SEQUENCE OF STAGES IN THE AROMATIZATION OF ETHYLENE ON HIGH-SILICON ZEOLITES

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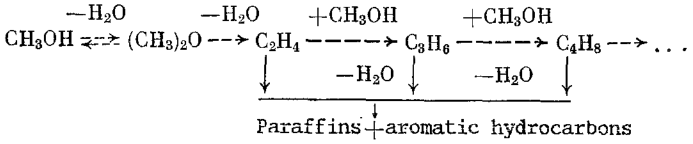
Based on a large number of data [1], the following scheme has been proposed for the synthesis of higher hydrocarbons from methanol on high-silicon zeolites (HSZ):



Several probable schemes of the mechanism of the first stage of the transformation — dehydration of ethers to olefins — have been described [2].

Since the sequence of the transformation of compounds the CH_3X type is not dependent on the nature of X (X = OH, Cl) [3], it should be expected that the transformation of olefins should determine the rate and selectivity of the process as a whole. It has been hypothesized [4, 5] that oligomerization is the first transformation of C_2–C_4 olefins on HSZ. The oligomers can then be isomerized, split into the initial olefins, and also transformed into aromatic and paraffin hydrocarbons, probably through aliphatic dienes [5, 6].

It has been hypothesized [3] that ethylene is aromatized with the lowest rate. In this respect, this reaction is of the greatest interest.

EXPERIMENTAL

Decationized high-silicon zeolite (HSZ) of the composition $0.12\ Na_2O \cdot Al_2O_3 \cdot 39SiO_2$ with a molar ratio of $SiO_2/Al_2O_3 = 39$, synthesized in the presence of tetrapropylammonium hydroxide according to the method in [7], was used as the catalyst. The catalyst was first calcined in a current of O_2 at 500-520°C and then decationized with a 0.1 N solution of $NH_4Cl + NH_4OH$. The fraction of 0.25-0.5 mm grains was formed from the powder obtained with no binder.

The rate and selectivity of transformation of ethylene were studied in a flow-circulation setup at 300-535°C with a 0.14-5.9 sec contact time. The contact time (τ) was calculated as the ratio of the volume of the catalyst (in cm^3/sec) to the feed rate of the initial gas mixture (in cm^3/sec) containing from 1 to 50 vol. % ethylene, and the remainder was helium. The composition of the reaction mixture at the inlet and outlet of the circulation circuit was analyzed by GLC with columns packed with γ-Al_2O_3 (500 m^2/g surface area) and polyphenyl ether on an S-22 carrier. The selectivity of the reaction for the i-th hydrocarbon (S_i) was calculated with the equation

$$S_i = \frac{W_i n_i}{2W_{\text{reagent}}} \cdot 100, \text{ mole } \%$$

where W_i is the rate of accumulation of the i-th hydrocarbon; W_{reagent} is the rate of consumption of ethylene in moles per unit of time per unit of weight of the catalyst; n_i is the number of carbon atoms in the molecule of the i-th hydrocarbon. The equilibrium constants of the reactions were estimated with the data in [8].

DISCUSSION OF RESULTS

An increase in τ at 370°C resulted in a rapid decrease in the yield of C_3–C_4 olefins with a simultaneous increase in the yield of paraffins and aromatic hydrocarbons.

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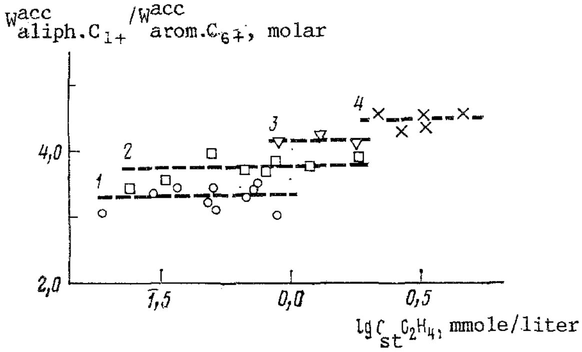

Fig. 1. Dependence of the ratio of the rates of accumulation of the sum of aliphatic and the sum of aromatic hydrocarbons in transformation of ethylene on HSZ on the steady-state concentration of ethylene, 370°C. Contact time, sec: 1) 5.9 ± 0.5; 2) 1.16 ± 0.03; 3) 0.42 ± 0.02; 4) 0.14 ± 0.01.

The fraction of olefins obtained under these conditions of transformation of ethylene (370°C, τ = 0.14-5.9 sec) primarily consisted of propylene. The concentration of C_4 and higher olefins in this fraction was small, even with the lowest contact time studied, and rapidly decreased to zero with an increase in τ. As a consequence, the formation of C_3–C_4 olefins is the first, fastest stage of transformation of ethylene which probably includes its oligomerization according to an equation of type (1) and splitting of the oligomers formed according to equations of type (2)-(5)

$$nC_2H_4 \rightleftarrows C_{2n}H_{4n} \tag{1}$$

$$C_6H_{12} \rightleftarrows 2C_3H_6 \tag{2}$$

$$C_8H_{16} \rightleftarrows 2C_4H_8 \tag{3}$$

$$C_8H_{16} \rightleftarrows C_3H_6 + C_5H_{10} \tag{4}$$

$$C_5H_{10} \rightleftarrows C_2H_4 + C_3H_6 \tag{5}$$

The analysis of oligomerization based on the data in [8] actually showed that it has no limitations with respect to the position of equilibrium for any degree of oligomerization for the reaction temperature studied (643°K). At the same time, splitting of the oligomers of ethylene (particularly C_8 and higher) to olefins of a higher molecular weight than ethylene [Eqs. (2)-(5)] is also thermodynamically favorable above 500°K.

As a consequence, with respect to thermodynamics, the general scheme of the first, fastest stage of transformation of ethylene can be represented by the sequence

$$C_2H_4 \rightleftarrows C_4H_8 \rightleftarrows \text{oligomers} \rightleftarrows C_3H_6 \tag{6}$$

An increase in the contact time results in the transformation of the oligomers of olefins into aromatic and paraffin hydrocarbons. The requirement of balance with respect to hydrogen and carbon in the transformation of olefins into monocyclic aromatic hydrocarbons and paraffins permits writing a general empirical equation for the second stage of transformation which is valid for any special cases of these types of hydrocarbons

$$\left(\frac{3p+ml+6}{n}\right)C_nH_{2n} = C_6H_{6-m}(C_lH_{2l+1}) + 3C_pH_{2p+2} \tag{7}$$

where n = 2, 3, 4, etc.; m = 0, 1, 2, 3, 4, 5; l = 1, 2, 3, etc.; p = 1, 2, 3, etc.

Equation (7) shows that the molar ratio of paraffin and aromatic products of the second stage of the transformation should always be equal to three. As Fig. 1 shows, the experimentally observed ratio of the rates of accumulation of aliphatic and aromatic hydrocarbons in the reaction mixture, constant for each τ, rapidly increases with an increase in τ, approaching the stoichiometric value with an increase in the contact time. The apparent difference from the expected stoichiometry observed with small values of τ should be attributed to the fact that the rate of accumulation of the sum of olefins is included in the value of the rate of accumulation of the sum of aliphatic C_{1+} hydrocarbons. An increase in the contact time results in a rapid decrease in the rate of accumulation of these products. For this reason, the ratio of the rates of accumulation of aliphatic and aromatic hydrocarbons in the transformation of ethylene on HSZ actually approaches the stoichiometric value, equal to three, with the highest contact times of the reaction mixture with the catalyst (5.9 ± 0.5 sec.

In the 300-535°C range with the highest contact time, i.e., with τ = 5.9 ± 0.5 sec, both the character of the change in the rate of consumption of ethylene (Fig. 2a) and the accumula-

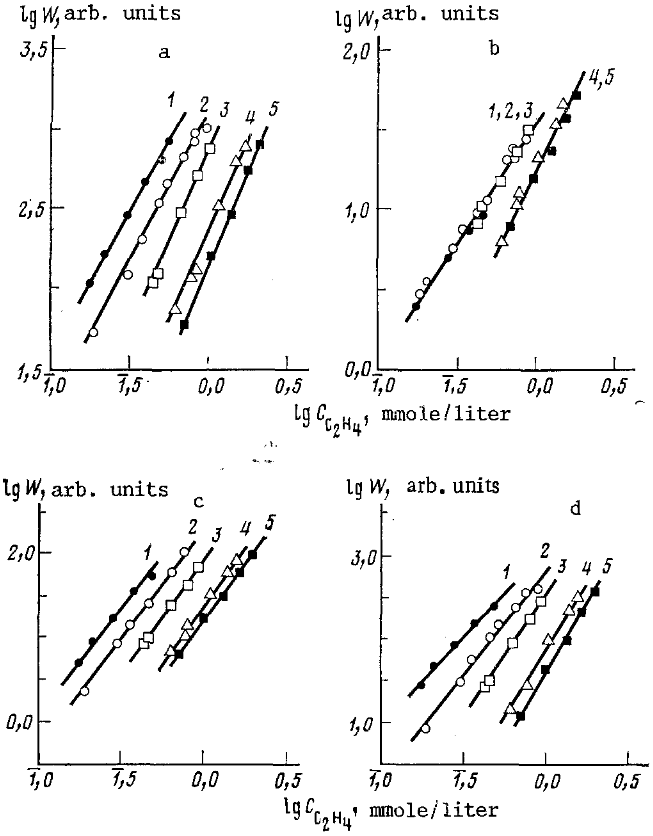

Fig. 2. Dependence of the rates of consumption of ethylene (a) and accumulation of products: propylene (b), aromatic C_6+ hydrocarbons (c), C_1+ paraffins (d), on HSZ on the steady-state concentration of ethylene in the reaction mixture with a contact time of 5.9 ± 0.5 sec and a reaction temperature of: 1) 340°C; 2) 370°C; 3) 440°C; 4) 495°C; 5) 535°C.

tion of the fractions of paraffin and aromatic products of the transformation of ethylene (see Fig. 2c, d) remain almost constant and can be described by a second-order equation with respect to the concentration of ethylene with good approximation.

At the same time, Fig. 2 shows that increasing the temperature from 340 to 535°C results in a decrease in both the rate constant of consumption of ethylene (Fig. 2a) and the rate constant of accumulation of the sum of aromatic (Fig. 2c) and the sum of paraffin hydrocarbons (see Fig. 2d) by more than one order of magnitude. The rate constant of accumulation of propylene decreases only insignificantly (by 1.5-2.6 times, see Fig. 2b).

A change in the temperature in the 300-500°C range does not affect the stoichiometry of the process. Since the character of the kinetic dependences of the accumulation of the products also does not change significantly when the temperature is varied (see Fig. 2), it can be hypothesized that no changes are observed in the sequence of the stages of transformation of ethylene in the temperature range studied.

At the same time, the selectivity of the process changes significantly in the 300-535°C range: an increase in the temperature results in a rapid decrease in the fraction of C_3 and higher paraffins and simultaneously to an increase in the yield of C_1–C_2 paraffins, i.e., to a rapid decrease in the average number of C atoms in the paraffin molecule (Table 1). Since the molar stoichiometry of the process remains unchanged ($W_{C_1+paraf}^{acc.}/W_{aromC_6+}^{acc.} = 3$), and the average number of C atoms in the molecules of the aromatic hydrocarbons only changes insignificantly (cf. Table 1), the increase in the selectivity of the reaction with respect to the sum of aromatic hydrocarbons observed with an increase in the temperature is the consequence of the changes in the selectivity for paraffins described above.

TABLE 1. Distribution (mole %) of the Final Products of Transformation of Ethylene on HSZ (SiO_2/Al_2O_3 = 39) for a Reaction Mixture with a Steady-State Concentration of Ethylene of 1.0 mmole/liter, Obtained with $\tau = 5.9 \pm 0.5$ sec and Different Temperatures

Product	340°	370°	440°	495°	535°
Methane	0,43	1,12	3,41	21,74	40,73
Ethane	3,77	5,47	11,02	22,03	20,19
Propane	37,67	39,63	43,86	26,86	12,56
Isobutane	17,62	17,50	10,05	2,29	0,40
n-Butane	8,24	6,14	3,73	0,99	0,06
Isopentane	1,50	1,81	2,41	0,40	0,28
n-Pentane	4,04	3,61	1,21	0,35	0,18
Aliph. C_{6+}	1,22	1,20	0,67	0,43	0,30
Benzene	0,92	1,30	2,41	6,27	8,93
Toluene	4,23	5,67	8,94	12,51	11,51
(m+p)-Xylenes	3,36	4,78	5,88	3,84	3,85
o-Xylene	0,73	1,21	1,35	1,02	1,04
(m+p)-Ethyltoluenes	4,64	4,60	1,15	0,33	0,28
Mesitylene	0,53	0,47	0,13	0,08	0,05
Pseudocumene	0,29	0,45	0,55	0,39	0,12
Arom. C_{10+}	10,82	5,04	3,24	0,48	0,04
Average number of C atoms:					
In paraffins	3,48	3,40	3,07	2,21	1,67
In aromatic hydrocarbons	8,82	8,31	7,77	7,07	6,92

The decrease in the selectivity for the total C_5 and higher paraffins could probably be related to parallel cracking of these hydrocarbons at high temperatures according to equations of type (8)

$$C_5H_{12} \rightleftarrows C_2H_6 + C_3H_6$$
$$C_6H_{14} \rightleftarrows C_3H_8 + C_3H_6 \text{ etc.} \qquad (8)$$

The occurrence of these reactions, which apparently does not affect the overall stoichiometry of the synthesis, should result in an increase in the selectivity of the process for lower olefins (propylene, for example) and lower paraffins [ethane, for example; cf. Eq. (8)], which is actually observed (see Table 1). However, correlating the decrease in the selectivity of the process for butanes and especially for propane observed with an increase in the temperature with the parallel cracking of these hydrocarbons according to equations of type (8) should not be considered very probable. The degree of transformation of n-butane on HSZ at 500°C with a contact time 5 times higher than in the present study does not exceed 10-12%, and the degree of transformation of propane in these conditions is only 1.4% [9]. The redistribution of the selectivities in the group of paraffin hydrocarbons with an increase in the temperature of the reaction found in the present study thus cannot be explained by the side reaction of cracking of paraffins alone.

The described redistribution of the selectivities in the group of paraffins (see Table 1) should probably be correlated with a change in the length of the carbon chain of the hydrocarbon molecule where paraffin products are formed in its transformation. Cracking of higher olefins [Eqs. (9)-(13)] to alkadiene and paraffin could be such a reaction if it takes place similar to cracking of paraffins:

$$C_5H_{10} \rightleftarrows C_4H_6 + CH_4 \qquad (9)$$

$$C_6H_{12} \rightleftarrows C_4H_6 + C_2H_6 \qquad (10)$$

$$C_7H_{14} \rightleftarrows C_4H_6 + C_3H_8 \qquad (11)$$

$$C_8H_{16} \rightleftarrows C_4H_6 + C_4H_{10} \qquad (12)$$

$$C_8H_{16} \rightleftarrows C_5H_8 + C_3H_8 \qquad (13)$$

The alkadienes simultaneously formed with paraffins in the aromatization of olefins are highly reactive products whose subsequent transformation can result in [5, 6] aromatic hydrocarbons through intermediate cycloolefins.

The analysis of the thermodynamic characteristics of reactions of type (9)-(13) based on the data in [8] shows that cracking of olefin oligomers to paraffin and diene is not thermodynamically limited for 300°C and above (i.e., for the temperature range investigated in the present study). However, the maximum probable chain length of the olefin oligomer rapidly decreases with an increase in the temperature, and above 450°C, the formation of C_8 and higher oligomers is thermodynamically significantly limited. Since the minimum chain length of alkadiene is four carbon atoms, an increase in the temperature should result in a decrease in the length of the carbon chain in the paraffin formed in the transformation of olefin oligomers according to the path examined [equations of type (9)-(13)], since the maximum chain length of the oligomer decreases.

The reactions of redistribution of hydrogen in olefins should probably be close to the well-known reactions of catalytic cracking of paraffins in nature and should take place with the participation of similar sites in catalysts with an acid–base action. In this case, the process of synthesis of aromatic hydrocarbons from olefins (and consequently from type CH_3X compounds) on zeolite catalysts on the whole can be represented as a sequence of the same type of reactions: alkylation and cracking.

CONCLUSIONS

Based on a study of the rate and selectivity of the reaction of aromatization of ethylene on high-silicon zeolite, the agreement of the experimentally observed distribution of the groups of products expected from the stoichiometry of the reaction was established for the temperature range studied.

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