PROPERTIES OF PENTASIL-CONTAINING CATALYSTS IN HYDROCARBON CONVERSIONS.

6.* FORMATION OF CONDENSATION PRODUCTS DURING AROMATIZATION OF PROPANE ON PENTASILS MODIFIED BY ZINC AND GALLIUM

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UDC 541.128:549.67:542.97:547.213

Condensation products (CP) formation during the aromatization of propane on pentasils modified by Zn and Ga (1-5%) has been studied by IR spectroscopy, and thermal and chemical analyses. The amount of CP increases with increasing Zn concentration but falls with increasing Ga concentration in the catalyst. CP are formed both in the channels and on the exterior surfaces and are of an aromatic nature. Coking occurs to a greater extent and the CP are more dehydrogenated for Zn-containing samples than for those containing Ga. A relationship has been noted between the processes of formation of condensed aromatic hydrocarbons, CP, and methane.

The formation of condensation products (CP) has been observed [2] during oligomerization and aromatization of ethylene on the catalytic system pentasil–Al_2O_3. Pentasils modified by zinc and gallium are effective catalysts for the aromatization of the lower alkanes, especially propane [3]. The aromatization process is accompanied by CP formation, which reduces the activity and the life of the catalyst. In this present work an investigation has been conducted into some of the problems of coking during propane aromatization on H-, Zn-, and Ga-forms of pentasils by IR spectroscopy, thermal and chemical analyses, and consideration of data on the activity and selectivity of the catalysts. The composition, nature, and amount of CP formed were studied in relation to the type and concentration of the modifier.

EXPERIMENTAL

The pentasil samples selected were ZVM with $SiO_2/Al_2O_3 = 42$, modified by zinc and gallium (1-5%). The catalysts were prepared from the NH_4-form ZVM by exchanging NH_4^+ ions with zinc or gallium with subsequent impregnation with the mother liquor. Prior to the experiments the samples were activated in a stream of dry air for 5 h at 300 and 520°C. Experiments on propane aromatization were conducted in a flow system at 500-600°C; volume feed rate of propane (V) 120 h^{-1}, length of experiments 5 h. At the end of the experiment the reaction products were removed from the catalyst by blowing a stream of argon through for 30-40 min at 550°C.

IR spectra of catalysts coked during the course of the reaction and of the regenerated samples (520-550°C, air, 1 h) were recorded on a Specord M-80. Thermal analysis in the form of TG–DTG–DTA was conducted using a MOM Q-1000 thermogravimetric instrument with a linear temperature increase (10 deg/min) in an atmosphere of air. The sample mass was 60-100 mg and the reference material was α-Al_2O_3. The coked catalysts were analyzed chemically for carbon and hydrogen by methods described in [4].

RESULTS AND DISCUSSION

The main results of the investigation are presented in Table 1 and Figs. 1-5. All the samples investigated exhibited high catalytic activity for propane conversion (Table 1).

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[*] For previous communication, see [1].

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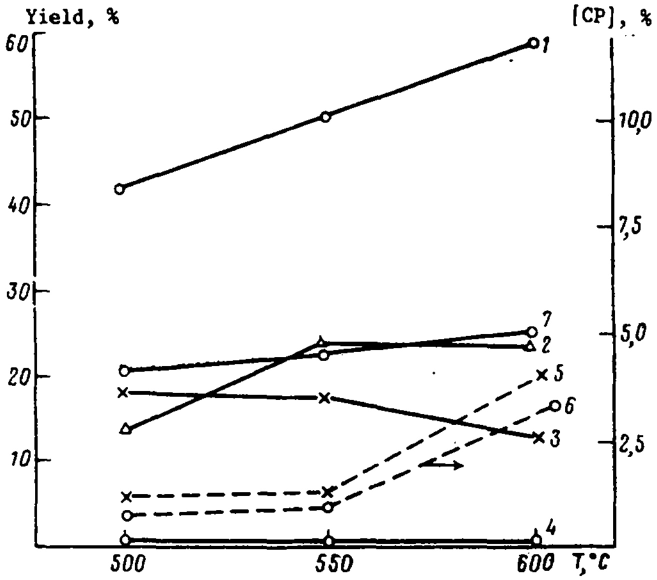

Fig. 1. Variation in product yield for propane conversion on 2% Ga/HZVM with reaction temperature. 1) Σ aromatic hydrocarbons (ArH); 2) benzene; 3) toluene; 4) C_9+ArH; 5) CArH; 6) CP; 7) CH_4.

TABLE 1. Propane Conversion on Modified (Zn, Ga) Pentasils (550°C, v = 120 h^{-1}, 5 h)

Catalyst	X, %	Yield, %									
		Σ ArH	Benzene	Toluene	Xylols	Condensed ArH*	CH_4	C_2H_4	C_2H_6	C_3H_6	C_3H_8
HZVM	94	31	14	14	2	1	47	5	8	3	6
1,0% Zn/HZVM	99	42	14	15	2	11	24	3	29	1	1
2,0% Zn/HZVM	99	40	13	12	3	12	28	2	28	1	1
5,0% Zn/HZVM	100	40	9	12	2	16	36	2	22	–	–
1,0% Ga/HZVM	93	38	14	13	4	7	32	3	18	2	7
2,0% Ga/HZVM	92	43	18	15	3	7	23	2	23	1	8
5,0% Ga/HZVM	91	41	17	13	3	8	20	1	28	1	9

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*Mainly naphthalene and its homologs; content of mononuclear ArH $C_9^+ \leq 0.5\%$.

Under the experimental conditions the conversion (X) was 91-100%. However, on introduction of the modifiers (Zn, Ga) to the H-form of the zeolite the selectivity toward the formation of different reaction components changed significantly; this was particularly noticeable in the case of methane and condensed aromatic hydrocarbons (CArH). There was vigorous methane formation during propane conversion on HZVM (the CH_4 yield reached 47%); the methane yield on the modified samples was significantly lower. Zinc and gallium do not exert the same modifying influence on methane formation: on Zn/HZVM the CH_4 yield increases with increasing [Zn]; in the case of the Ga samples it is the opposite, it decreases. Of particular significance is the difference in the action of the Zn and Ga samples on CArH formation. It can be seen from the table that with an increase in [Zn] the yield of naphthalene and its homologs increases but on Ga/HZVM the CArH yield is more or less independent of [Ga] and is two times lower than that on the Zn-containing samples. At the same time, in the presence of 2% Ga/HZVM, on raising the reaction temperature within the range 500-600°C a strong increase in the yield of naphthalene and its homologs is observed (Fig. 1): it increases by a factor of 4.5 and reaches 20% (600°C); mononuclear ArH of composition C_9^+ are negligible. The CP yield, like the CArH yield, increases with increasing reaction temperature. The similar character of the distributions of CArH and CP (Fig. 1) suggests that CArH can be considered to be one of the precursors of CP.

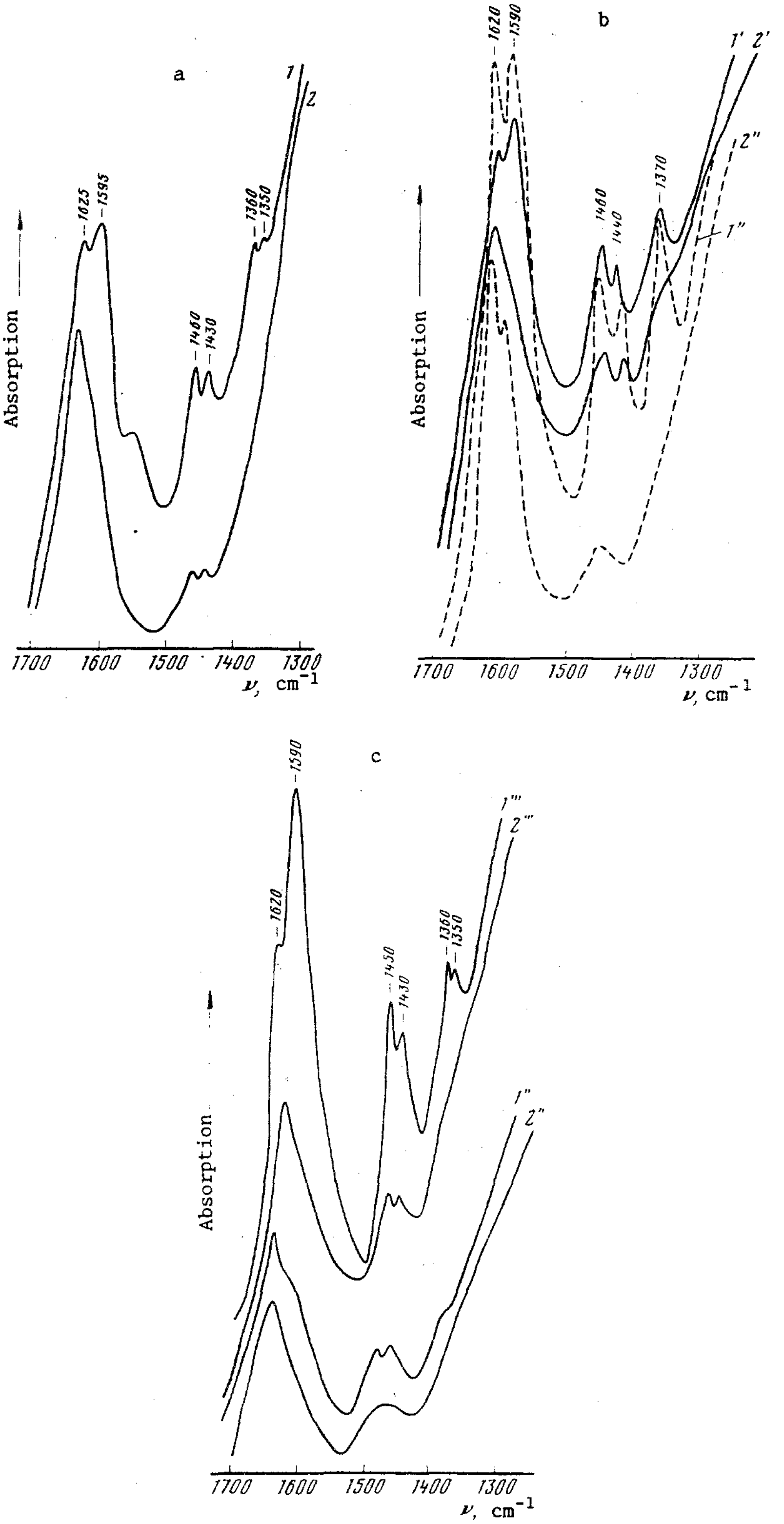

Fig. 2. IR spectra of CP on HZVM (a), Zn/HZVM (b), and Ga/HZVM (c): 1) after reaction with propane (550°C, 5 h), 2) after burning off CP (520-550°C, 1 h) at [M], %: 1', 2') 2; 1", 2") 5; 1"', 2"') 1.

The difference in the catalytic action of Zn and Ga-containing pentasils in propane conversion can be linked to differences in the nature and distribution of the modifiers in the zeolite matrix, the acid properties [3], and other factors.

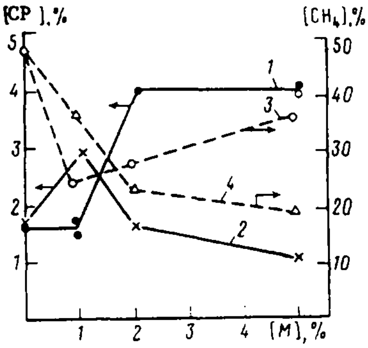

Fig. 3

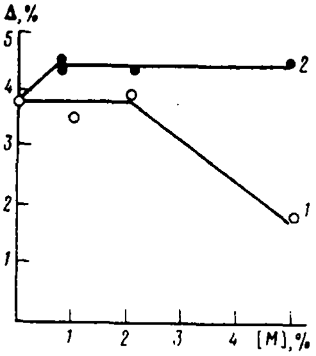

Fig. 4

Fig. 3. Variation in the amount of CP (1, 2) and the yield of CH_4 (3, 4) with concentration of zinc (1, 3) and gallium (2, 4) on modified pentasils.

Fig. 4. Variation in the mass loss during the elimination of sorbed water (Δ) with modifier concentration: 1) Zn, 2) Ga.

In order to investigate the reaction products of propane aromatization in more detail the nature, composition, and principles governing the formation of CP, were studied by means of IR spectroscopy, DTA–DGA, and chemical analysis.

IR spectra of the coked and regenerated samples are presented in Fig. 2a-c where it can be seen that in the region 1700-1300 cm^{-1} absorption bands (AB) at 1625, 1590, 1450, 1430, 1370-1350 cm^{-1} are observed for all the coked catalysts. In the samples modified by gallium the intensity of these AB varies significantly with [Ga]; the greatest intensity is observed for samples containing 1% Ga and the least for 5% Ga. In the case of the Zn samples the picture is reversed: the most intensive AB in the IR spectra were recorded for the 5% Zn sample and the least for 1% Zn. Thus the amount of CP decreases as the [Ga] in the zeolite increases but in the case of zinc it decreases. Regeneration of the catalysts in a stream of air with subsequent evacuation results in a significant reduction in these AB. The intensity of AB for bond vibrations of C–H at 2940 and 2870 cm^{-1} is comparatively low for all the coked samples. Results for the oxidative regeneration of the catalysts show that following the disappearance of AB in the region 1590, 1450, and 1360 cm^{-1} in the spectrum wide AB remain at 1680 and 1480-1420 cm^{-1}, which could indicate that two types of CP exist: low-temperature and high-temperature ones. Absorption bands at 1590, 1450-1430, and 1370-1352 cm^{-1} belong to C═C bond vibrations in polyaromatic systems and deformational vibrations in CH_2 and CH_3 groups in side chains [5-7]. It should be noted that in the IR spectra of all the coked samples AB for bridging OH groups are absent and consequently the CP form both inside the zeolite channels and on their exterior surface. No AB for OH-groups are observed after regeneration, which could be due to incomplete elimination of the CP under the selected conditions of regeneration, which was carried out directly in the cell.

Additional information about the properties and nature of CP were obtained by thermal and chemical analyses. Figure 3 shows the dependence of the sample mass loss during the burning off of CP on the modifier concentration. According to the IR data on Ga-containing samples the amount of CP falls with increasing modifier content and on Zn-containing catalysts it increases. It should be noted that the shape of the DTA curve also depends on the nature of the modifier: for the Zn samples a symmetrical peak is observed corresponding to the burning off of the CP; for Ga samples the peak is asymmetrical with a blurred leading edge. It can be assumed that these behavioral features of the CP are caused by differences in the gallium and zinc distributions in the pentasils [3]. The temperature of the exothermic peak (T_{max}) in the burning off stage of the CP is ~530-540°C on the H-form of ZVM and for the Ga-form it is almost the same (540-550°C) and independent of the gallium concentration; for the Zn-form it is 520°C for [Zn] = 2 and 5%, and reaches 545°C for [Zn] = 1%.

The nature of the distribution of gallium and zinc in the zeolite matrix [3] influences not only the nature of the formation and the distribution of the CP but also its adsorption capacity for water (low-temperature dehydration stage for coked samples in the DTA

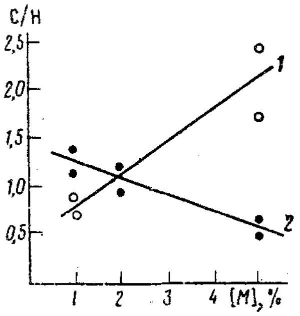

Fig. 5. Variation in CP C/H ratio on ZVM with modifier concentration, after aromatization has taken place: 1) Zn; 2) Ga.

experiments). Figure 4 shows the variation in mass loss during dehydration Δ with the modifier content of the catalyst. For samples with [Zn] ≤ 2% the adsorption capacity for water equals 4% (in terms of the sample mass), for [Zn] > 2% the adsorption capacity falls; at the same time for small [Zn] a relatively small amount of CP are formed (Fig. 3) but for [Zn] ≥ 2% the amount of CP reaches ~4% and then remains unchanged. It is evident that in the case of Zn-containing pentasils the zeolite channels present the same accessibility to CP and water. For Ga-containing pentasils the observed Δ are practically independent of [Ga], which could be due to localization of a significant portion of the Ga on the exterior zeolite surface [3]. Taking into account the fact that a section of the CP are found in the pentasil channels this could be an indication of the nonuniform character of the CP manifesting itself in the shape of the DTA curve.

Results of the chemical analysis (Fig. 5) were used to study the composition and nature of the CP further. It is clear that as the [Ga] increases the C/H ratio falls but with an increase in [Zn] it increases. It follows that in the case of gallium a higher modifier concentration will result in less, and in the case of zinc more, dehydrogenated CP. It should be noted that the C/H ratio equals 0.8 on HZVM, i.e., approximately the same as for 1% Zn/HZVM.

It can be seen from Fig. 3 that the variations in CP content and CH_4 yield with the concentration of each modifier differ from each other. Thus with an increase in [Zn] from 1 to 5% the amount of CP increases at first and then remains constant while the amount of methane formed increases steadily; for the same change in [Ga] these variations are similar to each other (the CP content and CH_4 yield both fall).

Thus during propane aromatization CP formation occurs both in the channels and on the exterior surface. The CP are not uniform in nature and some of them are retained very firmly by the zeolite. The nonuniform distribution of the modifiers in the zeolite matrix result in the CP also being distributed differently in the channels and on the exterior surface: in the case of gallium the internal volume of the zeolites is accessible for water adsorption but in the case of zinc it is somewhat smaller and is reduced sharply on introduction of 5% Zn, which blocks the channels and adsorption centers. An increase in the zinc content favors methane and CP formation; on the other hand an increase in the gallium content inhibits these and other processes. We can conclude that there is a link between the processes of CH_4 and CP formation. It should also be noted that on Ga-containing zeolites the amount of condensed ArH is small (7-8%) and is independent of [Ga]. In the case of zinc, ArH formation is significantly greater (11-16%) and with increasing [Zn] there is a noticeable tendency for the amount to increase. Taking spatial restrictions into account as well we can conclude that the uniform distribution of zinc in the zeolite matrix facilitates the formation of condensed ArH on the external surface, whereas the concentration of gallium on the external surface inhibits their formation. These conclusions agree with the data for the elemental composition of the CP, which show that with increasing modifier concentration the C/H increases for Zn-containing catalysts and decreases for Ga-containing ones.

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SOLVENT EFFECT ON THE RATE OF ESTER INTERCHANGE OF p-NITROPHENYLDIETHYLPHOSPHATE

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UDC 541.12.038.2:541.127:542.951.3:547.26'118

The reaction of p-nitrophenyldiethylphosphate with sodium phenolate takes place readily in aprotic polar solvents. Bimolecular rate constants of this reaction increase with increased concentration of the phenolate in such solvents as dimethylsulfoxide (DMSO), dimethylformamide (DMF), or hexamethylphosphoric amide (HMPA), but decrease in acetonitrile or acetone; this is caused by the association of sodium phenolate, and the different reactivities of free ions and ion pairs. The addition of 18-crown-6 to the reaction mixture decreases the reaction rate, because of the reduced reactivity of the complex formed by the crown ether with the phenolate ion pair.

Various authors have investigated the kinetics and mechanism of ester interchange of acids of tetracoordinated phosphorus [1-9]. A feature of such reactions with nucleophiles of the phenolate (PhO^-) type is the similarity of the chemical properties of the displaced groups to those of the anions entering into nucleophilic attack on the P atom. The complexity of the ester interchange mechanism is evinced by the fact that in a DMF medium, cis- and trans-2-p-nitrophenyl-5-chloromethyl-5-methyl-2-oxo-1,3,2-dioxaphosphoranes react with Na p-nitrophenolate and K p-cresolate to form products with inversion and retention of conformation [1]. The inverted product is obtained by a reaction proceeding through a trigonal bipyramidal intermediate, or else through a transition state of that same structure. The presence of a certain amount of product with retained conformation in [1, 2] was explained by a parallel reaction course including such possible variants of the mechanism as pseudorotation of ligands in the intermediate, splitting off of the leaving group from an equatorial position of the bipyramid, or the parallel formation of an intermediate with a square-pyramidal structure.

Phenolates readily react with esters of diphenylphosphinic acid [3, 4] and substituted phosphonic acids [5, 6] in aqueous solutions, but reactions of the esters with hydroxide ions and amines, present as buffering components, also occur. The rate constants of the phenyl ester interchange reactions depend on the nature of the phenolate ions participating in nucleophilic attack on the P atom, and of those splitting off as a result of the reaction; the rate constants show a Brönsted dependence on the basicity (pK_a values) of the nucleophiles and of the exiting groups [4, 6]. Esters of phosphoric acid usually react more slowly than esters containing alkyl groups on the P atom [7, 8].

Comparing the rate constants of the reaction of p-nitrophenyldiphenylphosphate with PhONa in water [8] and acetonitrile (AN) [9], it can be stated that changing the reaction medium from water to an aprotic polar solvent increases the reaction rate more than 1800 times. In this connection, it seemed interesting to do a broader study of solvent effects on the rate of ester interchange of esters of phosphorus acids. With this aim, we have

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0568-5230/91/4009-1738$12.50