

STUDIES ON THE INITIAL STAGES OF TRANSFORMATION OF C₁-C₄ ALCOHOLS
ON ZSM-5 ZEOLITES

M. DEREWINSKI^a, S. DZWIGAJ^a, J. HABER^a, G. RITTER^b

Institute of Catalysis and Surface Chemistry, Polish Academy of Sciences, Kraków, Poland (a)

Institut of Physical Chemistry, Technical University, Vienna, Austria (b)

ABSTRACT

Catalytic activity of ZSM-5 zeolite poisoned by adsorption of pyridine was studied in order to elucidate the role of C₂ and C₃ olefins in the transformation of methanol. Consecutive steps in the sequence: alcohol-olefins-oligomers-cyclopolyenes-aromatics/paraffins are catalysed by acid centers of increasing strength, but in case of methanol the initiation of the chain by the formation of the first C-C bond from C₁ species requires the presence of strongest acid centers. Ethylene is the first product in C₁ conversion and its appearance creates a new facile route consisting in methylation and bypassing the formation of C-C bond. Propylene and higher olefins are methylated more readily than ethylene and are responsible for the increasing rate of methanol consumption, but a parallel route to develop the reaction network is operating through oligomerization of propylene.

INTRODUCTION

It is well known that high silica type ZSM-5 zeolites show high catalytic activity in the conversion of alcohols and olefins [1-4]. Reactions of different alcohols in the presence of hydrogen form of ZSM zeolites result in the formation of the whole spectrum of hydrocarbon products containing olefins, cycloolefins, paraffins and aromatics. It is the characteristic feature of these catalysts that the composition of the products obtained is practically independent of the type of alcohols used what hints to the common reaction path of the transformations of all alcohols. The main difficulty in the identification of the elementary steps and in the construction of the

reaction network is due to the very high rate of these transformations in the presence of the very active hydrogen form of the zeolite. It seems thus of interest to reduce the activity of this catalyst by poisoning the active centers of acid character with appropriate base adsorbed before the catalytic tests in order to study the mechanism of the reactions of C_1 - C_4 alcohols and to determine the role of C_2 and C_2 olefins in the transformation of alcohols, in particular of methanol, into higher hydrocarbons.

EXPERIMENTAL

Zeolite Z-79 of the ZSM-5 type was synthesized according to the patent description [5] and its structure was identified as that of ZSM-5 by X-ray analysis. The hydrogen form was obtained by three fold ion exchange in 0.1 M NH_4Cl solution at 363 K and subsequent heating in the stream of nitrogen at 823 K for 5 hr. Preparations with reduced acidity were obtained by adsorption of pyridine, which was introduced into the carrier gas passing through the reactor with catalyst bed heated to the reaction temperature of 673 K until pyridine appeared in the gas at the outlet. Catalytic activity in the reaction of methanol (MeOH), ethanol (EtOH), isopropanol (iso-PrOH) and butanol (n-BuOH) was determined in the pulse microreactor 8 mm in diameter, filled with 0.28 g samples of the catalyst and kept at reaction temperature of 673 K. The flow rate of nitrogen as the carrier gas was 30 ml/min at the atmospheric pressure. Products were analysed using the on-line gas chromatograph with flame ionization detector and a 4 m column filled with Chromosorb W (60/80 mesh) and silicon oil DC 550 with 5 % addition of stearic acid as the active phase. Reagents were of analytical grade and were used without further purification. Pyridine (Fluka) used for poisoning of the catalyst was of spectroscopic grade.

In the Temperature Programmed Desorption (TPD) experiments the sample of 100 mg of the zeolite was first activated at 823 K for 3 hr at the pressure of $5 \cdot 10^{-3}$ Torr ($6.63 \cdot 10^{-1}$ N/m²). After cooling to room temperature 15 μ l of alcohol was introduced and its adsorption carried out for 15 min. The sample was then outgassed for 1 hr and TPD experiment was carried out in the temperature range 303-923 K at the heating rate of 10 K/min. Desorbing products were analysed with a mass-spectrometer.

RESULTS AND DISCUSSION

Our earlier studies showed [6] that adsorption of pyridine at

CH₃OH/ZSM-5-Pyridine

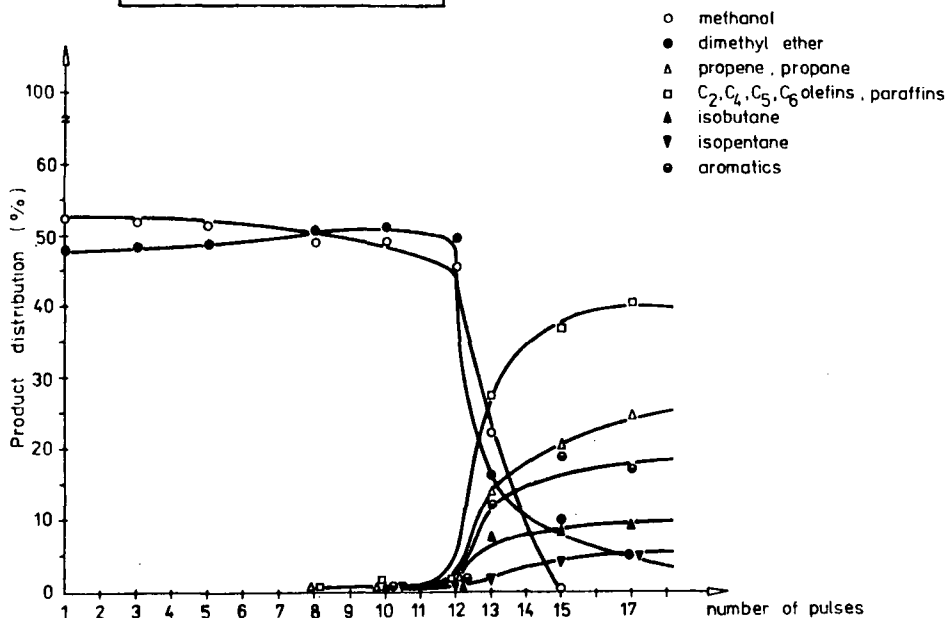


Fig. 1. Product distribution as function of number of pulses of MeOH introduced on ZSM-5 type zeolite poisoned by pyridine.

the surface of ZSM-5 zeolite results in drastic changes of the product distribution of the reaction of alcohols. Fig. 1 shows the changes of the composition of products obtained when pulses of MeOH were consecutively introduced on the initially poisoned zeolite. In the first pulses dimethylether (DME) is observed as the only product. Only after 10 pulses of MeOH traces of higher hydrocarbons appear. As the first products small amounts of C₂ and C₃ olefins are observed after 8 pulses. When more important amounts of propylene are formed immediately the whole spectrum of both paraffins and aromatics appears in the products. This is accompanied by the rapid decrease of the amount of unreacted MeOH and DME.

When reaction of EtOH was carried out in identical conditions, 100 % conversion to ethylene was observed already in first pulses, ethylene remaining as the only product through the whole experiment. Zeolite, which after partial removal of pyridine by consecutive pulses of the alcohol due to competitive adsorption of the reaction products and eluting effect of the carrier gas at high temperature developed the activity in the transformation of MeOH not only to DME but also hydrocarbons, remained inactive for the transformation of

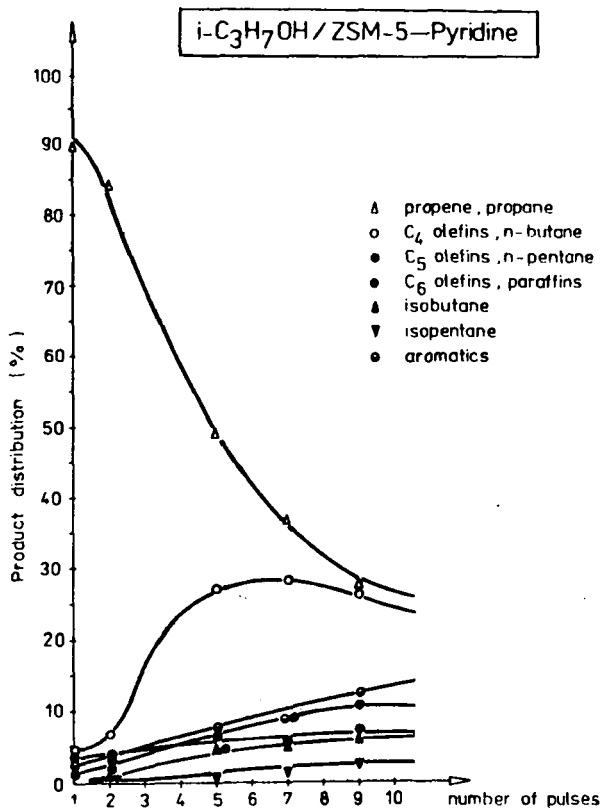


Fig. 2. Product distribution as function of number of pulses of iso-PrOH introduced on ZSM-5 type zeolite poisoned by pyridine.

At variance with the behaviour of C₁ and C₂ alcohols already after introduction of the first pulses of iso-PrOH not only propylene as the direct product of the dehydration of this alcohol on weak acid centres, but also the whole spectrum of hydrocarbons including paraffins and aromatics was observed, the conversion of iso-PrOH being 100%. At the beginning mainly propylene, products of its oligomerization and of the oligomer cracking are formed as indicated by high content of C₄-C₆ olefins. It may be mentioned that studies of the adsorption of propylene on HY zeolite [7] revealed the oligomerization of 4 molecules of propylene, and measurements of the adsorption of butene also on HY zeolite [8] indicated the formation of the oligomer from 3 molecules of butene.

Further removal of adsorbed pyridine by pulses of iso-PrOH results in gradual increase of the amount of products of cyclization

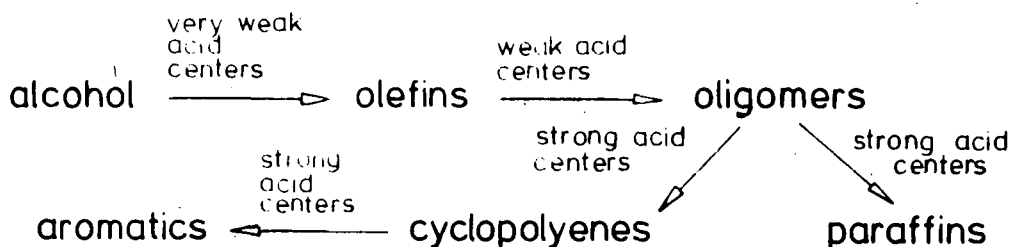
ethylene. Apparently it still lacks acid centers strong enough to convert ethylene into higher hydrocarbons. Their first trace amounts appeared only in the conditions in which methanol was already transformed into higher hydrocarbons to a considerable degree. After 20 pulses the conversion of ethylene was only 5% the main product (2%) being propylene.

Fig. 2 illustrates the results obtained when pulses of iso-PrOH were injected into the reactor with poisoned zeolite. At variance with the behaviour of C₁ and C₂ alcohols already after introduction of the

and hydride transfer i.e. paraffins and aromatics. It is noteworthy that in the case of iso-PrOH all these products appear in conditions in which in the case of MeOH and EtOH only products of their dehydration to DME and ethylene respectively are observed, but no compounds which require the formation of C-C bonds between C₁ or C₂ species.

Results obtained with n-BuOH were similar to those with iso-PrOH.

Comparison of the behaviour of MeOH and iso-PrOH clearly indicates that formation of the first C-C bond from C₁ species, necessary for further transformations and development of the whole reaction network, requires the presence of acid centers of the catalyst stronger than those, which are involved in the development of this network from propylene. It also shows that transformations of higher alcohols such as iso-PrOH or n-BuOH consist of a series of consecutive steps, catalysed by acid centers of increasing strength:

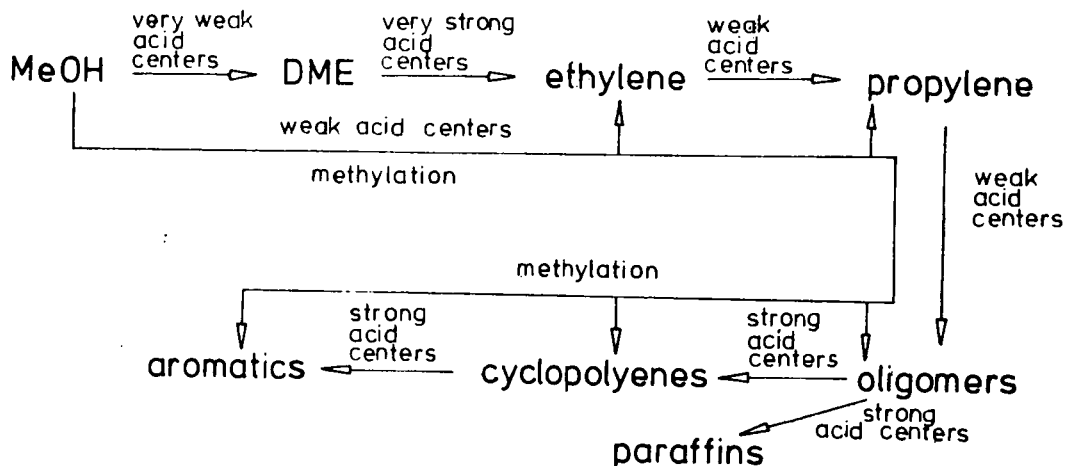


It can be namely concluded from the results presented in Fig. 2 that oligomerization and cracking, which are the first step in the series, require the presence of weaker acid centers and are therefore regenerated in the first instance on pyridine desorption. Further removal of pyridine uncovers stronger acid centers of the catalyst responsible for cyclization and hydrogen transfer.

The condition necessary to start the reaction chain in the case of methanol is the removal of pyridine from strongest acid centers required for the formation of the first C-C bond. Appearance of even small amount of such centers makes possible the formation of first portion of ethylene. Once they have been formed they undergo methylation by MeOH, which as shown before [6] proceeds with the participation of much weaker acid centers, from which pyridine has already been desorbed earlier. The absence of the products of dimerization or trimerization of ethylene at the early stages with the simultaneous presence of propylene indicates that no oligomerization of C₂H₄ takes

place, but only its methylation with MeOH. It may be concluded, that once small amounts of ethylene have been formed in the reaction of MeOH, the initial step consisting in the formation of C-C bond from C₁ species becomes bypassed by the much easier step of the methylation of the resulting carbon chain. It is obvious that also other products of the reaction sequence, higher olefins, cycloolefins, aromatics may undergo methylation by MeOH.

Thus, in the case of methanol the reaction network may be represented by a following scheme:



In the absence of MeOH, ethylene remains unreacted and therefore is the only product of the reaction of EtOH on zeolite catalysts which have not available very strong acid centers. The low reactivity of ethyl alcohol and ethylene was also postulated by other authors[3,4,9]

We have noticed that besides the intramolecular dehydration of EtOH also its intermolecular dehydration to diethylether (DEE) is possible in the first stages of the reaction. This is illustrated by Fig. 3, which shows the results of an TPD experiment after adsorption of EtOH on hydrogen form of the ZSM-5 zeolite, which has been previously activated at 823 K in vacuum of $(6.65 \cdot 10^{-1} \text{ N/m}^2) 5.10^{-3}$ torr. The values in brackets by the TPD curves of different m/e fragments indicate the sensitivity range used by registration. The curve m/e=45 corresponding to the fragment $\text{CH}_3\text{CH}=\overset{+}{\text{O}}\text{H}$ with maximum at 395 K represents the desorption of EtOH as confirmed by the appearance of a similar peak on curve m/e=31 ($\text{CH}_2=\overset{+}{\text{O}}\text{H}$), m/e=29 ($\text{HC}=\overset{+}{\text{O}}$) and m/e=46 ($\text{CH}_3\text{CH}_2\overset{+}{\text{O}}\text{H}$). The curve m/e=28 shows two maxima. The first, at 395 K is apparently related to the fragmentation of

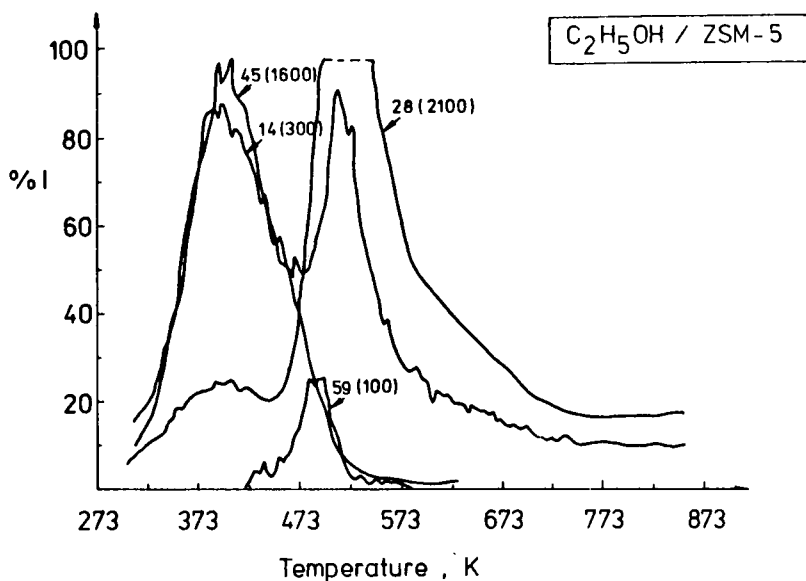


Fig. 3. TPD spectrum obtained after adsorption of EtOH on ZSM-5 zeolite.

desorbed alcohol, whereas the second maximum at 509 K may be assigned to the desorption of ethylene ($\text{CH}_2=\overset{+}{\text{C}}\text{H}_2$ fragment). The presence of other peak characteristic for the mass spectrum of C₂ olefin e.g. $e/m=27$ ($\overset{+}{\text{C}}\text{H}=\text{CH}_2$) $m/e=25$ ($\text{CH}\equiv\overset{+}{\text{C}}$), $m/e=14$ ($\overset{+}{\text{C}}\text{H}_2$), confirms the desorption of ethylene at this temperature. The curve illustrating the formation of a fragment with $m/e=59$ registered at the sensitivity 21 times higher than that of ethylene indicates the presence of diethylether ($m/e=59$ corresponds to the fragment $\text{CH}_2=\overset{+}{\text{O}}-\text{CH}_2\text{CH}_3$). The characteristic fragment $m/e=31$, which usually serves for identification of DEE is in our experiment screened by fragments originating from EtOH.

Results of TPD experiment clearly indicate that on the interaction of EtOH with ZSM-5 zeolite not only its intramolecular but also intermolecular dehydration with the formation of DEE takes place.

The studies of catalytic properties of the series of boron and aluminium phosphate of different composition [10] have shown that in the composition range, in which Brønsted acidity is present, only dehydration of EtOH to ethylene takes place, whereas in the composition range, in which pairs of Lewis acid-base centers are generated, ethanol is dehydrated mainly to DEE. It is possible that preactivation of the zeolite sample before the TPD run in comparatively severe conditions resulted in generation of some Lewis acidity. In normal conditions this reaction path is marginal in comparison with intra-

CH₃OH/ZSM-5—NH₃

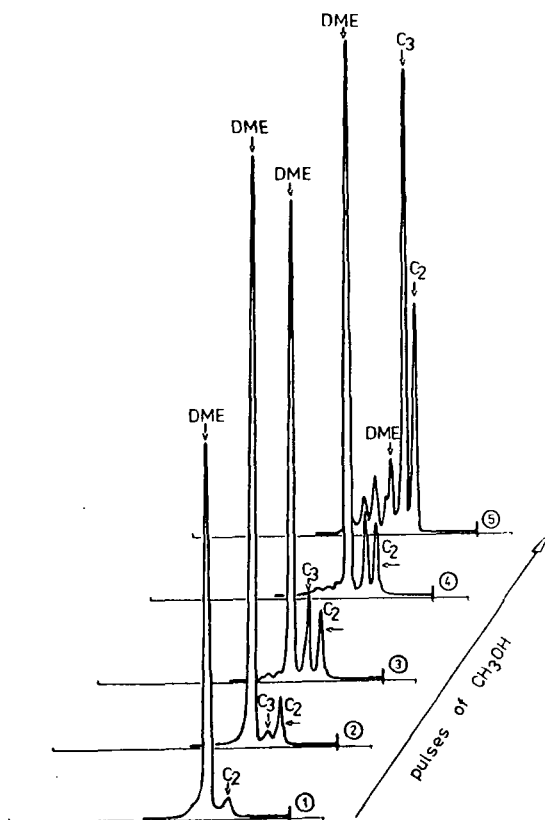


Fig. 4. Results of gas-chromatographic analysis after five consecutive pulses of MeOH introduced on ZSM-5 type zeolite poisoned with ammonia.

portion of ethylene which is responsible for initiation of the reaction sequence. The appearance of propylene results in rapid acceleration of the reaction and increase of the conversion of methanol which is consumed mainly through the methylation of the growing hydrocarbon chains. Simultaneously, as may be concluded from the results obtained with iso-PROH, propylene alone reacts rapidly, developing through oligomerization and cracking the whole reaction network. This contributes to further consumption of MeOH and results in its total conversion. On studying the influence of various alcohols

molecular dehydration. In order to confirm the role of ethylene as the intermediate which enables the bypassing of the first most difficult step in the transformation of MeOH—the formation of the first C-C bond, a series of experiments was carried out in which the state of the reaction was registered on the zeolite poisoned with ammonia (Fig. 4).

The first product appearing besides the DME at the beginning of the reaction is ethylene. The presence of ethylene does not yet lead to the appearance of higher hydrocarbons. The next rapidly growing product is propylene. As already mentioned the absence of C₄ and C₆ hydrocarbons as products of ethylene oligomerization and appearance of propylene indicates that it is methylation of the first

and olefins added in small amounts to MeOH on its conversion at the surface of the zeolite catalyst poisoned by pyridine [11] it was found that indeed propylene much easier undergoes methylation than ethylene and therefore accelerates the transformation of MeOH to a much greater extent. In later stages of the reaction ethylene is formed not only by direct formation of C-C bond from C_1 species, which is a difficult step and requires the presence of strong acid centers, but also as the result of cracking of larger olefins.

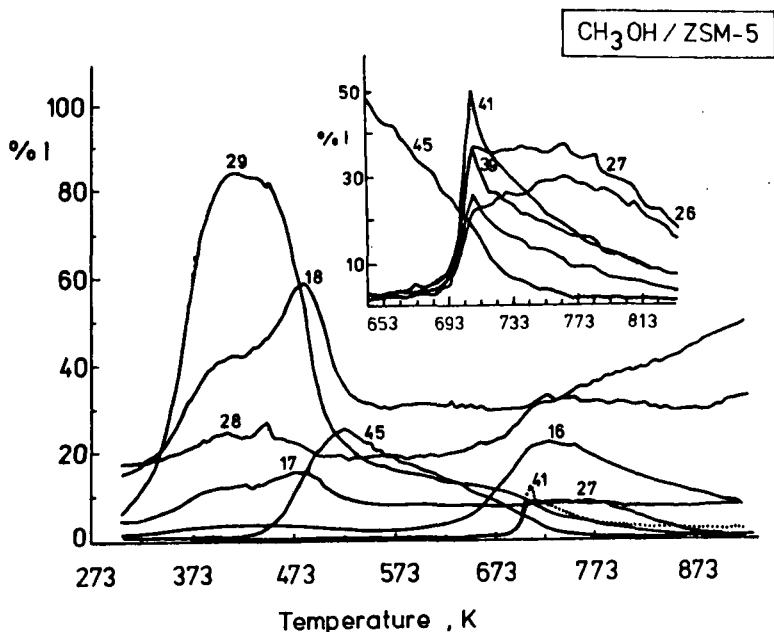


Fig. 5. TPD spectrum obtained after adsorption of MeOH on ZSM-5 type zeolite.

Additional information on the role of lower olefins in the transformation of MeOH was obtained from TPD experiments.

Fig. 5 illustrates the TPD curves registered after adsorption of methanol on active HZSM-5. The curve $m/e=29$ illustrates the desorption of the unreacted MeOH, curves $m/e=18$ and $m/e=17$ - desorption of water. Maximum at 481 K is related to the dehydration of methanol. The curve $m/e=45$ represents the formation of DME (maximum desorption temperature 523 K) and its disappearance on further heating. The magnified part of the temperature range 643 K - 823 K (shown in the insert) illustrates the desorption of ethylene $m/e=27$ ($CH_2=CH^+$), $m/e=26$ ($CH=CH^+$) and propylene $m/e=41$ ($CH_3-CH=CH^+$). It may be seen that methylation of ethylene is not difficult. On the other hand the very rapid disappearance of propylene at higher

temperatures with simultaneous accumulation of ethylene shows that propylene reacts further more rapidly than ethylene, through methylation and oligomerization. Apparently, the competition from higher olefins and aromatics for methylation results in the accumulation of less reactive ethylene. It is noteworthy that some amount of methane is also formed (curve representing the fragment with $m/e=16$).

REFERENCES

1. Chang, C.D., Silvestri, A.J., *J. Catal.*, 47, 249 (1977).
2. Derouane, E.G., Nagy, J.B., Dejaifve, P., van Hooff, J.H.C., Spekman, B.P., Vadrine, J.C., Naccache, C., *J. Catal.*, 53, 40 (1978).
3. Anderson, J.R., Foger, K., Mole, T., Rajadhyaksha, R.A., Sanders J.V., *J. Catal.*, 58, 114 (1979).
4. Dejaifve, P., Vadrine, J.C., Bolis, V., Derouane, E.G., *J. Catal* 63, 331 (1980).
5. Argauer, R.J., Landolt, G.R., US Patent 3 702 886 (1972) Mobil Oil Corp.
6. Derewiński, M., Dźwigaj, S., Haber, J., *Zeolites*, 4, 214 (1984).
7. Haber, J., Komorek, J., Romotowski, T., prepared for Inter. Symp. on Zeolite Catalysis, Siófok, May 1985.
8. Datka, J., *J. Chem. Soc. Faraday I*, 76, 2437 (1980).
9. Ahn, B.J., Armando, J., Perst, G., Guisnet, M., *C.R. Acad. Sci. Paris* 288c, 245 (1979).
10. Haber, J., Szybalska, U., *Disc. Faraday Soc.*, 72, 263 (1981).
11. Dźwigaj, S., Haber, J., Derewiński, M., in press.