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SELECTIVE CATALYTIC TRANSFORMATIONS OF METHANOL TO C_2–C_3 HYDROCARBONS OVER THE NEW ZEOLITE TYPE LZ 132

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The small pore zeolite HLZ 132 exhibits, in comparison with other zeolites, an increased selectivity for the transformation of methanol to ethylene in the reaction temperature range 350–500 °C: the weight ratio of C_2H_4 to C_3H_6 in the products ranges between 1 and 4 at WHSV = 2 h^{-1}. Besides the effect of the reactant shape selectivity this fact may be interpreted by the participation of the asymmetrical methoxy groups in the surface as well as by proton-donor centres of lower acidity which do not catalyze the oligomerization of ethylene but which do the more basic molecule of propylene, thereby generating polyene-type coke.

The LZ 132 zeolite described recently [1] is topologically related to the mineral levynite with an effective pore-size of the calcined product of 4.3 Å. These characteristics as well as the pore structure and surface properties of LZ 132 zeolite may be significant for its catalytic properties, which, from the point of view of the selectivity for methanol transformation to C_2–C_3 hydrocarbons, differ from those of ZSM zeolites and other, so called small pore zeolites (Nu-3, erionite, chabazite, ZK-5).

The LZ 132 zeolite was prepared by hydrothermal synthesis [1]. The raw product (Na^+ = 0.2 wt%, Si/Al = 33) was activated by decomposition of the structure-directing agent successively in N_2 and O_2 at 550 °C, followed by ion-exchange (with 0.5M-NH_4NO_3) and final transformation into the H^+-form at 350 °C in vacuo. The X-ray diffractographic data of the LZ 132 zeolite correspond to those given in the literature [1]. The IR spectrum characterizing HLZ 132 in the skeletal vibrations range is given in fig. 1.

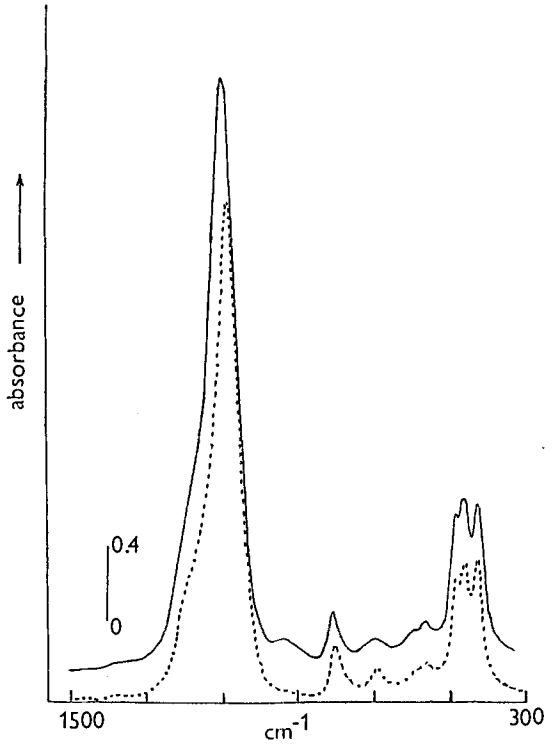

Fig. 1. IR spectra of the HLZ 132 zeolite in the frequency range of skeletal vibrations: in the original state (full line); and after the catalytic test (dashed line).

The transformation of methanol was performed in a catalytic microreactor at 400 °C and WHSV = 2 h^{-1} over a catalyst with 0.4–0.6 mm grain size. The feed contained 17 vol.% CH_3OH, 68 vol.% H_2O and 15 vol.% N_2 under 10 kPa total pressure. After 60 minutes on stream 96% methanol conversion was attained, the products containing 51 wt.% $C_2 + C_2^=$ ($C_2 < 1\%$), 3.5 wt.% C_3, 34.5 wt.% $C_3^=$, 10.5 wt.% $C_4 + C_5$ hydrocarbons and less than 0.5 wt.% i–$C_4^=$ and aromatics. The ratio of $(C_2 + C_2^=)/C_3^=$ after 60 minutes on stream as function of the reaction temperature is given in fig. 2. The dependence found shows that, with rising reaction temperature, the amount of ethylene in the product is increased. In a feed without water vapour a similar composition of the methanol transformation products was found, the presence of H_2O having a positive effect only on the lifetime of the catalysts. The IR spectra of HLZ 132 measured before and after the catalytic test in the skeletal vibrations range (see fig. 3) shows that, during the catalytic reaction, the ratio ${}^0A_{565cm^{-1}}/{}^0A_{460cm^{-1}}$ of the normalized absorbancies of the bands in question (and hence also the crystallinity of the zeolite catalysts) undergoes no change.

Catalytic tests over HZSM-5 zeolite (Si/Al = 17), performed under the same reaction conditions, led to a product containing significantly less $C_2 + C_3$ olefins.

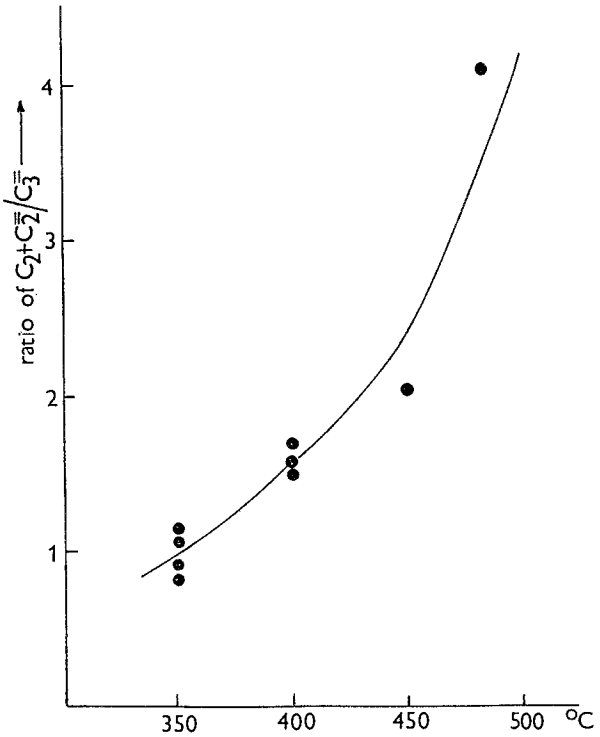

Fig. 2. The ratio $(C_2 + C_2^=)/C_3^=$ of hydrocarbons after 60 min on stream in dependence of the reaction temperature.

The product contained where: 22 wt.% $C_2 + C_2^=$ ($C_2 < 1\%$), 8.3 wt.% C_3, 26.5 wt.% $C_3^=$, 37.5 wt.% $C_4 + C_5$ hydrocarbons, the rest higher hydrocarbons and aromatics.

These results show that the yields of $C_2 + C_3$ olefins over HLZ 132 zeolite are significantly higher than those obtained with HZSM-5. The weight ratio $R = (C_2 + C_2^=)/C_3^=$ in the products at reaction temperatures of 350–500 °C attains the values of 1 to 4; at 400 °C $R = 1.6$, i.e. by nearly 100% higher than over HZSM-5 ($R = 0.83$) under the same reaction conditions. Analogical values of R over "small pore zeolites" (erionite, chabazite, ZK-5) as given by Chang [2] are also lower than those obtained over HLZ 132 at the same reaction temperature. Over HLZ 132 both the values of R and conversion sums to $C_2^= + C_3^=$ hydrocarbons are higher than over Nu-3 zeolite [3] which also belongs to the group of zeolites similar to levynite.

So as to gain insight into the causes of the higher selectivities of the HLZ 132 zeolite in the formation of lower olefins C_2–C_3 the initial rate of ethylene and propylene oligomeration was determined at 80 °C and $p_{olef.} = 2.66$ kPa (for further experimental details see ref. [4]). The IR spectra of the catalyst (using a Nicolet-MX1 FT-IR spectrometer) in the frequency range of structural OH

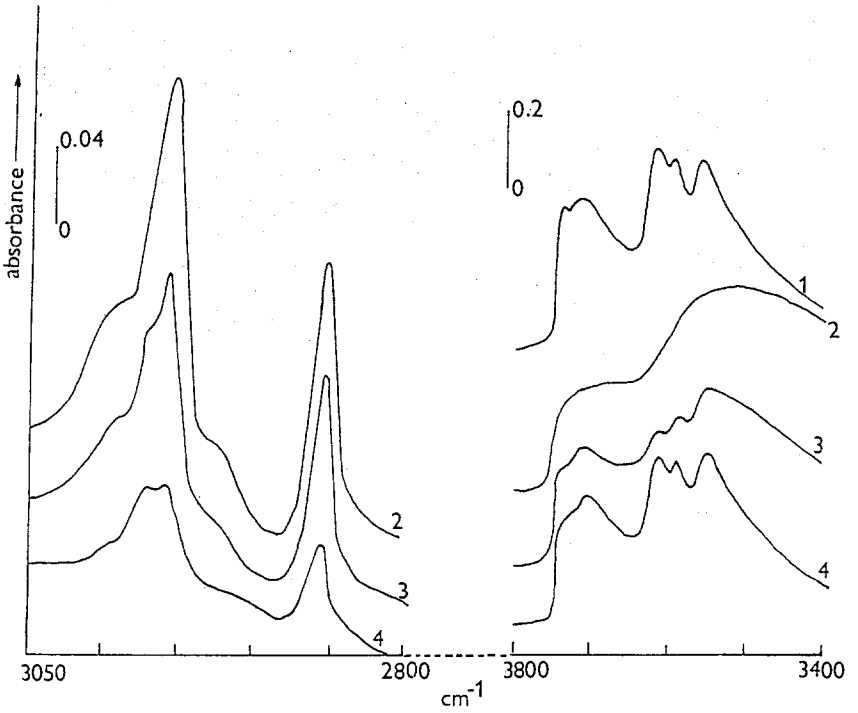

Fig. 3. IR spectra of the HLZ 132 zeolite evacuated at 350 °C overnight before the interaction with CH_3OH (curve 1), after the interaction with CH_3OH at 20 °C for 30 min (curve 2), after the interaction with CH_3OH at 100 °C for 30 min (curve 3) and finally after the interaction with CH_3OH at 400 °C for 30 min (curve 4).

groups and methanol surface complexes in the interaction temperature range 20–400 °C were also recorded. Measurements of IR spectra were performed with self-supported pellets (10 mg/cm^2 thickness) situated in a high-vacuum cuvette. The amount of preadsorbed methanol at 20 °C was 10 mmol/g zeolite (for the experimental details see ref. [5]).

The initial oligomeration rate of ethylene $r_0 < 0.2$ min^{-1} is lower by two orders of magnitude than that of propylene ($r_0 = 28.2$ min^{-1}) which is a more basic molecule. The different behaviour of HLZ 132 in the oligomeration of C_2H_4 and C_3H_6 indicates that the proton-donor centres of the zeolite which take part in the oligomeration on zeolites [6] are less acidic (or weaker) than e.g. on HZSM-5, where the ethylene oligomeration rate under the same conditions was $r_0 = 45.1$

Table 1
Comparison of the methanol conversion (%) to C_2–C_3 olefins at 450 °C and 84 min. on stream

	R	$C_2^= + C_3^=$ (%)
HLZ 132	2.1	97
HNu-3 [3]	0.92	60

min^{-1}. Supposing that on the HLZ 132 zeolite the difference between the oligomeration rates of C_2H_4 and C_3H_6 is maintained also at higher reaction temperatures we may interpret the high value of R in the methanol transformation products by the formation of coke from the greatest part of the propylene formed. From IR spectra it follows that the structure of this coke on HLZ 132 corresponds only to polyenes as expected (proved by the presence of a strong band at 1600 cm^{-1}–see ref. [6]), whereas on HZSM-5 the coke formed exhibits the structure of both polyenes and polyaromatics [6].

Figure 3 shows the IR spectra of HLZ 132 zeolite in the frequency range corresponding to the structural OH groups as well as in that one corresponding to the stretching vibrations ν(C–H) of these bonds before and after interaction with CH_3OH. In the original spectrum of the HLZ 132 zeolite four OH-bands are present, namely at 3710, 3620, 3600 and 3550 cm^{-1}. After CH_3OH adsorption at 20 °C and a short desorption of the gaseous phase at the same temperature the spectrum exhibits only two broad bands at 3710 and 3500 cm^{-1} indicating a strong interaction of CH_3OH with the OH groups of the zeolite. In the region of ν(C–H) vibrations two strong bands at 2925 and 2855 cm^{-1} are formed, accompanied by shoulders at 2987 and 2925 cm^{-1}, resp. When the interaction temperature is 100 °C, all four bands appear again in the spectrum. Their reduced intensity indicates that a part of CH_3OH has desorbed, whereas a part of it remained solidly bound on the zeolite. In the region of ν(C–H) vibrations both bands and shoulders found at 20 °C were preserved, only with a reduced intensity. Besides that, another intensive band at 2972 cm^{-1} appeared. When the interaction takes place at 400 °C, all four original OH-bands are preserved, their intensity being higher than after the interaction with CH_3OH at 100 °C, although lower than in the original spectrum. At this interaction temperature the intensity of all four bands in the ν(C–H) vibrations range including the shoulders is reduced, so that the shoulder at 2925 cm^{-1} could not be registered distinctly.

The decrease of the bands intensities (and of the absorbancies calculated from them) in the frequency range of ν(C–H) groups vibrations, accompanied by the increase of the OH bands intensities, indicates that a reaction between the previously formed surface methoxy-groups takes place at 400 °C during formation of gaseous hydrocarbon products and simultaneous regeneration of the OH groups.

The coordination of the above quoted bands found with the respective vibration groups in the IR spectrum facilitates a better understanding of the processes taking part in the CH_3OH interaction with HLZ 132 at higher temperatures (at 400 °C in this case). The bands in the frequency range of the vibrations of structural OH groups as well as their changes clearly correspond to OH groups with proton-donor properties, as it may be seen also from the IR spectra of HLZ 132 after its interaction with either acetonitrile or NH_3 (not presented in this paper). The bands in the frequency range of the vibrations ν(C–H) may, in all probability, be ascribed to two types of surface methoxy complexes zeolite-OCH_3

(designated A, B) formed during interaction of CH_3OH with proton-donor centers of the zeolite, just as it has been described in papers dealing with HX, HY and HZSM-5 zeolites [5, 7–10]. The bands at 2957 cm^{-1}, 2855 cm^{-1} and the shoulder at 2925 cm^{-1} would correspond to the symmetrical zeolite-OCH_3 species B. The unsymmetrical surface complex A is, according to Morrow [7], characterized by one strong and two weak C–H bonds. We may adopt the idea that those weak C–H bonds in the two neighbouring surface complexes enhance the elimination of water and the formation of ethylene.

Our results are in agreement with the ideas of Casci and Whitham [3] on the role of "shape selectivity" of the zeolite in the transformation of CH_3OH to lower olefins over a similar small-pore zeolite Nu-3 and complete them in the following aspects. Ethylene as product may be formed over HLZ 132 by a reaction either between two reactive surface complexes of type A or between one surface complex of type A and gaseous CH_3OH. This model agrees with the mechanism of the transformation of CH_3OH over ZSM-5 zeolite under participation of dimethyl ether, as suggested by Derouane et al. [11]. The methoxy groups found experimentally on HLZ 132 could serve as a precursor to the formation of dimethyl ether ("in statu nascendi") in agreement with the transformation mechanism quoted above. The subsequent transformation of ethylene to higher olefins then proceeds to a diminished degree, as expected from the lower acidity of the HLZ 132 zeolite. Because of its weak basicity, ethylene is not activated by the proton-donor centres for the next reaction, e.g. the oligomeration or the reaction with another CH_3OH molecule. The yield of higher olefins is therefore low. The content of propylene and further higher olefins (with molecules of higher basicity when compared with ethylene) in the products is further reduced by oligomeration leading to a progressive coverage of the zeolite by polyene–type coke.

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