MODIFIED HETEROSILICATES (Fe, B)–CATALYTIC CHARACTERISTICS AND IR SPECTRA

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The catalytic characteristics (in the aromatization of propane and propylene) and acidic characteristics (IR spectra in diffuse scattered light) of modified crystalline heterosilicates (Pt, Zn, Ga) were studied. It was shown that new centers, capable of substantially increasing (by 2-7 times) the yield of aromatic hydrocarbons from propane, are formed when Zn and Ga are introduced into ferri- and borosilicates. In the case of propylene the aromatizing characteristics of the modified heterosilicates show up particularly clearly in the region of relatively low temperatures.

Key words: *Heterosilicates, IR spectroscopy, acidic properties, modification, aromatization.*

One of the effective methods for the control of the properties of zeolites in order to modify their activity and selectivity is isomorphous substitution of Al ions in the lattice of crystalline aluminosilicate by the cations of other elements. The heterosilicates formed here retain the structure of the respective zeolite, e.g., of the Pentasil type but have a series of individual characteristics due to the nature of the ions entering into the framework of the zeolite [1]. Representatives of the most fully and widely studied heterosilicates are the crystalline high-silicon ferrisilicates (FS) and borosilicates (BS). Their acidic and catalytic characteristics [2-4] differ appreciably from the characteristics of the aluminosilicate analogs [5]. New representatives of the heterosilicates (Ga, Zn, Mo, and other metals) have been synthesized and vigorously investigated [1, 6]. Published data on heterosilicates mainly concern their decationated forms; modified heterosilicates have been investigated little. There is only a certain amount of information on them in [7-9]. In addition, it is known that the acidic and catalytic characteristics of zeolites can be controlled successfully by the introduction of various additives.

In the present work we studied the effect of the modification of heterosilicates (ferrisilicates, borosilicates) with platinum, zinc, and gallium on the activity and selectivity in the transformations of propane and propylene. At the same time the nature of the active centers in the H, Zn, and Ga samples was investigated by IR spectroscopy in diffuse scattered light. The obtained data were compared with the results from catalytic experiments.

EXPERIMENTAL

The decationated forms of ferrisilicates and borosilicates had the following molar ratios: $SiO_2/Fe_2O_3 = 234$; $SiO_2/B_2O_3 = 179$; Na_2O content <0.1%. Ferrisilicates and borosilicates modified with platinum, zinc, and gallium were prepared from the respective NH_4 forms under conditions of ion exchange with subsequent impregnation [10]. The platinum content amounted to 0.5%, and the zinc and gallium contents amounted to 2 wt.%.

The catalytic investigations were conducted in flow-type apparatus. Before the experiments all the samples were activated with air at 300°C for 1 h and at 500°C for 4 h. The amount of catalyst was 1.5-1.6 g (2.5 cm^3), and the volume delivery rate of the reagents was 120 h^{-1}.

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*Deceased.

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TABLE 1. Transformation of Propane on the H and Modified (Pt, Zn, Ga) Forms* of Borosilicate and Ferrisilicate (ν = 120 h^{-1})

Catalyst	T, °C	K, %	Yield, wt. %						S_{ApY}, %
			CH_4	C_2H_4	C_2H_6	C_3H_6	C_3H_8	ApY C_6—H_{10}	
HBS	550	7	2	2	1	tr	93	2	29
	600	38	10	13	5	tr	62	10	26
Ga/ BS	550	16	2	3	2	tr	84	9	56
	600	47	9	6	11	9	53	12	26
Zn/BS	550	32	5	2	11	tr	68	14	44
	600	66	10	5	12	15	34	24	36
HFS	550	27	4	3	5	tr	73	15	56
	600	55	12	8	13	3	45	19	35
Ga/FS	550	28	4	3	4	tr	72	17	61
	600	62	8	5	21	6	38	22	35
Zn/ FS	550	75	14	2	25	8	25	26	35
	600	89	17	4	24	10	11	34	38
Pt/ FS	550	68	11	1	21	16	32	19	28
	600	79	13	1	17	16	21	29	37

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*Zn, Ga 2.0, Pt 0.5 wt.% (calculated on the metal).

The transformation of propylene was realized according to the following scheme. On one sample of the catalyst we carried out experiments at 550, 500, and 400°C, and then on a new sample we carried out experiments at 250, 300, 350, and 400°C. This made it possible to assess the stability of the catalyst. Between the experiments the samples were regenerated in a stream of air at 500°C for 2 h. In the case of propane we used a fresh portion of the catalyst for each sample, since in this case a reduction in the activity of the catalyst was observed from experiment to experiment. The length of each experiment was 4 h. The reaction products were analyzed by GLC on two types of columns, i.e., with Silicone oil for analysis of the liquid products and with Porapak Q for the gaseous products.

The degree of coking on the heterosilicate was assessed by thermal analysis (TG–DTA) of a series of samples after reaction with propane (600°C). The amount of condensation products formed on the investigated samples was not greater than 3%, and the H forms were least subject to coking.

The diffuse scattering IR spectra were measured on Perkin-Elmer 580B and Beckman Acta MVII spectrophotometers [11, 12]. Molecular hydrogen and methane were used as probes for the acidic centers [13]. Before the spectral investigations the samples were calcined at 500°C under vacuum for 5 h.

DISCUSSION OF RESULTS

It is seen from Table 1 that the degree of transformation (*K*) of propane on HBS is only 7% (550°C); HFS is significantly more active under analogous conditions, the *K* value for propane amounts to 27%, and the yields of the aromatic hydrocarbons (ArH) are 2 and 15% respectively.

The introduction of zinc, gallium or platinum into the HFS and HBS substantially increases their catalytic activity. Zinc has the strongest promoting action both on the general activity and on the aromatizing characteristics of the ferrisilicate and borosilicate. In the presence of Zn/HFS the conversion of propane is increased by three times, while the yield of the aromatic hydrocarbon is increased by almost twice (550°C). The H form of the borosilicate (2% of the aromatic hydrocarbon), which is practically inactive in aromatization, acquires aromatizing characteristics as a result of modification; the yield of the aromatic hydrocarbon is increased by seven times and *K* by five times. The introduction of gallium into the borosilicate and ferrisilicate also leads to a positive effect. However, the gallium-containing samples are less active with respect to the transformations of propane. The conversion of propane and the yield of the aromatic hydrocarbon are half the values obtained on the zinc-containing samples. At the same time it is important to note that the heterosilicates modified by gallium have higher selectivity in the formation of the aromatic hydrocarbon (S_{ArH}) (Table 1). This fact can probably be explained by differences in the distribution of the zinc and gallium in the matrix of the heterosilicate and by the different acid characteristics of the zinc- and gallium-containing samples, as in the case of aluminosilicate Pentasils [14].

TABLE 2. Conversion of Propane on HFS, Zn/FS*, and Ga/FS* (ν = 120 h^{-1})

Catalyst	T, °C	K, %	Yield of liquid products, wt. %	Yield, wt. %								S_{ArH}, %
				CH_4	C_2H_4	C_2H_6	C_3H_6	C_3H_8	C_4–C_5	ArH C_6—C_{10}	AlkH C_6—C_{10}	
HFS	250	97	66	tr	tr	tr	3	11	20	62	4	4
	300	99	80	tr	tr	tr	1	8	11	70	10	10
	350	91	55	1	3	2	9	10	20	39	16	18
	400	92	52	1	3	2	8	17	17	22	30	33
	500	87	48	6	6	12	13	12	3	3	45	52
	550	92	47	12	9	17	8	7	tr	1	46	50
Zn/FS	250	95	60	tr	1	tr	5	6	28	55	5	5
	300	94	69	tr	1	tr	6	7	17	61	8	9
	350	90	57	1	2	tr	10	8	22	32	25	28
	400	83	56	1	3	1	17	9	13	24	32	39
	500	81	50	1	3	3	19	20	4	2	48	59
	550	92	32	15	2	25	8	18	tr	tr	32	35
Ga/FS	250	95	66	tr	tr	tr	5	8	21	56	10	11
	300	99	84	tr	tr	tr	1	8	7	63	21	21
	350	97	71	tr	1	tr	3	9	16	40	31	32
	400	92	44	tr	3	2	8	18	25	13	31	34
	500	80	41	4	6	9	20	16	4	2	39	49
	550	84	41	8	6	16	16	13	tr	1	40	48

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*2.0 wt.% calculated on the metal.

The Pt/HFS catalyst gives fairly high general conversion of propane (68%), but the yield of the aromatic hydrocarbon is low, and in this respect it is similar to the initial HFS. Platinum greatly intensifies the cracking and dehydrogenation processes, as a result of which many gaseous products (CH_4, C_2H_6) and propylene are formed (Table 1).

Increase in the reaction temperature to 600°C leads to substantial changes in the general activity of the catalysts and their selectivity. On all the investigated samples there is a considerable increase in the conversion of propane and a simultaneous increase in the aromatizing ability of the catalyst. Here in almost all cases the increase in the *K* values predominates over the yield of the aromatic hydrocarbon. This fact may be due both to the acceleration of the individual stages of the complex aromatization process, leading to the formation of blind products, and to increase in the cracking rate of the initial alkane as a result of the increase in temperature. As a result there is a substantial change in the composition of the reaction products; methane formation increases, the yield of the C_2-C_3 olefins and ethane is increased, and the yield of the aromatic hydrocarbon is increased by 1.5-2 times and by five times in the case of HBS (Table 1).

While comparing the effect of the modifying additives on the characteristics of the investigated heterosilicates it is necessary to note that they all lead to an increase in catalytic activity, while zinc in the present case is the most effective promotor of the transformation of propane to aromatic hydrocarbons. In addition, at the zinc- and platinum-containing heterosilicates the dehydrogenation and hydrocracking processes are intensified, leading to an increase in the yield of the olefins, on the one hand, and C_1-C_2 alkanes, on the other. Conversely, the introduction of gallium leads to some decrease in methane formation with a simultaneous increase in the aromatizing activity of the catalyst, and here the yield of the aromatic hydrocarbons on the Ga samples is appreciably lower than on the zinc-containing heterosilicates. This is probably due to the different mechanism for the action of the zinc and gallium catalysts [14].

We note that the comparatively low activity of the borosilicates and the modified catalysts based on them in the transformations of propane is primarily explained by the weak acidic characteristics of these heterosilicates [15].

The transformations of propylene, which is an intermediate product in the aromatization of propane, was studied on the H, Zn, and Ga forms of ferrisilicate in the range of 250-550°C. This made it possible to estimate the contribution from the modifiers both at the stage of oligomerization of propylene and during its subsequent transformations into the aromatic hydrocarbons. It can be seen from Table 2 how the ratio of the reaction products reflecting the processes that occur on the H and modified forms of ferrisilicates changes with increase in temperature. Thus, the oligomerization of the olefin takes place vigorously on the unmodified ferrisilicate at 250-300°C; the yield of the liquid hydrocarbons is 66-80% with almost complete conversion of the propylene. The main products are C_6-C_{10} olefins (AlkH). The yield of ArH and S_{ArH} are commensurable and do not exceed 10% (300°C). A change in the selectivity of the process is observed at higher temperatures. Above 300°C the

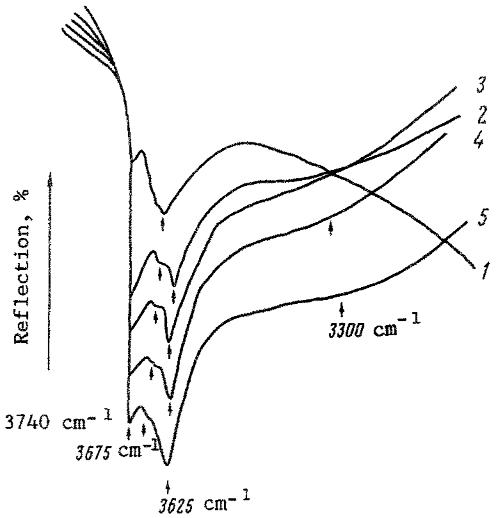

Fig. 1. IR spectra of the hydroxyl groups of ferrisilicates in diffuse scattered light: Zn/HFS (1) and Ga/HFS (2) after reaction with propane (600°C, 3 h) + regeneration (air, 500°C, 2 h); Ga/HFS (3), Zn/HFS (4), and HFS (5), initial samples after calcination under vacuum (500°C, 5 h).

cracking of the oligomers is intensified; the yield of the gaseous products is increased by more than twice mainly on account of the C_1-C_2 hydrocarbons. Beginning at 400°C the content of AlkH in the catalyzate is substantially reduced, and the yield of ArH is increased; here S_{ArH} is increased by 2-3 times. At 500-550°C the liquid reaction products mostly represent aromatic hydrocarbons, the yields of which amount to 45% (S_{ArH} is greater than 50%).

On the modified forms of the ferrisilicates at relatively low temperatures (250-300°C), when oligomerization and disproportionation of C_nH_{2n} mainly occur, the effects of zinc and gallium show up in different ways. In particular, on Zn/HFS the yield of the aromatic hydrocarbons and S_{ArH} are commensurable with the corresponding values for the initial H form. At the same time, the introduction of gallium into the HFS doubles the yield of the aromatic hydrocarbons and S_{ArH}. This effect is particularly significant at low temperatures. In the region of 350-500°C the promoting action of zinc appears. Under these conditions the effect of zinc on the aromatizing characteristics of the ferrisilicates is stronger than that of gallium (Table 2). Zn/HFS has the strongest aromatizing ability at 500°C (S_{ArH} = 59%); the gaseous reaction products only contain small amounts of volatile hydrocarbons (several times smaller than in the case of HFS and Ga/HFS). If the reaction temperature is increased to 550°C on Zn/HFS, the pattern changes abruptly; the yield of methane is increased by more than an order of magnitude, the yield of the C_2-hydrocarbons is increased by 4.5 times, and S_{ArH} decreases from 59 to 35%. In the case of Ga/HFS under analogous conditions S_{ArH} remains practically unchanged, and the yield of methane is only increased by twice. A pattern similar to Ga/HFS is observed on HFS (Table 2).

It is important to note that HFS and its modified forms (Zn and Ga) exhibit high stability in the experiments with propane; the characteristics of the catalysts did not change over the whole series of experiments (3-4 h). In view of the fact that little of the condensation products (3%), which can lead to deactivation of the catalyst, is formed during the transformations of propane, the low stability of the investigated samples can probably be explained by structural changes that occur at high temperatures in the lattice of the heterosilicate under the influence of the reaction medium [15].

On the whole the results indicate that the aromatizing activity of the H forms of ferrisilicates and borosilicates in the transformations of propane and propylene is substantially increased as a result of modification of the heterosilicate by platinum, zinc, or gallium. The promoting effect of the above-mentioned additives is particularly significant in the case of propane; the yield of the aromatic hydrocarbons is increased by 2-7 times. The detected differences in the catalytic action of the heterosilicates modified with zinc and gallium can probably be explained by analogy with the zinc- and gallium-containing aluminosilicates [14, 16] by the different distributions of zinc and gallium in the matrix of the heterosilicate and by the different mechanisms for the action of zinc and gallium samples. However, it must be borne in mind that the aluminum-containing Pentasils and their isomorphously substituted analogs (heterosilicates) differ substantially not only in their catalytic characteristics but also in their physicochemical characteristics [4, 5, 15]. In this connection the samples of the modified ferrisilicates and also the initial HFS

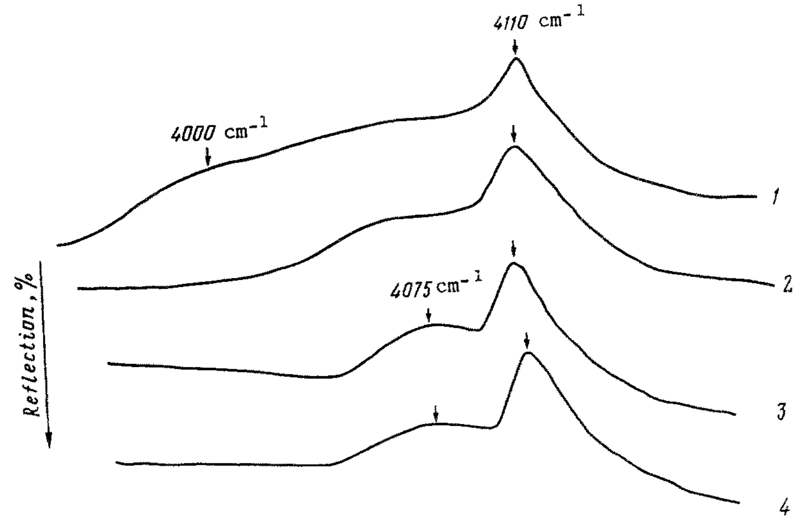

Fig. 2. IR spectra of hydrogen adsorbed on ferrisilicates at 77 K: 1) Zn/HFS after calcination under vacuum (500°C, 5 h); 2) Zn/HFS after holding in hydrogen (300 K, 10 min); 3) Ga/HFS after calcination under vacuum (500°C, 5 h); 4) HFS (P_{H_2} = 30 torr).

were investigated in detail by IR spectroscopy in diffuse scattered light with molecular hydrogen and methane as probes for the acidic centers.

The IR spectra of the hydroxyl groups of the H form of the ferrisilicate and of the samples modified by zinc and gallium ions are given in Fig. 1. For the ferrisilicates lines are observed at 3740, 3675, 3625, and 3300 cm^{-1}. The line at 3740 cm^{-1} belongs to the vibrations of the isolated Si–OH groups, and the line at 3675 cm^{-1} corresponds to the hydroxyl groups attached to the iron ions outside the framework [15]. In addition, in the case of the modified samples the hydroxyl groups attached to the modifying ions (Me–OH, where Me = Zn or Ga) can make a contribution to the intensity of the line at 3675 cm^{-1}. According to [3], the line at 3625 cm^{-1} belongs to bridging acidic hydroxyl groups of the $\mathrm{Fe{-}\overset{H}{O}{-}Si}$ type. The line at 3300 cm^{-1} in the spectrum of the ferrisilicates, which is also observed in zeolite HZSM-5 and other metallosilicates with the Pentasil structure, probably corresponds to the bridging hydroxyl groups of HFS perturbed by a hydrogen bond with the oxygen atoms of the lattice [17]. The introduction of the zinc or gallium ions somewhat changes the intensity of the absorption bands of the hydroxyl groups. The cycle that includes the catalytic aromatization of propane and subsequent regeneration has a more substantial effect. As seen from Fig. 1, such treatment leads to practically complete disappearance of the lines at 3625 and 3300 cm^{-1}, and this corresponds to escape of almost all the Fe ions from the metallosilicate framework.

Figure 2 shows the IR spectra of hydrogen adsorbed on the modified ferrisilicates at 77 K. For the Zn/HFS sample a broad unresolved band is observed in the range between 3930 and 4100 cm^{-1}, corresponding to the complexes of H_2 with the Lewis acid centers and coordination of the unsaturated cations. Treatment of the sample with adsorbed H_2 at ~20°C leads to disappearance of the lines with the envelope maximum close to 4000 cm^{-1}. Subsequent vacuum treatment of the Zn/HFS sample at 370 K and adsorption of hydrogen at 77 K lead to the appearance of lines with a maximum at 4000 cm^{-1} in the spectrum, and they then again disappear after holding at ~20°C. We note that no reduction in the intensity of any lines in the spectrum of hydrogen after holding at 300 K was observed in the initial H form of the ferrisilicate. It can be supposed that dissociation of hydrogen with the formation of zinc hydrides and hydroxyl groups occurs on Zn/HFS at 300 K. Dissociative adsorption of hydrogen by a similar mechanism was detected earlier on aluminosilicate zeolite HZSM-5 modified with Zn^{+2}, which is an active catalyst for the aromatization of lower paraffins [16, 18].

The spectrum of hydrogen adsorbed on Ga/HFS hardly differs at all from the spectrum of the initial H form of the FS. In both cases there are lines at 4110 cm^{-1}, corresponding to the complexes of H_2 with hydroxyl groups, and a band at 4075 cm^{-1}, belonging to hydrogen molecules adsorbed on the Fe^{3+} ions outside the framework [5]. Modification of the ferrisilicate with gallium does not lead to appreciable changes in the intensity of the lines or to the appearance of new bands in the spectra.

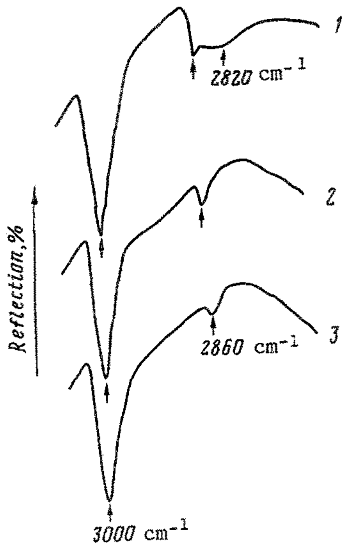

Fig. 3. IR spectra of methane adsorbed on ferrisilicates: Zn/HFS (1) and Ga/HFS (2) after calcination under vacuum (500°C, 5 h); 3) HFS (P_{H_2} = 30 torr).

In the spectra of methane (Fig. 3) adsorbed on HFS and Ga/HFS, in addition to the band at 3000 cm^{-1} characterizing physical nonspecific adsorption, there is a line at 2860 cm^{-1}. Earlier it was shown that lines with a close maximum (2855-2865 cm^{-1}) in the case of partially dealuminated zeolites HZSM-5 and gallosilicates with the Pentasil structure, containing gallium outside the framework, correspond to strongly polarized molecules of methane interacting with the metal ions outside the framework [19]. It can be supposed that the band at 2860 cm^{-1} in the spectrum of methane on the ferrisilicates also belongs to complexes of CH_4 with ions outside the lattice and with Fe^{+3} in particular. The intensity of this band does not change when the H forms are modified with Ga^{+3} ions. We note that additional bands are not observed in the spectrum of the methane after the introduction of Ga^{+3}.

Thus, acidic centers belonging to Ga were not detected in the channels of the ferrisilicate by IR spectroscopy with H_2 and CH_4 as probes. It is known that during impregnation in Metasils triply charged cations are localized preferentially on the outer surface of the microcrystallites [20]. During modification of ferrisilicates with the Pentasil structure with gallium a large part of the ions is probably situated on the outer surface of the metallosilicate crystals. The concentration of gallium ions in the channels during such modification must be small, and this agrees with the data obtained by IR spectroscopy.

In the spectra of methane adsorbed on Zn/HFS, in addition to the bands at 3000 and 2860 cm^{-1}, there is an additional band at 2820 cm^{-1}, probably belonging to complexes of CH_4 with the acid–base centers Zn–O, at which dissociative dissociation of the molecular hydrogen occurs at 300 K. This suggestion is confirmed experimentally. Thus, the adsorption of hydrogen on Zn/HFS at 300°C followed by dissociation leads to disappearance of the band at 2820 cm^{-1} during the adsorption of methane. Earlier a band with a close maximum (2805 cm^{-1}) was observed in the spectra of methane adsorbed on Zn/HZSM-5 [18].

Thus, the modification of ferrisilicates with zinc and gallium oxides leads to the appearance of centers that exhibit dehydrogenating characteristics and are capable of polarizing the molecules of saturated hydrocarbons. In the case of the zinc-containing samples these centers are situated in the channels of the ferrisilicates; in samples modified with gallium these centers are probably localized mainly at the outer surface of the ferrisilicate crystals. Migration of the gallium into the channels of the ferrisilicate and borosilicate under the influence of the reaction medium, as observed in the case of gallium Pentasils [21], is not excluded.

Thus, the data set out above make it possible to conclude that as a result of modification of the heterosilicates with zinc and gallium new active centers, capable of substantially increasing the aromatizing characteristics of the catalysts based on ferrisilicates and borosilicates in the transformations of propane and propylene, appear.

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