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Production, Physicochemical and Catalytic Properties of Gallium-Containing Zeolite Catalysts

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Abstract

Crystalline galloalumino- and gallosilicates with pentasil structure were synthesised under hydrothermal conditions. The influence of gallium concentration and binder amount both on physicochemical and catalytic properties of a zeolite in the process of C_2-C_4 light alkanes aromatization and on catalyst deactivation due to carbidization has been studied. Acidic properties of gallium-containing pentasils with different composition were studied using the method of thermoprogrammed ammonia desorption. The formation of strong aproton acidic sites whose composition includes gallium ions was found. It has been shown that isomorphic aluminium replacement by gallium in the pentasil lattice leads to a significant increase in aromatizing activity and period of stable catalyst operation. A decrease in intensity of coking and the formation of less condensed coke deposits with a wide distribution by the structure are observed with the increase in gallium concentration. The introduction of a binder to galloaluminosilicate results in a significant increase in mechanical strength of a catalyst. It was established that the most efficient catalyst of the above process is a zeolite containing 2.2% of gallium oxide and 1.3% of aluminium oxide and mixed with 20% of the pseudobeumite. The selectivity of the formation of aromatic hydrocarbons reaches 55-60%, the period of stable operation exceeds 350 h. In accordance with the data obtained suggested are the principles of the selection of efficient catalysts of light alkanes aromatization and optimum conditions of the process.

Introduction

High-silica zeolites of pentasil type are promising catalysts of a whole range of important chemical processes. Fixed structure of the crystal lattice and the presence of acidic sites of different types on its surface allows applying the zeolites in different chemical reactions, including the conversion of light alkanes into aromatic hydrocarbons. Nevertheless, at the application of an unmodified zeolite of ZSM-5 type the selectivity of aromatic hydrocarbons formation does not exceed 30%. That is why, to improve the formation of aromatic hydrocarbons, promoting additives, preferentially Pt, Zn, Ga or Cd [1-9], are introduced into the zeolite composition. At the same time, the catalysts produced, despite of their high activity and selectivity, may not be used under commercial conditions because the sample properties do not meet the requirements of interlaminar and wear strengths. Mechanical strength of the catalysts may be improved by introducing a binder into the composition of a zeolite. Moreover, the existing zeolite catalysts are characterised by a short life between regenerations, which requires a simultaneous application of several reactors in the process scheme and the modification of the design and the regeneration system [2-4]. In this connection the development and creation of a high-stability catalyst to be used in the conversion of light alkanes, which preserves a high activity and stability for aromatic hydrocarbons is an urgent task.

This paper presents the results of investigations of physicochemical and catalytic properties of galloalumino- and gallosilicates differing by the content of lattice atoms of aluminium and gallium, in the process of conversion of C_2-C_4 light alkanes mixture into aromatic hydrocarbons as well as on the catalyst deactivation resulting from its carbidization.

Experimental

The initial aluminosilicate (AS) that did not contain gallium (SiO_2/Al_2O_3=60) was synthesised under hydrothermal conditions at the temperature of 175°C

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*corresponding author. E-mail: pika@ipc.tsc.ru from alkaline aluminosilicagels of the following composition: 17.5 $Na_2O \cdot 6.1 R \cdot Al_2O_3 \cdot 60 SiO_2 \cdot 3275 H_2O$.

Hexamethylene diamine (HMDA) was used as an organic component (R). AS produced in the synthesis process was converted into an active H-form via double decationization by 25% NH_4Cl solution at 90°C for 2 h followed by drying at 100°C and air calcination at 550°C for 6 h (Na_2O content in AS was less than 0.02%). AS modification by gallium was carried out via isomorphic replacement of Si^{4+} ions by Ga^{3+} ions in the zeolite crystal lattice at the stage of hydrothermal synthesis by a partial or total replacement of aluminium by gallium in the initial aluminosilicagel $SiO_2/(Al_2O_3+Ga_2O_3)$. Gallium oxide content in the reaction mixture changed from 0.6 to 4.9 wt.%, that of Al_2O_3 changed from 0.7 to 2.4 wt.%. To prepare a catalyst with a binder, a catalytic mass was obtained by mixing galloaluminosilicate (Ga_2O_3=2.2 wt.%), pseudobeumite (PB) and water, nitric acid (0.1-0.15 mol/mol Al_2O_3) was added for plastification. The plastic mass obtained was subjected to extrusion. Catalyst grains (d=2 mm) were dried for 24 h on air, then in an air drier at 110°C for 24 h and calcined at 600°C for 6 h. The amount of a binder in a galloaluminosilicate was changed from 10 to 30 wt.%. To carry out the test, a catalyst fraction of 0.25-0.50 mm was taken.

During loading and operation, the catalyst should not be destroyed, that is why the index of its mechanical strength is of a great importance. To assess the mechanical strength of the catalysts, different methods and devices are applied, nevertheless, for the catalysts produced as the grains via extrusion forming only the methods of cutting or splitting and crushing are used [10]. Mechanical strength of catalyst grains was determined by the load provoking their destruction at splitting. To compare the catalysts, the value of specific strength or the strength factor, *i.e.*, the value of the breaking load per 1.0 mm of the grain diameter, was used. The sample grains were split using a steel knife with the blade 0.1 mm wide.

The quality of the samples produced was tested by IR-spectroscopy (IRS) and X-ray structure analysis (XSA). IR-spectra of the samples were obtained using a UR-20 spectrophotometer ("Carl Zeiss") within the range 2000-400 cm^{-1} in KBr pellets on air. The amount of the zeolites was assessed by their characteristic absorption bands. Thus, the formation of zeolite phase in the samples synthesised is indicated by the absorption band in the region 550-560 cm^{-1} relating to the vibrations along the external bonds of AlO_4 и SiO_4 tetrahedrons of the framework and conditioned by the presence of doubled 4-, 5- and 6-cycled rings. The crystallinity degree determined using IR-spectroscopy by the procedure described in [11] points to the degree of the phase purity of high-silica zeolites obtained.

X-ray study of the zeolites synthesised was carried out using a DRON-3 installation (Cu K_α radiation, Ni-filtered). The data of X-ray photographs allowed us to determine the structural type of the zeolites obtained. The position and the relative intensity of the lines of X-ray photographs are identical to the set of the lines of the reference sample of ZSM-5 type.

The elementary composition of the catalyst samples obtained was determined using atomic absorption spectrophotometry.

Acidic properties of the catalyst surface were tested using thermoprogrammed ammonia desorption (TPD). The procedure of TPD experiments is described in [5]. To calculate the values of activation energy, ammonia desorption from the samples was carried out at different heating rates (5, 10, 15 and 20 deg/min). Activation energies were determined in accordance with the procedure described in [12].

To determine total specific surface of the samples, we used the method of thermal argon desorption. The installation for the determination of the specific surface of catalysts was assembled on the base of a "Micromeritics" installation (France).

Aromatization of a mixture of light alkanes (ethane – 2.2; propane – 73.7; *i*-and *n*-butane – 24.1 wt.%) was performed on a flow type installation with the reactor volume of 5 cm^3 at atmospheric pressure, reaction temperature was 350-600°C, the feedstock space velocity was 50-400 h^{-1}. Before the tests galloaluminosilicates (GAS) and gallosilicates (GS) were treated by air at 300°C for 2 h and at 520°C for 3 h, then they were reduced in hydrogen flow at 520°C for 2 h, the space velocity of air and hydrogen was 1 dm^3/h. The reaction products were analysed by gas chromatography. When determining the period of a stable catalyst operation, the tests were run continuously for several days, the reaction products were analysed at certain intervals that were equal for all the samples. The stability of catalyst operation was assessed by the changes both in the degree of feedstock conversion and in the selectivity of aromatic hydrocarbons formation.

DTA-DTG patterns of coked catalysts were recorded on "C" DTA-DTG instrument (MOM, Hungary) within 20-1000°C. The sample (400-500 mg) was heated in a platinum crucible on air at the rate of 10 deg/min.

Results and Discussion

The data on the composition of gallium-containing zeolites and their crystallinity degree are given in Table 1. As is seen, the increase in gallium content of the catalysts results in a small decrease in crystallinity degree of a zeolite catalyst that was high for all the samples.

Table 2 shows the results of the study of acidic properties of gallium-containing zeolite catalyst, specific surface values and factors of catalyst strength. The initial AS has two types of acidic sites which is confirmed by the presence of two forms of ammonia desorption in the pattern. The maximum temperatures (T_{max}) of weak and strong acidic sites are 210°C and 425°C, respectively. The concentrations of weak acidic sites are 271 and 244 μmol/g, respectively. The activation energies of form I and form II of ammonia desorption are, respectively, 33.3 and 123.3 kJ/mol.

Table 1

Characteristics of crystalline gallium-containing zeolite catalyst.

Catalyst	Concentration, wt.%				Molar ratio		Crystallinity, %
	Ga_2O_3	Al_2O_3	Na_2O	SiO_2	SiO_2/Al_2O_3	SiO_2/Ga_2O_3	
AS	-	2.7	0.02	97.28	60	-	90
GAS-1	0.6	2.4	0.02	96.98	70	488	90
GAS-2	1.2	2.0	0.04	96.76	82	245	90
GAS-3	2.2	1.3	0.06	96.44	122	122	88
GAS-4	3.7	0.7	0.08	95.52	245	82	85
GS-60	4.9	-	0.02	95.08	-	60	67
GS-120	2.5	-	0.08	97.42	-	120	70

Table 2

Characteristics of gallium-containing zeolite catalyst

Catalyst	T_{max} (°C)		Concentration, (μmol/g)			$E_{dec.act.}$ (kJ/mol)		S, (m^2/g)	k
	T_I	T_{II}	C_I	C_{II}	C	E_I	E_{II}		
AS	210	425	271	244	515	33.3	123.3	514	0.24
GAS-1	210	430	250	215	465	32.1	125.5	-	-
GAS-2	205	435	237	183	420	31.6	126.7	-	-
GAS-3	200	440	215	178	393	30.8	138.9	504	-
GAS-4	200	425	202	174	376	30.2	123.9	-	-
GS-60	195	360	120	137	257	25.6	105.3	-	-
GS-120	185	355	84	54	138	22.1	99.9	-	-
GAS-3/10%-PB	200	400	202	121	323	-	-	390	0.30
GAS-3/20%-PB	200	390	176	114	290	29.4	105.3	365	0.54
GAS-3/30%-PB	195	380	149	104	253	-	-	343	0.73
pseudobeumite	180	-	226	-	226	-	-	286	-

Note. T_I, T_{II} are the temperatures of peak maximums for the forms I and II; C_I, C_{II} and C are the concentrations of acidic sites of the form I and form II and total concentration, respectively; E_I and E_{II} are activation energies of ammonia desorption for forms I and II; S is specific surface; k is specific strength value, kg/mm of diameter.

As is seen from Table 2, the introduction of gallium into a zeolite during hydrothermal synthesis leads to the changes in acidic properties, first of all to a decrease in concentration of acidic sites of both types. On the increase of gallium content and decrease of aluminium content in a zeolite the concentration of strong and weak acidic sites is decreased as well, as evidenced by the shift of peak maximum of form I of ammonia desorption into the region of lower temperatures. At the same time with the increase in Ga_2O_3 concentration in a galloaluminosilicate to 2.2 wt.% an increase in strength of high-temperature sites and in activation energy of ammonia desorption for II adsorption form are observed. This is explained by the formation of new stronger active sites with a high energy of ammonia retention, although their concentration is not high, on gallium introduction. The formation of strong aproton acidic sites containing gallium atoms determines an increased activity of galloaluminosilicates in the reactions of light alkanes aromatization because their formation is followed by a drastic increase in reaction rate of the first process stage, *i.e.*, dehydrogenation of low saturated hydrocarbons. The oligomerization of olefins formed occurs by proton mechanism. Both proton and aproton acidic sites are involved in further cyclization of oligomers and their unsaturated fragments. The increase in gallium oxide concentration in a zeolite to 3.7 wt.% and decrease in aluminium oxide to 0.7 wt.% or a total replacement of Al atoms by Ga in the crystal lattice of a zeolite lead to the decrease in strength of high-temperature acidic sites and activation energy of ammonia desorption for II adsorption form. Obviously, it is connected with the formation of minor quantity of coordination spheres of active sites containing neighbouring atoms of gallium, aluminium, and silicon and the formation of less active catalysts. So far, to produce the most effective catalyst of light alkanes aromatization, it is of a great importance to take into account aluminium moiety in zeolite framework, although its quantity may be very low.

Mixing GAS with a binder leads to the reduction in its acidity, PB introduction exerts an especially significant influence on the strength and concentration of high-temperature sites. Thus, when mixing GAS-3 with 10% PB, T_{max} of the high-temperature peak is shifted to the region of lower temperatures (by 40°C), the concentration of strong acidic sites decreases by 57 μmol/g. The further increase in PB concentration in GAS-3 results in a smoother reduction in strength and concentration of acidic sites. Activation energy also decreases upon binder introduction into GAS-3, thus, the values of I and I forms of ammonia desorption for the sample GAS-3/20%-PB are 29.4 and 105.3 kJ/mol, respectively. The initial pseudobeumite is characterised by the presence of a low-temperature peak only, with T_{max} at 180°C and a relatively high content of weak acidic sites. That is why at its introduction into GAS-3 the active acidic component of the sample is diluted by pseudobeumite possessing lower acidic properties. The catalysts containing PB are characterised by significantly lower values of the specific surface, as compared with the initial GAS-3. The specific surface decreases mostly at the introduction of 10% PB, the further increase in binder concentration leads to a gradual reduction in the value of the specific surface of galloaluminosilicate catalyst. With the increase in PB concentration in GAS-3 a significant improvement of the mechanical catalyst strength is observed (Table 2). The samples containing 20 and 30% PB are characterised by fair mechanical properties because it is necessary to apply significant efforts to destruct the catalyst grains: respective strength factors are 0.54 and 0.74 kg/mm of diameter.

Initial AS converts the mixture of C_2-C_4 light alkanes into aromatic hydrocarbons at a selectivity of about 30%. Maximum arenes amount is formed over this catalyst at 600°C and space velocity of 100 h^{-1}. Galloaluminosilicates perform the aromatization of light alkanes more effectively than aluminosilicates. In this case, they exhibit already a high catalytic activity at 450°C, at 500°C the initial gaseous raw material is converted almost completely on GAS-2 and GAS-3 (Fig. 1). The selectivity of formation of aromatic hydrocarbons significantly depends on gallium content in a zeolite. The aromatization activity of a catalyst increases with gallium concentration in GAS, the maximum yield of the product is observed on GAS-3 containing 2.2% Ga_2O_3. Further increase in gallium concentration in GAS or a total replacement of Al by Ga leads to a slight decrease in aromatization activity of a catalyst and increase in its cracking activity. Thus, the selectivity of the formation of aromatic hydrocarbons on GAS containing an optimum gallium concentration reaches almost 60%, whereas on AS and GS it does not exceed 20 and 45% at 500°C and flight rate of 100 h^{-1}, respectively. This evidences the prospects of application of galloaluminosilicate catalysts in the process of aromatization of light alkanes.

One of the important goals of oil processing is the creation of highly stable catalysts, *i.e.* the catalysts retaining their catalytic activity and selectivity for

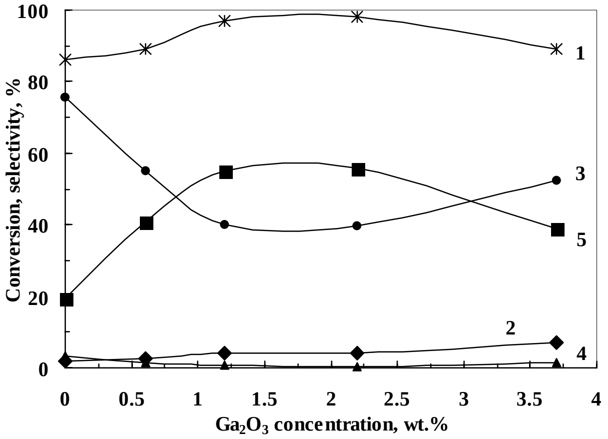

Fig. 1. Relationship between the conversion (1) of light alkanes and selectivity of the formation of hydrogen (2), alkanes (3), alkenes (4), and aromatic hydrocarbons (5) and Ga_2O_3 concentration in a zeolite (T=500°C, GHSV= 100 h^{-1}).

desired end products as long as possible. In this connection, we studied the stability of operation of gallium-containing zeolite catalysts prepared in the process of light alkanes conversion into aromatic hydrocarbons.

Table 3 shows the data on the effect of the period of GAS and GS operation on catalytic properties. Aluminosilicate retains its catalytic activity constant for approximately 24 h, and then the conversion degree and selectivity of aromatic hydrocarbon formation are decreased. At the same time the selectivity of light olefins formation is increased, the selectivity of alkanes formation changes insignificantly.

Gallium introduction into a zeolite during hydrothermal synthesis leads, along with a significant increase in aromatization stability of a catalyst, to a significant increase in the period of its stable operation. Investigations of catalytic GAS and GS properties showed that depending on gallium content the time of stable catalyst operation changes from 50 to 200 h at a process temperature of 500°C and flow rate of 100 h^{-1}. In addition, we should note that an insignificant increase in the selectivity of formation of aromatic hydrocarbons is observed during the first 24 hours that is related to GAS and GS operation under the action of the reaction medium (Fig. 2). A catalyst containing 2.2% of Ga_2O_3 demonstrated the highest catalytic stability in the process of light alkanes aromatization. Its period of stable operation is more than 200 h, the selectivity of aromatic hydrocarbon formation remains high even after 200 h test that makes it possible to carry on the process further. Temperatures rise to 550°C leads to the recovery of initial activity and selectivity of GAS-3, although, as shown by further studies, catalyst deactivation occurs faster at this temperature.

Nevertheless, despite of high activity and selectivity of GAS-3 in the aromatization of light alkanes, it may not be used in a commercial installation because it does not meet the requirements imposed to interlaminar and wear strengths. As a result, a significant entrainment of catalyst particles by the reac-

Table 3

Changes in catalytic properties of AS, GAS and GS in the process of light alkanes aromatisation with operation time (t) (GHSV=100 h^{-1}).

Catalyst	t (h)	$T_{reaction}$ (°C)	X (%)	A (%)	S_1 (%)	S_2 (%)	S_3 (%)
AS	1	600	98	28.0	28.3	68.1	1.4
	16	600	97	29.8	30.7	58.2	7.4
	24	600	96	30.6	31.9	56.4	8.2
	30	600	89	27.8	31.2	53.5	12.2
	48	600	77	18.7	24.5	51.1	22.1
GAS-2	1	500	97	53.3	54.9	40.0	0.6
	24	500	99	55.1	55.7	39.5	0.5
	30	500	95	51.0	53.7	40.3	0.9
	48	500	91	45.3	49.8	43.1	1.9
	72	500	81	38.9	48.0	43.8	3.8
	96	500	69	31.0	44.9	43.9	7.5

Table 3

Continued

Catalyst	t (h)	$T_{reaction}$ (°C)	X (%)	A (%)	S_1 (%)	S_2 (%)	S_3 (%)
GAS-3	1	500	98	54.8	55.9	39.6	0.3
	24	500	99	57.3	57.9	37.5	0.3
	48	500	99	57.3	57.9	37.1	0.4
	72	500	98	52.6	53.7	41.3	0.6
	96	500	98	51.7	52.8	42.2	0.6
	120	500	97	50.9	52.5	42.3	0.8
	144	500	94	50.6	53.9	39.3	1.3
	168	500	93	41.8	45.3	47.5	1.7
	192	500	90	40.2	44.7	47.7	2.2
	216	500	84	38.5	45.8	43.5	3.9
	217	550	98	53.3	54.4	37.0	1.7
	240	550	91	49.8	54.8	33.9	4.9
GAS-4	1	500	89	34.6	38.9	52.3	1.6
	24	500	92	50.2	54.6	36.9	1.8
	48	500	92	45.5	49.5	42.0	2.0
	72	500	89	42.8	48.1	43.0	2.5
	96	500	85	40.0	47.0	43.5	3.1
	120	500	80	36.0	45.1	44.1	4.4
GS-60	1	500	94	41.1	43.7	48.6	1.1
	24	500	93	51.2	55.1	38.3	1.5
	48	500	91	47.4	52.1	40.8	1.9
	72	500	86	41.4	48.1	42.9	2.9
	96	500	85	39.3	46.2	44.9	3.2
	120	500	77	35.6	46.2	43.1	4.7
GS-120	1	500	73	28.1	38.5	52.1	3.6
	24	500	75	34.9	46.5	41.5	4.9
	48	500	74	34.1	46.1	41.8	5.3
	72	500	71	31.4	44.2	42.8	6.3
	96	500	70	30.4	43.4	43.2	6.4
	120	500	68	29.0	42.7	43.1	7.1

Note. X is conversion degree; A is yield of aromatic hydrocarbons; S_1, S_2 and S_3 are selectivities of the formation aromatic hydrocarbons, C_1-C_2 alkanes and C_2-C_3 alkenes, respectively.

tion products takes place. Mechanical properties of the catalyst may be improved by the introduction of a binder (pseudobeumite) into the zeolite composition. On the basis of the study performed it was established that an optimum binder content in GAS-3 is about 20 wt.%. GAS-3/20%-PB is characterised by the activ-

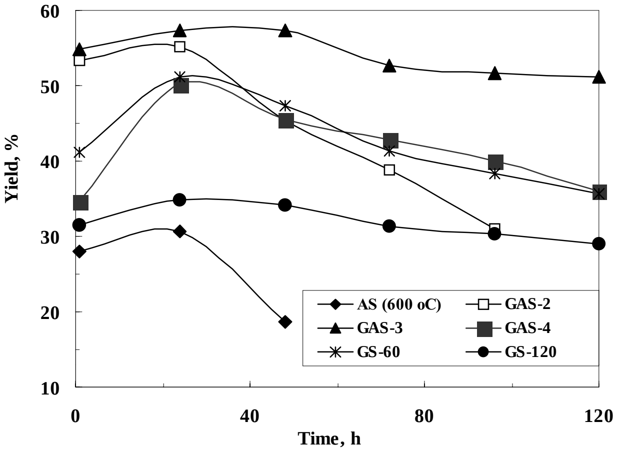

Fig. 2. Relationship between the yield of aromatic hydrocarbons and the operation time of Ga-containing zeolites (T=500°C, GHSV =100 h^{-1}).

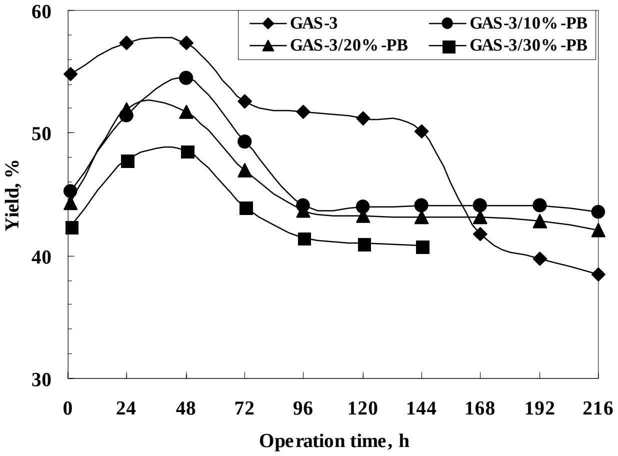

Fig. 3. Relationship between the yield of aromatic hydrocarbons and the operation time of GAS-3 containing different amounts of the binder (T=500°C, GHSV=100 h^{-1}).

ity and selectivity comparable to those of other catalysts, and the stability of its operation surpasses that of GAS-3/30%-PB and compares well with GAS-3/10%-PB, it possesses a much higher mechanical strength (Fig. 3).

In accordance with thermal analysis data, the total weight of coke deposits for AS after a complete operating cycle (48 h) in the process of light alkanes conversion is 16% (Table 4). This is a rather high content because all the other catalysts studied contain a significantly lower coke amount, although they have operated several times longer. In addition, the structure of coke deposits formed on AS during the process significantly differs from that of the condensed products formed on GAS and GS. For AS on DTA curve a peak smearing is observed, higher temperatures of the forms of burnout of coke deposits are characteristic (470-670, 670-850, 850-900°C) pointing to the presence of a wide range of coke deposits structure and a high degree of their polycondensation. An increased content of highly condensed products on AS is connected obviously with the fact that on its surface there is a large number of strong acidic sites immediately participating in the reactions leading to an intensive catalyst carbidization and a quick loss of its activity. AS regeneration due to the formation of coke deposits with a high polycondensation degree on AS is very problematic.

Table 4

Characteristics of coked catalysts

Catalyst (operation period, h)	T_{max}, forms of the coke burn-out (°C)			T_b, (°C)	Coke amount (%)
	I	II	III		
AS (48)	630	775	880	900	16.0
GAS-2 (96)	605	690	760	800	10.9
GAS-3 (240)	600	690	760	800	11.9
GAS-4 (120)	600	695	-	720	8.2
GS-60 (120)	580	-	-	640	8.2
GS-120 (120)	585	-	-	660	8.2
GAS-3/10%-PB (240)	550	610	-	a shoulder to 770	12.0
GAS-3/20%-PB (340)	580	700	-	a shoulder to 1020	19.6
GAS-3/30%-PB (200)	540	640	-	a shoulder to 925	16.4

Note. T_b is the temperature of the coke burnout

Condensed products formed on GAS with different Ga_2O_3 content differ by their structure. In case when it is possible to distinguish 3 exoeffects on DTA curve for GAS-2 in the regions of 450-650, 650-720 and 720-800°C with respective maximum points at 605, 690 and 760°C, GAS-4 is characterised by the presence of 2 exoeffects in the regions of 450-660 and 660-720°C with respective maximums at 600 and 695°C. This evidences the formation of less condensed coke on GAS-4 as compared to GAS-2. It is worth noticing that GAS-4 contains a lower amount of coke deposits (8.2%), despite of a longer service time. The service time of GAS-3 sample was 2.5 times longer than that of GAS-2 sample, nevertheless, the quantity and properties of coke formed on it slightly differ from corresponding characteristics of the coke formed on GAS-2. GS thermograms show only one exothermal peak within 450-650°C with a marked maximum at 580-585°C, the temperature of the coke burnout does not exceed 660°C (Table 4).

Thus, the data of differential thermal analysis evidence that the increase in gallium concentration and decrease in aluminium concentration in a gallium-containing zeolite catalyst lead to the decrease in intensity of coke formation and to the formation of less condensed coke deposits that allows one to carry out the oxidative regeneration readily. The data obtained agree well with the results of the tests of catalytic samples activity. Thus, the increase in gallium concentration in GAS leads to the increase in catalyst life between regenerations, which is explained by a reduced rate of the coke formation process. At the same time it is worth noticing that a sufficient decrease in aromatizing GAS activity occurs while a certain aluminium concentration is reached, that is why, to produce the most efficient catalyst of light alkanes aromatization, it is necessary to determine an optimum gallium-aluminium ratio.

Among the catalysts mixed with a binder, GAS-3/20%-PB contains the highest coke amount, which is explained by a longer operation time. On DTA curve for GAS-3/20%-PB one may allocate two exothermal peaks in the region 400-640 and 640-740°C with respective maximums at 580 и 700°C and a wide shoulder to 1020°C. The temperature of the coke burnout (1020°C) evidences a high polycondensation degree. The nature of the coke deposits formed on GAS-3/20%-PB and GAS-3/30%-PB is very close. The initial GAS-3 and GAS-3/10%-PB contain significantly lower amounts of coke, and the condensed products formed are less condensed which is confirmed by a lower temperature of the coke burnout. GAS-3/10%-PB is characterised by the presence of two exothermal peaks in the region 400-580 and 580-680°C with respective maximums at 550 and 610°C, and a small shoulder to 770°C. The amount of coke formed in 240 h of operation is 12.0%.

Thus, the data of differential thermal analysis demonstrate that the increase in the period of a continuous catalyst operation above 250 h leads to a slow formation of highly condensed products, as a result, its regeneration will be very problematic. A prolonged life between regenerations of a galloaluminosilicate catalyst followed by a slight decrease in activity, leads to its irreversible deactivation, an excess accumulation of highly condensed coke deposits leads to catalyst overheating during the regeneration process. That is why the service cycle of GAS-3/20%-PB should not exceed 240-250 h, then it is necessary to perform an oxidative regeneration. Coke formed on GAS-3/30%-PB is characterised by a high polycondensation degree though it has operated for a shorter time.

Summarising the above results for galloalumino- and gallosilicate catalysts, one may construct a histogram as follows (Fig. 4).

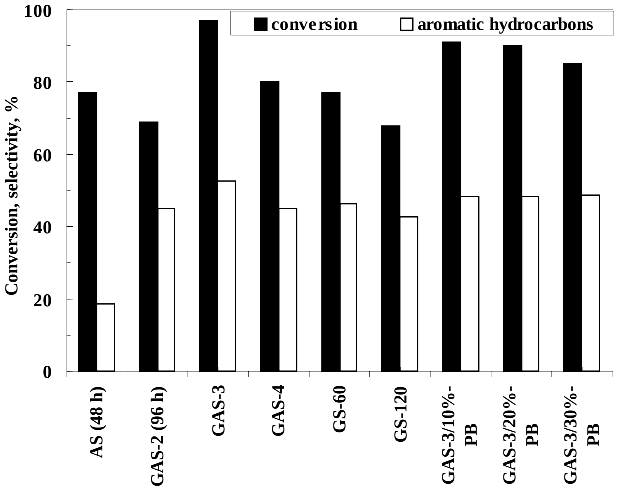

Fig. 4. Conversion of light alkanes and selectivity of aromatic hydrocarbons formation on Ga-containing zeolites within 120 h of operation at 500°C and 100 h^{-1}.

The most efficient catalyst among all the studied catalysts of C_2-C_4 light alkanes aromatization is a zeolite containing 2.2% of gallium oxide introduced at the stage of the hydrothermal synthesis and 1.3% of aluminium oxide, and mixed with 20% of pseudobeumite used as a binder. The selectivity of aromatic hydrocarbons formation reaches 55-60%, the reaction cycle should not exceed 250 h of operation for a complete coke removal using the method of oxidative regeneration. At the same time it is worth noticing that the service life of GAS-3/20%-PB is more than 350 h.

Conclusion

Under hydrothermal conditions gallium-containing zeolites of different compositions were synthesised from alkaline aluminosilicagels with the introduction of gallium nitrate and hexamethylene diamine as a structure-forming template.

Gallium introduction into a zeolite on the stage of hydrothermal synthesis results in the formation of strong aproton acidic sites characterised by a high energy of ammonia retention.

Crystalline galloaluminosilicates with pentasil structure possess higher catalytic activity and stability in light alkanes aromatization as compared to alumino- and gallosilicates.

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