STUDY OF THE CATALYTIC PROPERTIES OF PENTASIL-CONTAINING COMPOSITES IN TRANSFORMATION OF HYDROCARBONS.

4.* FORMATION OF PRODUCTS OF CONDENSATION DURING OLIGOMERIZATION AND AROMATIZATION OF ETHYLENE ON THE PENTASIL-ALUMINUM OXIDE SYSTEM

V.I. Yakerson, V.D. Nissenbaum, T.V. Vasina,
L.I. Lafer, S.A. Isaev, E.L. Denisova,
Zh.L. Dykh, and O.V. Bragin

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The process of formation of products of condensation (PC) during oligomerization (280°C) and aromatization (500°C) of ethylene in the presence of H-pentasil (HTsVM)-γ-Al_2O_3 was studied by IR spectroscopy, DTA, DTG, and chemical analysis. The mutual effect of the components of the composite on the formation of PC in aromatization of C_2H_4 was detected. PC are formed with the participation of acid sites both inside the channels and on the outer surface of the zeolite. Three types of PC were found: linear polyene structures with C/H = 0.8 (oligomerization), aromatic structures with C/H = 1.5 (aromatization on HTsVM), and cross-linked polyene structures with C/H = 2.45 (aromatization on Al_2O_3). The composition and structure of the PC formed on HTsVM during transformations of ethylene are a function of the molecular-sieve properties of the pentasil and the experimental conditions.

The formation of coke during heterogeneous catalytic reactions results in a reduction in the running time of the catalysts and a decrease in the activity and selectivity [2, 3]. Coke formation on zeolite-containing catalysts is examined in [4-6]. In some cases, controlled coking is a method of increasing the para selectivity in preparation of alkylaromatic hydrocarbons on zeolites [7]. It was shown in [8] that the H-pentasil-γ-Al_2O_3 catalytic system exhibits high activity and selectivity in the 350-500°C temperature range in aromatization of ethylene; oligomerization of ethylene takes place below 350°C. The process of coking of the HTsVM-γ-Al_2O_3 composite was investigated in the present study by the methods of IR spectroscopy, thermal, and chemical analyses combined with data on the catalytic activity in reactions of transformation of C_2H_4.

EXPERIMENTAL

Samples with different HTsVM-γ-Al_2O_3 ratios were selected for the study [8]; the final temperature of heat treatment of the samples before the experiments was 550°C. The experiments on oligomerization and aromatization of C_2H_4 were conducted in a flow-type setup at 280 and 500°C; the volume feed rate of C_2H_4 was 120 h^{-1}, and the duration of the experiments was 4-25 h. The IR spectra were recorded on a Specord M-80 instrument, and KBr pellets (7 mg of sample per 500 mg of KBr) or pellets with no binder in the form of self-molded pellets in a vacuum cuvette were used. The thermal analysis was conducted by TG-DTG-DTA methods on a Q-1000 thermal analyzer (Hungary); the weighed portion of sample was 50-100 mg, and α-Al_2O_3 was used as the standard; heating was conducted in air up to 1000°C with linear elevation of the temperature (10 K/min). The chemical analysis of the samples for the concentration of carbon and hydrogen was conducted by the method in [9].

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*For previous communication, see [1].

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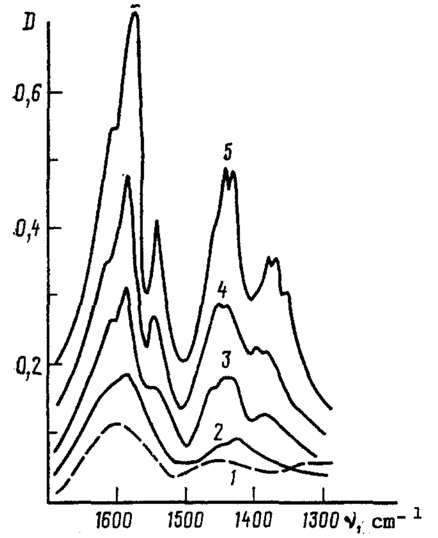

Fig. 1

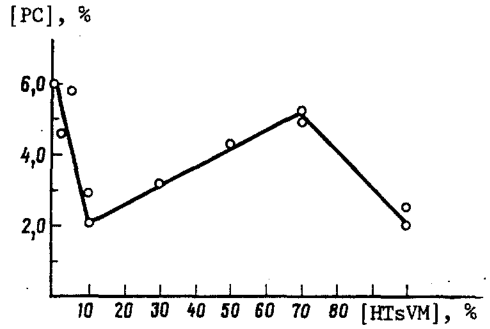

Fig. 2

Fig. 1. IR spectrum of HTsVM-Al_2O_3 after aromatization of C_2H_4 at 500°C for 15 h with [HTsVM]: *1*) 0; *2*) 10; *3*) 30; *4*) 70; *5*) 100.

Fig. 2. Dependence of the amount of PC on HTsVM-Al_2O_3 formed in transformations of C_2H_4 (500°C, 4 h) on the composition of the composite.

RESULTS AND DISCUSSION

A series of samples of HTsVM-Al_2O_3 with a concentration of 0.5, 2, 5, 10, 30, 50, 70, 95% HTsVM was prepared; the individual components of HTsVM and γ-Al_2O_3 undergoing the same treatment as the composite were also investigated.

The IR spectra of the samples in the 1700-1300 cm^{-1} region after conducting aromatization of C_2H_4 for 15 h are shown in Fig. 1. The following are the most characteristic absorption bands (a.b.): 2930, 2860, 1616, 1590, 1542, 1465, 1448, 1440, 1428, 1405, 1380, 1364, 1350 cm^{-1}. The intensity of all a.b. increases with an increase in [HTsVM]. These a.b. do not disappear from the spectrum after blowing an inert gas through the sample, and they belong to products of condensation (PC). A similar spectrum was observed in [10] in transformations of C_2H_4 on HZSM at 770°C after 19 h. The spectral data indicate the presence of aromatic structures and CH_2 groups. The 1590 cm^{-1} band, as well as the accompanying a.b. at 1450-1350 cm^{-1}, should be assigned to strongly adsorbed precursors of PC of the allyl carbocation type, whose formation requires a series of stages, including transfer of a proton from the acid OH groups (3610 cm^{-1} a.b.) to the molecule of the hydrocarbon (type I PC). Actually, even in the case of partially coked samples (2-3% PC), the 3610 cm^{-1} a.b. is totally absent in the IR spectrum, and pyridine does not form PyH^+. Since the OH groups are located both on the outer surface and in the bulk of the zeolite, the absence of the 3610 cm^{-1} a.b. in the spectrum indicates that coking takes place in the channels and on the outer surface of the zeolite, in agreement with [11]. Bands corresponding to OH groups appear in the IR spectrum only after treatment with air at 550°C. The optical density of the a.b. characterizing PC (type I) increases practically from zero with an increase in the concentration of HTsVM in the composite, which indicates that type I PC appear on HTsVM and are absent on Al_2O_3. In the case of Al_2O_3, only a broad band at 1600 cm^{-1} characteristic of polyene structures (type II) is found. Further information on the nature of the PC on HTsVM and on Al_2O_3 was obtained based on methods of thermal and chemical analyses. PC are removed in two stages on samples of HTsVM-Al_2O_3 coked during aromatization of C_2H_4: exothermic effects with $T_{max} \approx 510$-530°C and $T_{max} \approx 570$-600°C, and both exothermic effects are accompanied by loss of weight.

The chemical analysis showed that CO_2 appears in the products of combustion at temperatures of 500°C and consequently, the exothermic effects at $T_{max} \geq 510$°C correspond to combustion of PC. It was found that an exothermic effect with $T_{max} \approx 510$°C is characteristic of PC formed on Al_2O_3, versus at 570°C on HTsVM. Since in a first approximation PC are formed independently on HTsVM and Al_2O_3 and knowing the amount of coke individually on Al_2O_3

TABLE 1. Amount of PC on HTsVM-Al_2O_3 based on TG Data (C_2H_4; 500°C, 15 h)

HTsVM	PC on HTsVM	Concentration of Al_2O_3	PC on Al_2O_3	Amt. of PC on composite	
				calculated	experimental
			%		
0	0	100	13,2	–	13,2
10	0,8	90	11,9	12.7	13,1
30	2,3	70	9.2	11,5	10,6
70	5,3	30	4,0	9,3	10,55
100	7.7	0	0	–	7.7

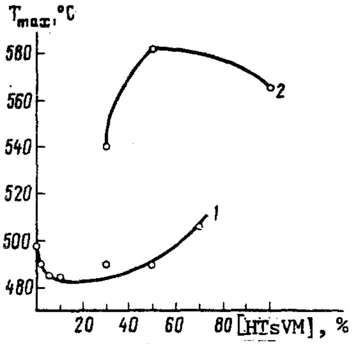

Fig. 3

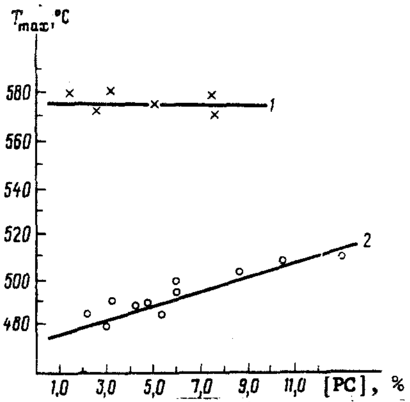

Fig. 4

Fig. 3. Dependence of T_{max} of combustion of PC on Al_2O_3 (*1*) and HTsVM (*2*) on the composition of the HTsVM-Al_2O_3 composite (500°C, 4 h).

Fig. 4. Dependence of T_{max} of combustion of PC on HTsVM (*1*) and Al_2O_3 (*2*) on the concentration of products of condensation.

and HTsVM (T_{max} = 510 and 570°C, respectively), it is possible to calculate the amount of PC on the composite and compare the calculated and experimental amount of PC (Table 1). The calculation assumes the formation of different types of PC individually on HTsVM and Al_2O_3. The total amount of PC on the composite is the sum of the amounts of coke on each component in the case of coked samples (500°C, 15 h). The results reported in Table 1 demonstrate the overall satisfactory agreement of the calculated and experimental data. However, the effect of the components on each other is observed, which is clearly manifested in the incompletely coked sample (Fig. 2).

Addition of 10% HTsVM to Al_2O_3 causes a sharp decrease in the amount of PC in aromatization of C_2H_4 and an increase in the catalytic activity [12], while addition of up to 30% Al_2O_3 to HTsVM on the contrary causes an increase in the amount of PC. Figure 2 actually demonstrates the first period of formation of PC when the effect of the components is manifested, and Table 1 illustrates the second period, the period of saturation, when this effect is masked. The change in T_{max} illustrates the effect of the mutual influence (Fig. 3): on addition of up to 10% HTsVM in Al_2O_3, the temperature of combustion of PC on Al_2O_3 (type II) decreases from 500°C to 480°C, and on addition of up to 30% Al_2O_3 to HTsVM, the temperature of combustion of PC on HTsVM (type I) increases from 565 to 580°C. The amount of PC formed on Al_2O_3 is greater than on HTsVM (see Table 1 and Fig. 2); however, PC burns more easily on Al_2O_3 than on the zeolite (Fig. 3). It is possible to hypothesize that HTsVM inhibits the formation of polyene structures in PC, while Al_2O_3 promotes the formation of aromatic structures in PC. T_{max} of combustion of PC on Al_2O_3 is a linear function of the amount of PC formed (Fig. 4); this indicates an increase in the C/H ratio as PC accumulate, since the structures joined by hydrogen burn with more difficulty, causing an increase in T_{max} [2, 3]. For type I PC, T_{max} virtually does not change (570 ± 5°C) (Fig. 4) outside of the dependence on the coking time (4-25 h), which indicates the constancy of the C/H ratio. (This conclusion is confirmed by the result of the chemical analysis.) As a consequence,

TABLE 2. Catalytic Activity and Carbonization of HTsVM-Al_2O_3 in Oligomerization of C_2H_4 (280°C, 4 h)

HTsVM, %	Conversion of C_2H_4 into liqlid hydrocarbons, %	T_{max}, C	Weight loss, %	HTsVM, %	Conversion of C_2H_4 into liquid hydrocarbons, %	T_{max}, C	Weight loss, %
100	40,0	480–490	5,7–6,0	10	0	*	1,7
70	22,5	490	5,8	5	0	*	2,4
50	24,0	470	4,9	2	0	*	2
30	6.0	490	2.8	0	0	*	1.75

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*Combustion in the 300-600°C temperature range.

TABLE 3. Catalytic Activity of HTsVM-Al_2O_3 in Aromatization of C_2H_4 (500°C, 4 h)

HTsVM/ %	X, %	Yield of liquid products, %						Yield of gases, %			
		AlH	ArH				ArH	CH_4	C_2H_4	C_2H_6	C_3H_8
			C_6	C_7	C_8	C_9+					
100	95	1	12	17	7	15	51	17	5	18	8
70	98	–	13	15	5	15	48	25	2	22	3
50	98	1	10	13	6	12	41	19	2	23	14
30	96	1	6	13	8	7	34	21	4	23	17
10	90	2	5	14	11	5	35	10	10	15	28
5	85	2	5	14	11	5	35	12	15	16	20
2	44	1	2	9	7	3	21	5	56	9	8
0*	16	–	1	4	6	3	14	1	84	1	0

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*Analysis after 1 h of the experiment.

type I PC have a constant composition, and they are not dehydrogenated with an increase in the coking time, as is observed for most catalysts [2, 3].

Coking is also observed in the case of occurrence of oligomerization of C_2H_4 at 280°C. The presence of an exothermic effect with T_{max} = 480 ± 10°C is a distinctive feature of such PC (type III), and its position is not a function of the composition of the composite; a monotonic increase in the amount of PC with an increase in the concentration of HTsVM is observed (Table 2). The IR data indicate the formation of polyene structures. The simultaneous intensification of coking and the catalytic activity (Table 2) with an increase in the concentration of HTsVM suggests that the formation of PC and oligomerization take place on both B and on L sites. According to [13], carbonization of dealuminated mordenite by the products of conversion of ethylene is determined by B sites. Additional information on the character of the coking processes was obtained by comparing the data from the chemical analysis and the TG data for a series of HTsVM-Al_2O_3 after a 15-h run at 500°C in the reaction of aromatization of C_2H_4. The values of [PC], %, and C/H (atomic) are reported below.

Sample	HTsVM	70% HTsVM	30% HTsVM	10% HTsVM	Al_2O_3
Data from chemical analysis	7,5	9,4	10.4	12,0	12.0
Thermogravimetry	7.7	9.6	10.6	13.1	13.2
C/H	1.5	1,9	2.3	2.4	2,5

The data indicate the good agreement of the results of the two independent methods, which simultaneously indicate higher coke deposition on Al_2O_3. In going from HTsVM to Al_2O_3, the C/H ratio increases from 1.5 to 2.5, i.e., dehydrogenation of PC takes place. Based also on the data from the IR spectroscopic study, it is possible to conclude that in conditions of aromatization of C_2H_4 at 500°C, type I PC are aromatic structures, while type II are apparently cross-linked dimeric and trimeric polyene structures comparatively impoverished in hydrogen. Type III PC formed in conditions of oligomerization of C_2H_4 have C/H of 0.8; the IR spectra of type III PC indicate the presence of double bonds; this could be a comparatively hydrogen-rich structure of the type of linear polyene with the formula C_nH_{n+2}, and 5 < n <

15. The constancy of T_{max} for type III PC means the constancy of C/H for all compositions of the composite. Passage from conditions of oligomerization (280°C) to aromatization (500°C) of C_2H_4 on HTsVM is accompanied by a change in the C/H ratio from 0.8 to 1.5, partial dehydrogenation, conversion of polyene structures into mononuclear aromatic structures, and an ~100°C increase in the temperature of combustion of PC.

Note that in aromatization of C_2H_4, the amount of PC increases with an increase in the concentration of Al_2O_3 (Table 1), and on the contrary, the amount of PC increases with an increase in the concentration of HTsVM in oligomerization of C_2H_4 (Table 2); in other words, formation of PC in these reactions, which takes place in different temperature conditions as a function of the composition of the composite, is antibatic in nature.

In aromatization of C_2H_4 on HTsVM (500°C), 2.5% PC is formed, 8% is formed after 8 h, 7.7% after 15 h, and 8% after 25 h. Thus, 8% PC with C/H of 1.5 corresponds to saturation (maximum coking).

Let us now consider which ratio of C/Al will correspond to total blockage of the active sites of the zeolite. We will use the basis for the calculation that linear phenylene rings located in the channels of the zeolite (number of rings ≤ 3) are contained in type I PC. Total saturation will correspond to 0.086 g of PC per 1 g of zeolite, which constitutes 3.4-$2.2 \cdot 10^{20}$ molecules per 1 g of zeolite. Since there are $5.5 \cdot 10^{20}$ aluminum ions per 1 g in zeolite with modulus M-35, we obtain ≈7.2 carbon atoms per 1 aluminum atom. It follows from this that: a) such carbon-containing structures can easily be located in the channels of the zeolite; b) not filling of the volume of the zeolite with PC but only blockage of active sites evidently takes place. According to [14], the number of active sites per unit cell (u.c.), divided by the number of Al atoms in the u.c. is <1, and in our concrete case is ~0.35; as a consequence, we are speaking of formation of PC with ~21 carbon atoms per active site. The mutual effect of the components in the Al_2O_3–HTsVM composite confirms the hypothesis in [8] from the point of view of coke formation that Al_2O_3 is not only a binder but also actively participates in the reactions of conversion of olefins.

Let us analyze how the catalytic activity of oligomerization and aromatization of ethylene and the process of coke formation are dependent on the composition of the HTsVM-Al_2O_3 composite. The data on the catalytic activity of HTsVM-Al_2O_3 at 500°C after 4 h of work are reported in Table 3.

During oligomerization of C_2H_4 at 280°C (Table 2), the yield of liquid aliphatic hydrocarbons (AlH) increases beginning with 30% HTsVM and attains the maximum value for 100% HTsVM. The formation of PC begins on individual Al_2O_3 and subsequently increases with an increase in the concentration of HTsVM in the composite. As a consequence, with a low concentration of zeolite in the composite, a significant part of the reactant is consumed for formation of PC, and is partially converted into AlH with high concentrations. Both reactions and coke formation take place with the participation of B and L sites in the zeolite and L sites in Al_2O_3.

Methane is not formed in the absence of HTsVM during aromatization at 500°C (Table 3); the formation of CH_4 increases on addition of more than 10% HTsVM and it remains at the level of 20% for [HTsVM] ≥ 30%. The total yield of aromatic hydrocarbons (ArH) increases even on addition of small amounts of HTsVM, and the change in the concentration of PC has a more complex dependence.

Since PC on HTsVM are also aromatic in nature, this dependence is natural: the maximum for the yield of AlH (together with ΣC_4 of 4%) for 10% HTsVM coincides with the minimum for formation of PC. Note the totally antibatic character of the change in the yield of C_3H_8 and the amount of PC as a function of the composition of the composite: the less ArH, the higher the yield of C_3H_8.

The following are characteristic of the reaction of formation of PC on zeolite (in contrast to Al_2O_3) and outside of the dependence on the process, oligomerization or aromatization, in which the PC appear.

a. The constant composition of PC during the entire process both in aromatization and in oligomerization; in the first case, type I PC with C/H of 1.5 (aromatic structures) are formed; in the second case, type III PC with C/H of 0.8 (polyene groups) are formed; on the contrary, during formation of PC (type II) on Al_2O_3, its composition changes.

b. The participation of all acid OH groups, most of which are located in the bulk of the zeolite, in the formation of PC indicates the occurrence of the process in the channels.

In our opinion, the formation of PC on HTsVM can be considered a reaction with a molecular-sieve effect precisely like the target reactions, oligomerization and aromatization.

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