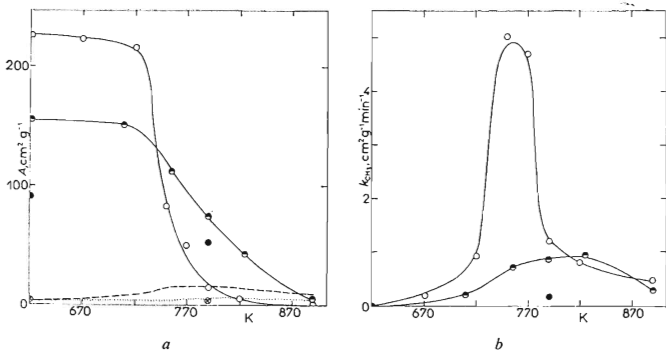


FIG. 1

Dependence of HF and SiOH Band Height *a* and of the Catalytic Activity *b* on the Activation Temperature of the Zeolites

○ HY-70, ● HY-40, ● HY-20, band SiOH: - - - - HY-70, ······ HY-40, ⊙ HY-20.

group bands over the activation temperature range 620–770 K increases significantly with the HY-70 zeolite, slightly with the HY-40 zeolite, and it does not change with the HY-20 zeolite; this can be seen from Fig. 1a, too.

With HY-70 and HY-40 the amount of carbon formed after their activation *in vacuo* from carbonate complexes and organic impurities was measured. ESR spectra of the free electron of $g = 2.004$, localized on carbon, were used in its detection. The signal intensity was constant over the activation temperature range 670–970 K.

Interaction of Ethylene and Propylene at 310 K

As shown in the previous paper³, ethylene adsorbs physically on fully hydroxylated forms of T_{620} zeolites HNaY. It follows from Fig. 1a,b that dehydroxylation of the samples results in oligomerization of ethylene. The oligomerization rate in dependence on the activation temperature of the sample *in vacuo* exhibits a maximum at 760 K for HY-70, and at 790–820 K for HY-40. The maximum oligomerization rate related to one Lewis centrum is 0.74 for HY-70 T_{750} , 0.23 for HY-40 T_{790} , for HY-20 T_{790} the value $0.08 \text{ cm}^2 \text{ g}^{-1} \text{ min}^{-1}$ was found. The number of Lewis centers was determined using infrared data from the loss of structural OH groups with respect to the number of OH groups in the hydroxylated form. These results point to a significant influence of decationization on the zeolite activity, decreasing with the increasing content of Na^+ ions.

A typical spectrum of partly dehydroxylated zeolites during the interaction with ethylene is shown in Fig. 2. Here, the bands at 3086 and 1446 cm^{-1} belong to the adsorbed ethylene, a part of which is H bounded to HF hydroxyls. The band maximum of these H bounded OH groups appears at the same wave number as with fully hydroxylated samples (3290 – 3260 cm^{-1} in dependence on the degree of decationization). During the reaction of ethylene branched oligomers are formed in zeolite cavities and these contain $-\text{CH}_2-$ groups (band 2930 cm^{-1}) and also CH_3-R , $\text{R}-\text{CH}(\text{CH}_3)-\text{R}$, $(\text{CH}_3)_2\text{CH}-\text{R}$, and $\text{R}-\text{C}(\text{CH}_3)_2-\text{R}$ (cf. bands 2955 , 1382 and 1368 cm^{-1}). The ratio of the band intensities of CH_3 (2955 cm^{-1}) and CH_2 (2930 cm^{-1}) was 1.3 to 1.2; the lowest measured value was 1.1 with a sample of the HY-70 T_{890} zeolite without structural hydroxyls. The oligomers during their growth cover the HF hydroxyls and in the region of high coverage also the SiOH groups. Both type of OH groups are weakly perturbed by this interaction, as can be seen from the positions of the corresponding OH vibrations, 3550 and 3690 cm^{-1} , respectively. As a result of the adsorption equilibrium, the decrease of the accessible free HF hydroxyls is accompanied by a lowering of the total number of hydrogen

complexes³ $\text{OH} \cdots \begin{array}{c} \text{C} \\ \parallel \\ \text{C} \end{array}$. The time dependence of the band intensities of CH_3- in oligomers, free HF, and HF interacting with ethylene or with saturated chains of the

oligomers is illustrated in Fig. 3 for HY-40 T_{790} zeolite. With HY-70 T_{790} and T_{820} we observed an increase of the reaction rate after the initial, slower stage. In the region of high ethylene conversions there was observed in the spectra also a weak band at 1590 cm^{-1} pointing to the presence of polyene structures.

The ethylene bands disappeared from the infrared spectra after an about 15 min desorption, but the bands of CH_2 - and CH_3 -groups decreased only negligibly. Thus, a substantial portion of oligomers remains in the zeolite and their decomposition and desorption takes place only at higher temperatures. This can be seen from Fig. 4: with HY-70 T_{770} (the zeolite of maximum activity) the gaseous phase between 370 and 470 K contains prevailing alkenes C_4 – C_7 (a comparatively small amount of propane) and smaller amounts of alkenes C_3 – C_7 . At higher temperatures there appear in the gaseous phase cycloalkanes and cycloalkenes and above 570 K a very small amount of aromatic compounds is present, too. After the decomposition and desorption of the oligomers at 570 K the infrared spectrum of the OH groups did not differ substantially from the initial spectrum of the zeolite before the interaction with ethylene. The following oligomerization of ethylene at 310 K occurred at a substantially slower rate than that one in the first cycle: $k(\text{CH}_3)$ (1st cycle) = $4.7\text{ cm}^2\text{ g}^{-1}\text{ min}^{-1}$, $k(\text{CH}_3)$ (2nd cycle) = $0.44\text{ cm}^2\text{ g}^{-1}\text{ min}^{-1}$.

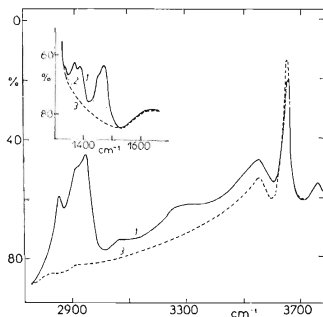


FIG. 2

The Influence of Interaction with Ethylene on the Infrared Spectrum of the HY-40 T_{750} Zeolite

3 Initial spectrum, 2 after 1 min interaction with 6.6 kPa of ethylene at 310 K, 1 after 35 min of interaction, the same pressure and temperature.

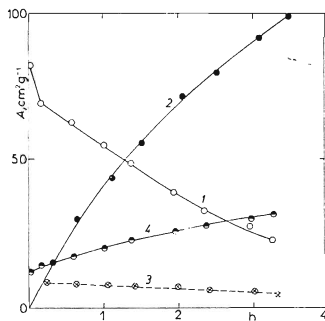


FIG. 3

Band Heights in the Infrared Spectrum of the HY-40 T_{790} Zeolite during the Interaction with Ethylene

Pressure 6.6 kPa, temperature 310 K; 1 free HF (3640 cm^{-1}), 2 $-\text{CH}_3$ (2955 cm^{-1}), 3 OH...C (3280 cm^{-1}), 4 $-\text{OH}$...sat. + LF (3550 cm^{-1}).

The oligomerization of propylene was investigated on samples activated under similar conditions as those under which the maximum catalytic activity was reached with ethylene. With the HY-70 zeolite also the interaction with a sample activated at 890 K was followed; this sample did not contain practically any structural OH groups. The positions of bands in the spectra and the over-all character of the intensity changes in them during the reaction was the same as with fully hydrated samples³. The activity of the HY-70 zeolite did not show any substantial changes with the increasing dehydroxylation, as long as structural OH groups were not removed at a high activation temperature: then it decreased substantially. However, with less decationized zeolites (HY-40 or HY-20) the over-all activity in the propylene oligomerization decreased with the increasing dehydroxylation.

These dependences can be clearly seen from Table I which gives also the numbers of HF hydroxyls and positions of the HF bands of hydrogen complexes with propylene. No changes in the spectra could be unambiguously assigned to the presence of allylcarbonium complexes formed by H^- removal on L centers.

Isotopic Exchange of Propylene- d_6 and Ethylene- d_4 with OH Groups at 570 K

The isotopic exchange of propylene- d_6 occurs in the same way as with hydroxylated forms, *i.e.* by the multiple mechanism with five equivalent hydrogens of the propylene molecule. We found that the labilization of the sixth hydrogen of propylene is similar in HY-70 dehydroxylated and in its hydroxylated forms³. However, the dependence of its labilization on the decationization degree was not investigated because of the reasons mentioned in the Experimental. The propylene- d_6 exchange rates were of the same order of magnitude (10^{18} atoms min^{-1}) as with the hydroxylat-

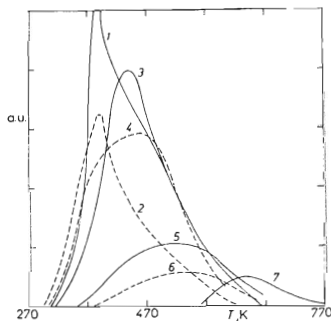


FIG. 4

Thermal Decomposition of Oligomers after the Adsorption of Ethylene on HY-70 T_{770} at 295 K (in arbitrary units)

1 Saturated hydrocarbons C_4-C_5 , 2 unsaturated hydrocarbons C_3-C_5 , 3 saturated C_6-C_7 , 4 unsaturated C_6-C_7 , 5 cycloalkanes, 6 cycloalkenes, 7 substituted aromatic hydrocarbons. Decomposition at the maximum pressure of $5 \cdot 10^{-4}$ Pa, temperature increase 1 K/min.

ed forms. However, the dependence on the decationization degree was not followed due to a different amount of SiOH groups.

The isotopic exchange of ethylene- d_4 was faster with HY-70 T_{770} than with the hydroxylated form, despite a larger fraction of SiOH groups which slow down the exchange: $4 \cdot 10^{17}$ atoms min^{-1} for HY-70 T_{770} and $2 \cdot 10^{17}$ atoms min^{-1} for HY-70 T_{670} . The single mechanism of the exchange and the induction period were preserved for the partly hydroxylated sample.

DISCUSSION

An increase of the catalytic activity of HNaY zeolites with the activation temperature was observed earlier for several types of reactions, *e.g.*, cracking of cumene, n-hexane, n-heptane, transalkylation of toluene, alkylation of benzene *etc.* This increase was explained by the action of dehydroxylated sites and/or by an increase of the acidity of the remaining OH groups⁴.

Our results with ethylene have shown that with hydroxylated forms of HNaY

TABLE I
Interaction of Propylene with HNaY Zeolites Activated at Various Temperatures

Zeolite	HF/u.c. ^a	ν OH . . CC ^b cm^{-1}	$k_{\text{CH}_3}^c$ $\text{cm}^2 \text{g}^{-1} \text{min}^{-1}$
HY-70			
T_{620}	22	3 180—90	5.8
T_{770}	4.8	^d	5.9
T_{880}	0	—	2.5
HY-40			
T_{620}	15	3 200	2.9
T_{770}	6.3	3 200	1.8
HY-20			
T_{620}	8.4	3 230	0.35
T_{770}	3.6	3 230	0.30

^a Number of HF hydroxyls in a unit cell, calculated from infrared spectra; ^b Position of HF hydroxyl bands in the H-complex with propylene; ^c Initial oligomerization rate of propylene at 310 K; ^d HF groups were quickly covered by saturated compounds and thus the position of this band could not be determined.

zeolites the interaction between OH groups and ethylene is so weak that at 310 K no formation of the primary carbonium ion takes place and, therefore, no oligomerization of ethylene occurs³. In agreement with other papers^{1,2}, it follows from our study that oligomerization of ethylene does proceed on samples containing dehydroxylated sites -- Lewis acid-base pairs. However, we found that with the dehydroxylated samples, in comparison with those fully hydroxylated, the position of the vibrational bands of the HF group bound in the hydrogen complex does not change. This experimental observation shows that no substantial increase of the acidity of OH groups through an indirect effect of Lewis centers takes place which would lead to the formation of the primary carbonium ion of ethylene through the hydrogen complex ethylene-HF group, thus initiating the oligomerization. An increase of the acidity of OH groups would have also influenced positively the oligomerization of propylene- however, the rate of this process either does not change or even decreases in comparison with the fully hydroxylated form. Therefore, the initiation of the ethylene oligomerization results evidently from a direct influence of Lewis acid-base pairs on ethylene. The skeletal isomerization which accompanies the oligomerization of ethylene points to the cationic mechanism of the reaction with a participation of carbonium ions. The catalytic action of Lewis centers presumably consists in their strong electron-accepting ability and in their polarization effect on the ethylene molecule. This molecule then reacts with another ethylene molecule to form the C₄-compound. This product has in turn the ability of forming, after the hydrogen transfer, secondary carbonium ions active in the further chain growth. The catalytic activity of Lewis acid-base centers increases with the increasing decationization, *i.e.* with the decreasing Na⁺ ion content in the zeolite.

The maximum activity in the ethylene oligomerization at a certain activation temperature may be explained by a collective action of the zeolite on the over-all reaction which includes not only chain initiation, but also its propagation and termination. In these latter two steps presumably play a role also lattice oxygen atoms, changes of the electrostatic field, and OH groups whose acidity increases with increasing decationization. Ions of Na⁺ themselves neither initiate the cationic polymerization nor support the chain growth, as follows from the preceding paper³. The maximum activity evidently requires a certain optimum ratio of Lewis centers and remaining OH groups. With HY-70 the activity maximum was at about 18–35% of structural OH groups (with respect to their number in the fully hydroxylated zeolite), with HY-40 its was at about 25–50%. The activity maximum shifted with the decreasing decationization to higher activation temperatures. This evidently hangs together with a higher stability of less decationized zeolites with respect to dehydroxylation. Further loss of structural OH groups behind the activity maximum leads to a steep decrease of the oligomerization rate. It follows from this fact that while Lewis centers are necessary in initiating the reaction, they are not the only centers which influence the oligomerization of ethylene.

The possibility that the activity decrease after reaching the maximum hangs together with amorphization of the samples, with the concentration of carbon during the activation *in vacuo*, or with trace amounts of iron (400–600 ppm in the samples under study) was excluded by determining the sorption capacities and by measuring signals of carbon and Fe^{3+} in the ESR spectra.

The oligomer species formed are stable with respect to the desorption at 310 K, while ethylene desorbs easily under these conditions. The decomposition of the oligomers starts above 470 K and it is accompanied by the intermolecular hydrogen transfer: in the gaseous phase saturated hydrocarbons prevail over unsaturated hydrocarbons, while in the zeolite polyene structures are formed and carbonization takes place, this all leading to a loss of its activity.

Oligomerization of propylene is influenced by the presence of Lewis centers, too. The process takes place even on the HY-70 T_{880} zeolite which shows in the infrared spectra no presence of structural OH groups. The presence of these hydroxyl groups forming with propylene the H-complex – the precursor of the secondary carbonium ion active in the oligomerization – thus is not only necessary condition of the oligomerization of propylene. Despite all this, Brønsted centers evidently play the dominant role in the oligomerization of propylene; the activity of partially dehydroxylated HY-40 and HY-20 is lower than that one of their fully hydroxylated forms.

The partial dehydroxylation did not substantially change the rate of the isotopic exchange of propylene- d_6 . As we assume – following the results of our previous study³ – that the exchange of five terminal hydrogens in propylene occurs directly with hydrogens of zeolite OH groups, and as we know that the character of structural hydroxyls is preserved in partly dehydroxylated zeolites, this experimental result is understandable. Any further conclusions are difficult to make in view of the substantial influence of slowly exchanging SiOH groups on the exchange rate.

Despite the fact that the oligomerization of ethylene proceed already on partly dehydroxylated zeolites, the single mechanism of exchange is preserved in the isotopic exchange of ethylene- d_4 ; thus, this mechanism is not connected directly with the ability of the zeolite to oligomerize ethylene. However, the rate of the isotopic exchange of ethylene does not correspond to the difference in the oligomerization activity of the hydroxylated and partly dehydroxylated HY zeolites: for the hydroxylated zeolite zero oligomerization activity was found³. Thus the transition state of the isotopic exchange differs from that one which stimulates the oligomerization of ethylene; this fact was noted by the authors of ref.¹ on the basis of other experimental data.

It can be said in conclusion that the initiation of the oligomerization of ethylene requires the presence of Lewis acid–base centers. The presence of remaining structural OH groups and of Na^+ ions strongly influences the maximum of the oligomerization activity. On dehydroxylated zeolites also the oligomerization of propylene proceeds; however, a more important role in this oligomerization play Brønsted centers,

namely with less decationized zeolites. The presence of Na^+ ions has a negative effect on both ethylene and propylene oligomerization; the activity of zeolites decreases with increasing amount of Na^+ ions, *i.e.* with the decreasing decationization.

REFERENCES

1. Liengme B. V., Hall W. K.: *Trans. Faraday Soc.* 62, 3229 (1966).
2. Kubelková L., Nováková J., Bosáček V., Patzelová V., Tvarůžková Z.: *Proc. Symp. on Zeolites, Szeged; Acta Phys. Chem. Szeged* 24, 189 (1978).
3. Nováková J., Kubelková L., Dolejšek Z., Jirů P.: *This Journal*, in press.
4. Poutsma M. L. in the book: *Zeolite Chemistry and Catalysis* (J. A. Rabó, Ed.), p. 437. ACS Monograph 171, Washington, D.C., 1976.

Translated by Z. Herman.