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Conversion of hydrocarbons over zeolites and phosphoric acid

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Abstract

The influence of the SiO_2/Al_2O_3 ratio and decationation degree on the process of adsorption of ethylene–temperature-programmed decomposition of the oligomers on the surface of NaHZSM-5, HM, HY was studied. It was found that the specific rate of ethylene adsorption (formation of oligomers) did not depend upon decationation degree whereas the activity in reaction of hydrogen redistribution (formation of paraffins) decreased with increase of sodium content or SiO_2/Al_2O_3 ratio. A similar behavior was observed for HY and phosphoric acid in conversion of ethylene. It was proposed that it is the multi-point adsorption centres which are responsible for the hydrogen transfer reactions while oligomerization takes place on isolated acid centres.

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1. Introduction

Zeolites are used for different processes of hydrocarbon conversion because of their extraordinary acidic and structural properties. Despite this the detailed mechanism of acid-catalysed reactions of lower C_2–C_3 olefins is still a subject of discussion. The principal point that remains obscure at the moment is the nature of the active hydrocarbon species which are responsible for the conversion. The nature of the active centres which corresponds to the reactions of hydrogen transfer and isomerisation is also unrevealed. A few types of active centres is believed to participate in light olefin activation and conversion on hydrogen forms of zeolites: structural Brønsted and/or Lewis acid centres formed under decationation–calcination procedure or acid–base pair; one electron red-ox (radical) centres which was found to exist in zeolites; extra-framework Al-containing species [1–3]. It is evident that because of the unique zeolite structure not only the nature of active centres can have an influence on the reaction course but also their location in the framework. One can expect some kind of cooperative effect for the samples with high 'surface density' of centres.

The objective of the paper is to reveal a possibility of such a cooperative effect and to study an influence of 'surface density' of centres on different reaction which can take place over zeolites. Because of the very complex set of transformation of the parent olefins two main processes were monitored:

i) a rate of olefin consumption by zeolites which reflects the rate of oligomer formation (oligomerization);
ii) an amount of saturated and unsaturated hydrocarbons evolved under TPD condition (temperature programmed desorption) which characterizes an activity in the reaction of hydrogen redistribution.

In the present paper a process of ethylene adsorption on hydrogen forms of pentasil, mor-

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denite and faujasite type zeolites followed by temperature programmed desorption decomposition (TPD) of adsorbed olefin and formed oligomers was carried out. SiO_2/Al_2O_3 ratio and decationation degree was changed to obtain different surface density of active centres. A thorough GC analysis of hydrocarbons evolved under TPD condition was employed to characterize catalytic activity of the samples studied because it was shown that the composition of the hydrocarbons is very sensitive to the nature of the active centres [4].

2. Experimental

Phosphoric acid (64–85% P_2O_5) and hydrogen forms of mordenite ($SiO_2/Al_2O_3 = 11–60$), faujasite (4.6) and ZSM-5 (39–136) were used. Pentasil was obtained by direct synthesis while mordenites and faujasites were prepared by dealumination of starting material with HCl and $SiCl_4$ correspondingly [5]. Decationation of the zeolites with aqueous with aqueous solution of ammonium acetate was employed to obtain desired sodium content. Before an experimental run a sample was treated in oxygen flow at 480°C then in a static vacuum system at $P = 0.1$ Pa and $T = 500°C$ followed by C_2H_4 adsorption at $P = 80 \pm 3$ kPa and $T = 50°C$. The amount of ethylene adsorbed and the rate of adsorption were calculated from the pressure drop. After the ethylene coverage reached the desired value of about $1–2 \cdot 10^{21}$ molecules C_2H_4/g the sample was purged with helium flow for 30 min at 50°C followed by linear temperature programming 3°/min to 600°C. The oligomers desorbed and the products of the oligomer decomposition were analyzed by on-line gas chromatograph on packed and capillary columns. A number of acid sites was calculated from temperature programmed desorption of ammonia.

A conversion of ethylene over phosphoric acid was carried out at 170–260°C and 0.16 MPa in a sealed glass tube with subsequent chromatographic analysis of the gas phase.

3. Results and discussion

3.1. Ethylene adsorption studies

The rate of ethylene uptake for all samples of mordenite and faujasite is very high and decreases with the increase of olefin coverage whereas a dependence of the rate of ethylene adsorption upon time or coverage on H-NaZSM-5 zeolites have an unusual shape (Fig. 1). An initial portion of C_2H_4 (about $4–5.5 \cdot 10^{20}$ molecules C_2H_4/g) is adsorbed very quickly and then a decrease of adsorption rate occurs. After a certain period of time (which depends upon the sodium content) an acceleration of reaction was observed. The rate of adsorption approaches a maximum at $6–8.5 \cdot 10^{20}$ molecules C_2H_4/g and falls slowly to zero.

The fist fast uptake of ethylene appears to be caused by physical adsorption of olefin because it occurs also on sodium form of pentasil (NaZSM-5). In this case ethylene is removed from the surface quantitatively under TPD condition.

Special experiments with propene and cis-butene-2 adsorption on 14%H-NaZSM-5 showed that maximal amount of olefin which can be sorbed on the surface of the sample was $11 \cdot 10^{20}$ molecules C_3H_6/g and $8.5 \cdot 10^{20}$ molecules C_4H_8/g. If we consider the density of oligomers to be

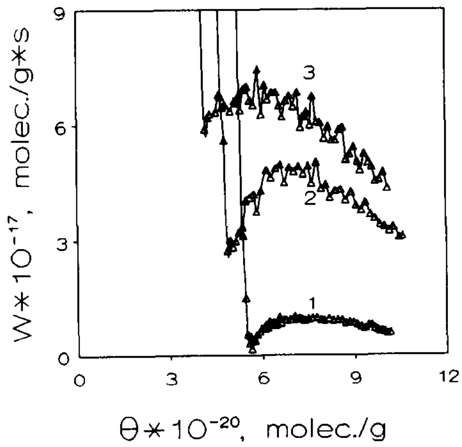


Fig. 1. Variation of adsorption rate W as a function of ethylene coverage Θ for H-NaZSM-5(45), $SiO_2/Al_2O_3 = 45$, decationation degree: 1 – 14%H; 2 – 50%H; 3 – 68%H.

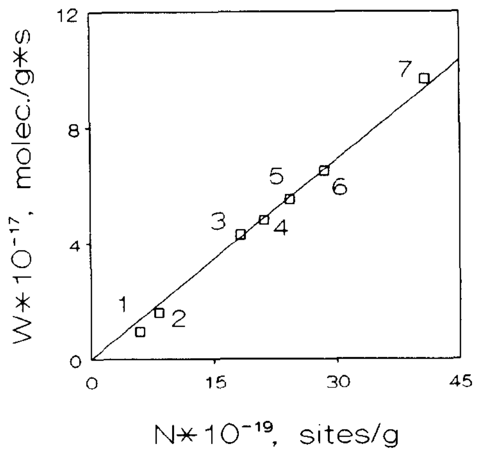


Fig. 2. Variation of adsorption rate in maximum W as a function of number of acid sites N for H-NaZSM-5. 1 – 14%H; 2 – 20%H; 3 – 43%H; 4 – 50%H; 5 – 58%H; 6 – 68%H; 7 – 100%H.

equal to the value of 0.8 g/cm^3 then the total volume of adsorbed hydrocarbons is 0.096 cm^3/g and 0.099 cm^3/g for propene and butene. These estimations are very close to the known free volume of the lattice of ZSM-5 type zeolite which is equal to the value of 0.1 cm^3/g. Therefore we can conclude that the progress of the reaction of oligomerization is limited by blocking of the internal volume of the lattice and the drop of the rate of ethylene adsorption is caused by the same reason.

The gradual increase of oligomerization rate of C_2H_4 (Fig. 1) can be explained if we consider that the reaction of ethylene oligomerization is a sequence of reactions which include a slow step of active surface species formation followed by fast process of oligomer chain growth. The nature of the active surface species is unknown but we can speculate that the slow step of the reaction includes either activation of ethylene molecules $C_2H_{4(surf)} \rightarrow C_2H_4^*$ or formation of C_4 species, which are more reactive than C_2 one.

It is interesting that the rate of ethylene oligomerization in maximum is proportional to the number of acid sites measured by ammonia adsorption or calculated from the sodium content assuming that removal of one Na atom produces one acid site (Fig. 2). This linear correlation suggests that a specific activity of an active centre remains constant and does not depend upon the decationation degree. It means that the reaction of ethylene oligomerization takes place on an isolated centre, at least for the samples studied. As far as decationation leads to the formation of Brønsted acid sites and at low decationation degree one can not expect any dealumination of zeolite framework producing extra-framework species it is the isolated structural Brønsted acid centres which are responsible for the oligomerization reaction of ethylene.

3.2. Temperature programmed desorption studies

It was shown that complex mixture of C_2 C_8 hydrocarbons evolved under TPD condition from the surface of zeolites with preadsorbed C_2H_4, the product composition depending on zeolite framework type [6].

The desorption of the hydrocarbons from the surface of HZSM-5 starts at about 130°C. One peak of desorption is observed for all the products excluding butanes which possess two defined maxima at 140–150 and 210–220°C (Fig. 3a). The rate of the hydrocarbon evolution reaches the maximum value of 230–250°C. The principal products are C_3–C_6 alkenes; small amount of alkanes, higher hydrocarbons and trace amount of methane and ethane are formed. As it was shown by us the increase of Si/Al ratio from 19 to 74 does not influence the position of the TPD curves and decreases a value of alkane/alkene ratio [6]. A similar effect is observed for H-NaZSM-5 with different degree of decationation. The increase of sodium content lead to the decline of low temperature peak of C_4H_{10} and alkane/alkene ratio. Parallel to these changes the peaks of unsaturated hydrocarbons become sharper (Fig. 3b). The disappearance of the saturated hydrocarbons from the TPD products means that no hydrogen transfer and creaking reactions occur on ZSM-5 with high SiO_2/Al_2O_3 ratio and low decationation degree under TPD condition studied.

More pronounced effect of SiO_2/Al_2O_3 ratio on product of TPD is observed for H-faujasite type zeolites (Fig. 4). Only paraffins (2-methylpro-

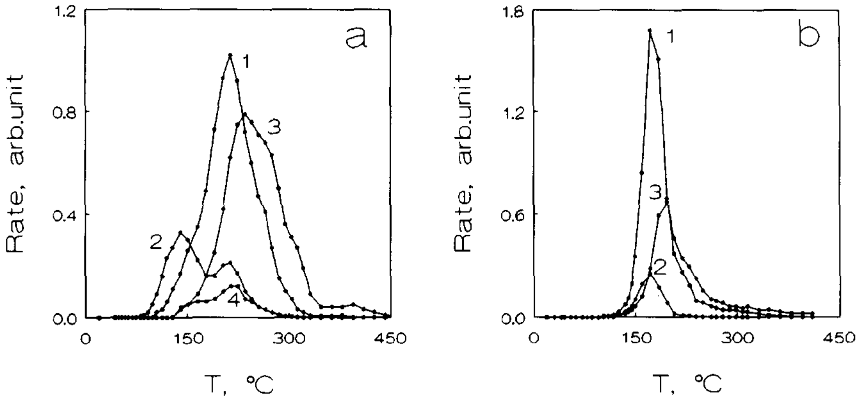


Fig. 3. Variation in the rate of the evolution of (1) – butenes, (2) – butanes, (3) – propene, (4) – propane under TPD condition as a function of temperature for H-NaZSM-5(45): (a) – 100%H, $\theta = 8.9 \cdot 10^{20}$ molecules C_2H_4/g; (b) – 14%H, $\theta = 5$. $\theta = 8.5 \cdot 10^{20}$ molecules C_2H_4/g.

pane and CH_4) are formed under TPD condition on HY ($SiO_2/Al_2O_3 = 4.6$–17). The increase of SiO_2/Al_2O_3 from 4.6 to 190 lead to complete disappearance of paraffins from TPD products. Similar to ZSM-5 type zeolites a sharp peak of olefin evolution arises at 140°C on HY-63 (Fig. 4b). This peak replaces one of 2-methylpropane observed on HY-17 (Fig. 4a). As for HZSM-5 a downfall of saturated hydrocarbon formation for HY with high Si/Al ratio corresponds to the diminished activity in reaction of hydrogen redistribution. The same dependence of activity of paraffin formation upon Si/Al ratio is observed for H-mordenite type zeolites with $SiO_2/Al_2O_3 = 10$–60.

The conducted studies show that for all zeolites studied a decrease of paraffin/olefin ratio occur with increase Si/Al ratio. The observed dependence of activity in reaction of saturated hydrocarbon formation (hydrogen redistribution) upon SiO_2/Al_2O_3 ratio on ZSM-5, HM and HY can be attributed to i) difference in zeolite lattice; ii) different sodium content leading to inhomogeneous distribution of acidity of active centres; iii) formation of extra-framework Al-containing species or iv) cooperative effect of acid sites.

It seems to be very unlikely that the structure of zeolite lattice (or changes of the structure) are the reason for observed activity variation because the same dependence is typical for zeolites with different framework and for H-NaZSM-5 containing various amount of sodium.

Existence of a few types of acid sites with different acidity (weak, intermediate, strong) can

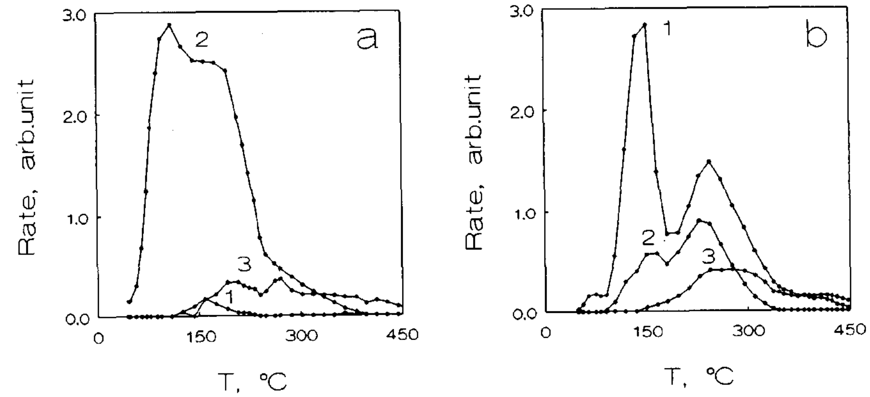


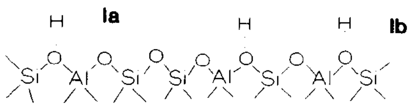
Fig. 4. Variation in the rate of the evolution of (1) – butenes, (2) – butanes, (3) – propene, under TPD condition as a function of temperature for (a) – HY ($SiO_2/Al_2O_3 = 17$), (b) – HY ($SiO_2/Al_2O_3 = 63$), $\theta = 1.8 \cdot 10^{20}$ molecules C_2H_4/g.

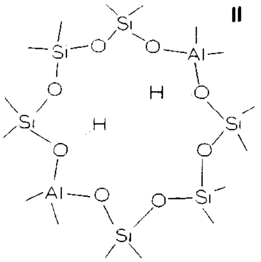
explain catalytic behaviour only for HM and HY. It is known that removal of aluminium atom from lattice alters the number of acid centres such as $H_n^+[(Si(OAl)_n(OSi)_{4-n}]^{n-m}mAl^{3+}$ (n = 0–4) which are known to possess different acidity. These centres were proposed to exist in a framework of the zeolites [7], the number depending upon the value of the Si/Al ratio [8]. Change of the heat of ammonia adsorption observed for partially decationated mordenites and faujasites [9] also evidences that Si/Al ratio and decationation degree influence the strength and number of acid cites. In the case of H-NaZSM-5 type zeolite that is not true. No changes of the heat of ammonia adsorption was observed for HZSM-5 with different Si/Al ratio or for partially decationated H-NaZSM-5 [9] corresponding to the uniform strength of acid centres. It means that it is not a change of acidity which determines the dependence of activity upon SiO_2/Al_2O_3 ratio or decationation degree in the reaction of hydrogen redistribution.

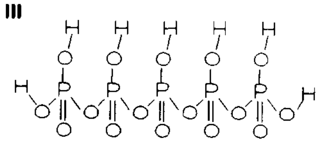
Formation of saturated hydrocarbons also can not be connected with an existence of extra-framework species which could facilitate the cracking and hydrogen transfer reactions [10]. High vacuum treatment employed apparently results in some dealumination of zeolite lattice in the case of HY and HM leading to the formation of extra-framework particles but one can hardly expect this in the case of HZSM-5 and H-NaZSM-5 which are very stable under temperature treatment. Moreover a special experiment with HZSM-5 ($SiO_2/Al_2O_3 = 45$) which was leached with NaOH solution to remove extra-framework species followed by decationation shows that this treatment produces only minor changes in TPD pattern. Therefore we can conclude that existence of extra-framework active sites can influence a course of reaction but can not account for the hydrogen transfer reaction on all samples studied.

An alternative explanation is that reaction of hydrogen redistribution requires at least binary active centre. In this case one could expect that the samples which possess a considerable number of such centres would be more active in the reaction compared with those which have only isolated one. Assuming random distribution of Al atoms in the framework (which corresponds to the most of NMR studies [11]) it is obvious that at high Si/Al ratio isolated acid centres (Ia, figure below) prevail and the decrease of Si/Al ratio result in gradual conversion of individual separate acid centres to more dense located group (Ib) which can act as a multi-point adsorption centre. Because of the unique structure of zeolite lattice at intermediate values of Si/Al ratio even statistically isolated acid centres $H^+[Si(OAl)(OSi)_3]^-$ can act as a binary centre when they are located on the opposite sides of a channel of the zeolite framework (II).

The gradual decationation of the zeolite samples with relatively low Si/Al ratio appears to have the same effect on the density of acid centres, this influence being structure-independent. The experimental data given above are consistent with the assumption that reaction of hydrogen transfer requires these type of active centres. A substantial yield of saturated hydrocarbons are observed for all sample of zeolites with low Si/Al ratio and







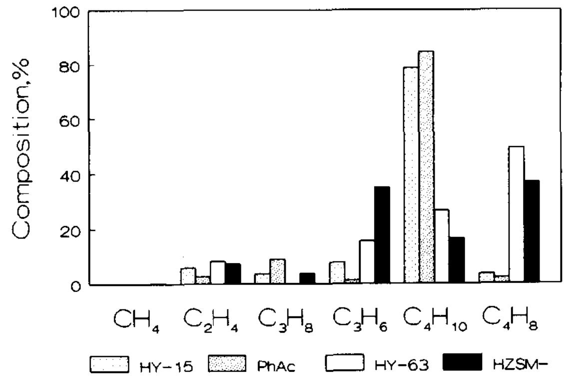


Fig. 5. Composition of C_1–C_4 hydrocarbons obtained under TPD condition on zeolites HY-17 ($SiO_2/Al_2O_3=17$), HY-63 ($SiO_2/Al_2O_3=63$), HZSM-5 ($SiO_2/Al_2O_3=45$) and over 85% P_2O_5–H_2O (PhAc, 190°C, 3 h, 0.16 MPa C_2H_4).

high decationation degree (Figs. 3a, 4a). A reversed picture are observed for the samples with high Si/Al ratio or with low degree of decationation (Figs. 3b, 4b) and only olefins are removed under TPD condition from zeolites with the highest Si/Al ratio ($SiO_2/Al_2O_3=136$ for HZSM-5, 96 for HY).

If it is the density of acid centres that determines the activity in reaction of hydrogen transfer than analogy in catalytic behaviour must exist between the zeolites and systems which possess a similar structure. It is known that phosphoric acid forms polyphosphoric chains at high P_2O_5 content which resemble zeolites in respect of density of the centres (III).

A comparison of ethylene conversion on homogeneous phosphoric acid (74–85% P_2O_5) with that on zeolites showed that there are similarities for these two systems. Ethylene conversion occurs at 170–250°C and the principal products observed are saturated branched hydrocarbons C_3–C_8 with minor amount of olefins (Fig. 5).

Orthophosphoric acid H_3PO_4 (72.4% P_2O_5–H_2O) has no activity. Conversion of ethylene increases with increase of P_2O_5 content, the product composition being very similar to that obtained over HY with low Si/Al ratio (Fig. 5). The main hydrocarbon of C_4 fraction is 2-methylpropane (more than 90%) in both cases. An isomeric composition of hexanes C_6H_{14} obtained is also very similar. Relative amounts of n-hexane, 2-methylpentane, 3-methylpentane 2,3- and 2,2-dimethylbutane are 1:48:33:2:16 and 0:49:22:0:29 for 85% P_2O_5 – H_2O (10^5 Pa C_2H_4, 190°C, 3h) and HY ($SiO_2/Al_2O_3=30$, initial $\theta_{C2H4}=1.1\cdot10^{20}$ molecules C_2H_4/g, TPD from 170 to 180°C) correspondingly.

NMR ^{31}P show that inactive orthophosphoric acid contains predominantly mono specie H_3PO_4 ($\delta\approx0.0$ ppm) while the most active system (83.2% P_2O_5) contains complex mixture of polyforms ($\delta\approx$ 14.75, 15.06, 31.01 ppm) and an activity in the reaction was found to be proportional to the content of polyphosphoric acids.

The similarity of product composition observed for polyphosphoric acid and zeolites with low Si/Al ratio indicate that mechanism of saturated hydrocarbon formation can be also similar for these two systems. Polyphosphoric acids (III) imitate zeolites with dense location of acid groups (Ib, II) whereas zeolites which possess isolated ones (high Si/Al, low decationation degree) have no or little activity in the reaction of hydrogen transfer and therefore produce only or predominantly olefins (Fig. 5). We can assume that reaction of hydrogen redistribution involves multiple Brønsted centres in the case of P_2O_5–H_2O as far as only Brønsted acidity are characteristic for phosphoric acid. For zeolites the active centre can include not only Brønsted but also Lewis acid site (located in the lattice or on extra framework species) but the main factor which determines activity in the reaction seems to be the density of acid centres.

4. Conclusion

Reaction of ethylene oligomerisation on hydrogen forms of mordenite, faujasite and ZSM-5 take place on the isolated acid centres. Reaction of hydrogen transfer which lead to paraffin formation involves binary acid centre.

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