DIFFERENT ACTIVITY OF HZSM-5 AND HNaY ZEOLITES IN THE INTERACTION WITH ETHYLENE: EFFECT OF WATER VAPOUR

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The reaction of ethylene on HZSM-5 and HNaY zeolites, differing widely in acidity, was compared by means of IR and MS methods. Different surface and gaseous products were observed. The presence of water vapour effected mainly the activity of the HZSM-5 zeolite.

In the formation of gasoline from methanol on ZSM zeolites ethylene has been assumed to be an active intermediate[1,2]. Therefore, it was interesting: *a*) to compare the ethylene reaction on the HZMS-5 zeolite with the ethylene reaction on a classical HNaY zeolite, and *b*) to study the influence of water vapour on the ethylene interaction, since water is a by-product in the methanol conversion.

EXPERIMENTAL

Properties of the zeolites of both types are summarized in Table I. Interaction of ethylene (Fluka, 99·99%) with both zeolites was followed at the temperature 310 K by means of infra-red spectroscopy (Perkin–Elmer 621). The oligomerization of ethylene in zeolitic cavities was observed

TABLE I

Properties of the Zeolites Used

Property	HZSM-5[a]	$H_{70}Na_{30}Y$[b]
Sorption capacity, mmol Ar/g	2	10·5
Pretreatment temperature, K	670	770
Conc. of OH groups (from D_2 exchange[4,5])	$2{\cdot}2 \,.\, 10^{20}$	$8{\cdot}7 \,.\, 10^{20}$
Brönsted acid conc., sites per gram (from PY sorption at 570 K[4,5])	$3 \,.\, 10^{19}$	$3 \,.\, 10^{20}$
Lewis acid conc., sites per gram	$2 \,.\, 10^{19}$	$3 \,.\, 10^{20}$

[a] Prepared according to[3]; [b] supplied by the Research Institute for Petroleum and Hydrocarbon Gases, Bratislava.

(Fig. 1): with HZSM-5 mainly straight-chain oligomers were found (bands at 2930 and 1470 cm^{-1}, assigned to vibrations of saturated —CH_2— bonds), while with HNaY branched oligomers, resulting from skeletal isomerization, were detected (additional bands at 2955, 1366 and 1382 cm^{-1}, assigned to methyl groups). With both zeolites, no bands of —C=C— vibrations were observed.

Additionally, the oligomers formed on the two zeolites at 310 K were subjected to thermal decomposition and the gaseous products formed were analyzed mass-spectrometrically (a modified MI 1305 spectrometer, USSR).

RESULTS AND DISCUSSION

Composition of the products and the observed differences between the two types of zeolites can be seen from Fig. 2*a*, *b*. Both zeolites evolved aliphatic hydrocarbons C_{3-7} when heated to temperatures 370–470 K, alicyclic hydrocarbons at 470–570 K, and methyl-substituted aromatic hydrocarbons around 600–700 K. Two main differences between the products can be noticed: *a*) with HNaY, saturated hydrocarbons represent the dominant product; on the other hand, unsaturated hydrocarbons prevail with HZSM-5; *b*) the formation of substituted aromatic compounds and benzene is more significant with HZSM-5 than with HNaY.

Similar differences in the composition of gaseous products were found in the reactions of both zeolites with ethylene at the temperature 670 K. The formation of satu-

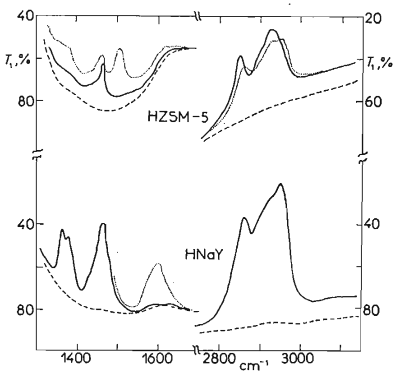

Fig. 1

IR Spectra of HZSM-5 and HNaY Zeolites after Interaction with Ethylene

------ Zeolites before interaction, ——— after interaction with ethylene at 310 K and 7·75 kPa, ·········· after heating with ethylene at 670 K and 7·75 kPa for 60 min and cooling to 310 K.

rated products with HNaY and unsaturated products with HZSM-5 is significant (see Fig. 3*b*, *c*). The consumption of ethylene is shown in Fig. 3*a*: the shape of these curves for both zeolites is practically identical at the beginning of the reaction, but the con-

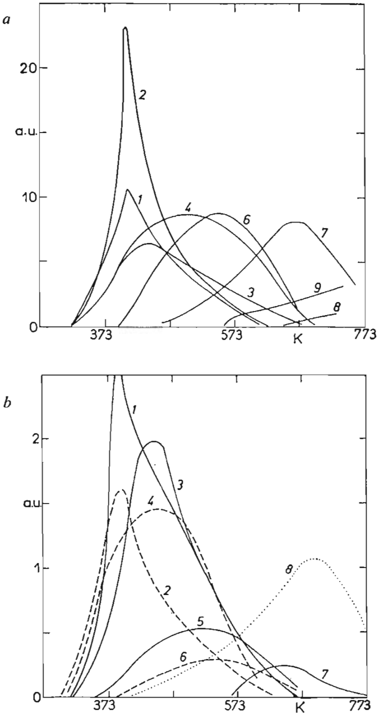

FIG. 2

Thermal Decomposition of the Ethylene Oligomer Formed at Room Temperature on HZSM-5 and HNaY Zeolites

a HZSM-5, *b* HNaY; both *in vacuo* of the mass spectrometer (max. $5 . 10^{-4}$ Pa), heating rate 1 K min^{-1}; *1* saturated C_{4-5}, *2* unsaturated C_{3-5}, *3* saturated C_{6-7}, *4* unsaturated C_{6-7} hydrocarbons, *5* cycloalkanes, *6* cycloalkenes, *7* aromatic hydrocarbons, *8* water, *9* benzene.

sumption of ethylene almost stops with HNaY after some time. In addition to this fact, new surface compounds were detected by means of IR after heating the zeolites at 670 K in the presence of ethylene. On HNaY a band at 1595 cm^{-1}, assigned to polyene structures, was found (Fig. 1). The character of the other bands remained the same as during the oligomerization at 310 K. On the contrary, analogous heat treatment of HZSM-5 with ethylene resulted in the appearance of new bands at 1505, 2955, and 1365–1385 cm^{-1}, assigned to aromatic compounds and CH_3 groups, but no substantial amount of polyene structures was observed.

The presence of water vapours (1 : 1 mixture with ethylene) did not significantly influence the reaction of ethylene with the HNaY zeolite. With the HZSM-5 zeolite, water vapours not only facilitated the release of products into the gaseous phase, but also changed the saturated/unsaturated hydrocarbon yield ratio which approaches the value found for HNaY. The facilitated release of products was also significant for aromatic compounds (not shown in Fig. 3): after several minutes 3% of aromatic compounds (from the total amount of products) appeared in the gaseous phase, while without water several hours were needed for the observation of the same amount.

The reaction of ethylene on the HNaY zeolite was related in our previous paper[6] to collective properties of this zeolite. The dominant role of the Lewis acid–base pair

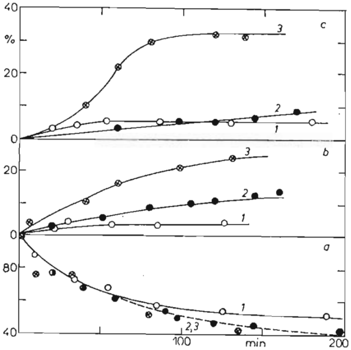

FIG. 3

Composition of the Gaseous Phase during the Interaction of Ethylene with HZSM-5 and HNaY Zeolites at 670 K

1 HNaY, *2* HZSM-5, *3* ethylene + water (1 : 1) over HZSM-5; *a* ethylene, 1·3 kPa, *b* unsaturated hydrocarbons C_{3-7}, *c* saturated hydrocarbons C_{4-7}.

centers was supposed in the initiation of oligomerization. The Brönsted acid centers were considered to be mainly responsible for the hydrogen and methyl transfer and for secondary reactions at higher temperatures. The formation of polyene structures was connected with coking of the surface and leaded to a desactivation of the zeolite.

With the ZSM-5 zeolite other factors are likely to play a dominant role in the reaction with ethylene, since the content of both types of acid centers is by one order of magnitude lower than in the HNaY zeolite. In agreement with this fact, qualitatively different products (straight surface chains, unsaturated compounds in the gaseous phase, aromatic compounds on the surface) and no observable desactivation are found. Several factors may be responsible for the different reaction path of HZSM-5 with ethylene: *a*) the electrostatic field which is different from that of HNaY (ref.[7]); *b*) the large Si : Al ratio[3] which makes the HZSM-5 zeolite similar to reactive silica for which a radical mechanism in the ethylene interaction was assumed[8]; *c*) the specific crystal structure and pore opening[9]. Water vapour is important not only for the enhancement of the product release into the gaseous phase, but it also increases the fraction of saturated hydrocarbons, probably as an additional source of protons.

In the interaction of ethylene on the HZSM-5 zeolite in the presence of water vapours the same products were formed as in the interaction of methanol with this zeolite[4]. Therefore, the assumption of ethylene being an active intermediate in the conversion of methanol[2] seems to be justified. However, the influence of water vapours on the reaction path must be taken into consideration.

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