

Conversion of C₂-C₄ Low Alkanes on ZSM-5 Containing Zn Nanoparticles

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Abstract

Mixed catalysts were prepared on the basis of a synthesized high-silica ZSM-5 zeolite and an electroexplosion nanosized zinc powder. The influence of Zn concentration in a zeolite on its acidic and catalytic properties in the reaction of C₂-C₄ low alkanes aromatization as well as the catalyst deactivation resulting from carbonization were studied.

Introduction

Catalysis of chemical reactions is an important and wide field of application of metal nanosized particles [1-3]. A high catalytic activity of these particles is explained by electron and geometric effects resulting from a small particle size [4-6]. A high dependence of the catalytic activity on the particle size emphasizes the need to develop selective methods to produce nanosized particles with a precision of 1-2 atoms. One of the rapidly developing methods for the synthesis of nanocrystal powders is the conductor electroexplosion carried out by passing a powerful current pulse with a width of 10⁻⁴-10⁻⁶ A/mm² [7,8]. As a result, the formation of energetic and geometric structures occurs at extremely high temperature gradients that leads to an insignificant non-equilibrium of physicochemical processes. Metastable particles formed are characterized by structure deficiency, a developed inner surface and a high energy saturation. Obviously, this complex of the properties of nanosized powders (NSP) produced by electroexplosion determines their high catalytic activity in chemical processes. In this connection the study of physicochemical properties of nanosized metal powders and establishment of the catalysis fields where they would find a practical application is a very important and urgent task.

Experimental

The synthesis of ZSM-5 with a silicate modulus SiO₂/Al₂O₃=50 was carried out by hydrothermal

crystallization of alkali aluminosilicagels at 175°C for 4-6 days. A 30% sol of silica acid or water glass (29% SiO₂, 9% Na₂O, 62% H₂O) was the silicon source, aluminum nitric salt was aluminum oxide source. The initial reaction mixture had the composition as follows: 17.5 Na₂O · 6.1R · Al₂O₃ · 60 SiO₂ · 3275 H₂O, where R is hexamethylenediamine. After the crystallization the zeolites were washed by the distilled water and dried at 100°C for 24 hours. To change the samples over the active H-form they were twice decationized by 25 % aqueous NH₄Cl solution followed by drying at 110°C and calcined on air at 540°C for 6 hours. (Na₂O content in H-ZSM-5 was less than 0.02%).

The quality of the samples produced was checked by infrared spectroscopy (IRS), electron microscopy and X-ray structure analysis (XSA). Microscopic studies were carried out on SEM LEO-420 microscope at the resolution of 15 Å. In accordance with IRS (SPECORD M80) and XSA (DRON-3 and CuK_α irradiation) data the samples synthesized have a high crystallinity degree (96%), do not contain amorphous phase admixtures and are qualified as ZSM-5 type.

A nanosized Zn powder was produced on a laboratory installation by the electroexplosion of a wire 0.1-0.2 mm in diameter in argon atmosphere. Wire electroexplosion is a drastic change in the physical state of a metal due to an intensive energy release when passing a high-density pulsed current [9]. On the condensation in the flow of a rapidly broadening vapor a zinc powder was produced with an average particle sized of approximately 100 nm which had a spherical shape. Using a ball vibrating mill the samples having different contents of the promoter were pre-

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pared by dry mixing of a zeolite and Zn NSP on air for 2 hours. To carry out comparative studies we prepared zeolite catalysts where the commercial zinc was introduced by ion exchange or mechanical mixing. Catalyst characteristics and their codes are given in Table 1. The catalysts were pressed into pellets. A fraction of 0.25-0.50 mm was taken for tests using special sieves.

Table 1
Characteristics and codes of the catalysts

Catalyst codes	Zn concentration in a zeolite (wt%)	Method for Zn introduction into a zeolite
C	0	-
C-1	0.125	mixing with Zn NSP
C-2	0.25	mixing with Zn NSP
C-3	0.5	mixing with Zn NSP
C-4	0.75	mixing with Zn NSP
C-5	1.0	mixing with Zn NSP
C-6	2.0	mixing with Zn NSP
C-7	3.0	mixing with Zn NSP
C-8	0.5	mixing with commercial Zn mixing
C-9	0.5	with ZnO
C-10	0.5	ion exchange followed by impregnation
C-11	1.5	a commercial sample

The testing of acidic properties of the catalyst surface was carried out by temperature-programmed desorption (TPD) of ammonia. The procedure of TPD experiments has been described in [10]. To calculate the values of activation energy, ammonia desorption from the samples was carried out at different heating rates – 5, 10, 15 and 20 grad/min. Activation energies were determined in accordance with the procedure described in [11].

The catalytic activity and stability of zinc-containing zeolites were studied in the process of the conversion of C₂-C₄ alkanes mixture into aromatic

hydrocarbons. The tests were carried out on the flow type installation, with the reactor volume of 5 cm³ at atmospheric pressure, reaction temperature of 350-600°C and volumetric flow rate of 50-400 h⁻¹. The reaction products were analyzed by gas chromatography. The stability of the catalyst operation was assessed by the changes in the degree of the initial raw material conversion and in the selectivity of the formation of aromatic hydrocarbons.

DTA-DGA patterns of carbided catalysts were recorded using «C» DTA-DGA 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 grad /min.

Results and Discussion

Table 2 shows the results of the investigations of acidic properties of zeolites modified by Zn nanosized powders.

An unmodified zeolite has two types of acidic centers that is evidenced by the presence of two forms of ammonia desorption on a TD spectrum: weak acidic sites with the temperature of the peak ($T_{\max}$) of 210°C and strong acidic sites with $T_{\max}$ of 425°C. The concentration of weak acidic sites is 270.5 μmol/g, that of strong acidic sites is 243.7 μmol/g. Activation energy is 33.3 and 123.3 kJ/mol for I and II forms of ammonia desorption, respectively. When adding a small amount of Zn NSP to a zeolite, the strength and the concentration of strong acidic sites decrease. When zinc concentration is brought to 4%, the smoothening of the high-temperature maximum on the thermodesorption spectrum is observed and its exact determination becomes impossible. In addition, the strength and the concentration of weak acidic sites as well as the activation energy of ammonia desorption decrease (Table 2).

Therefore, the investigations of acidic properties of a catalyst demonstrated that on the introduction of Zn NSP into a zeolite the redistribution of acidic sites by strength and concentration as well as the formation of new acidic sites with a higher energy of ammonia retention occur. The most significant influence is caused by Zn NSP on strong acidic sites of a zeolite; a pronounced decrease in strength and concentration of weak acidic sites is observed at the zinc content more than 1%. As a result the ratio between weak and strong acidic sites of a zeolite changes that influences its catalytic properties and hydrocarbon conversion because specific active sites are responsible for the oc-

Table 2

Acidic properties of the initial zeolite and a zeolite containing different amounts of Zn NSP

Catalyst	$T_{\max}$ (°C)		Concentration ^a (μmol/g)			$E_{\text{dec.act.}}$ ^b (kJ/mol)	
	form I	form II	C_1	C_2	C	E_I	E_{II}
C	210	425	270.5	243.7	514.2	33.3	123.3
C-1	210	425	270.5	243.7	514.2	33.3	124.6
C-2	210	420	270.5	240.6	511.1	33.3	146.8
C-3	210	415	266.9	235.6	502.5	32.8	157.9
C-4	210	415	265.5	228.1	493.5	32.8	157.9
C-5	210	410	260.5	221.3	481.8	30.4	164.5
C-6	210	400	241.3	180.6	421.9	28.4	103.6
C-7	200	-	225.3	-	225.3	18.2	-

^a C_1 , C_2 and C: concentration of acidic sites of form I and form II and total concentration, respectively.^b E_I and E_{II} : activation energy of ammonia desorption for form I and form II, respectively.

currence of one or other chemical reaction.

In the presence of a novel class of heterogeneous catalysts – ZSM-5 high-silica zeolites – C_2 - C_4 saturated hydrocarbons are converted into a mixture of C_6 - C_9 aromatic hydrocarbons (mainly, benzene, toluene, xylenes) and higher that may be used as high-octane additives to motor fuels or as individual components after rectification. Gaseous products contain hydrogen, methane, and C_2 - C_4 hydrocarbons of different homologous series. The selectivity of aromatic hydrocarbon formation on the initial ZSM-5 is usually about 30% at the process temperature of 550-600°C. It is possible to improve the catalyst selectivity toward the formation of aromatic hydrocarbons by introducing promoters. Zn belongs to such promoters; in this case the concentration of the metal introduced determines the catalyst activity.

Preliminary tests of the catalytic activity of Zn NSP in the process studied have shown that the feedstock conversion does not occur under the above operation conditions. The rise in the temperature above 600°C leads to the occurrence of the reactions of thermal cracking. It is connected with the fact that alkanes conversion occur only in the presence of a bifunctional catalyst with an optimum combination of dehydrogenating and acidic properties.

Fig. 1 shows the results of the study of C_2 - C_4 alkanes on a modified zeolite catalyst. On the introduction of 0.125 wt% of Zn NSP into a zeolite an increase in the total catalyst activity (evaluated by the degree of the feedstock conversion) is observed at 500°C, at 550°C the initial mixture of C_2 - C_4 n-al-

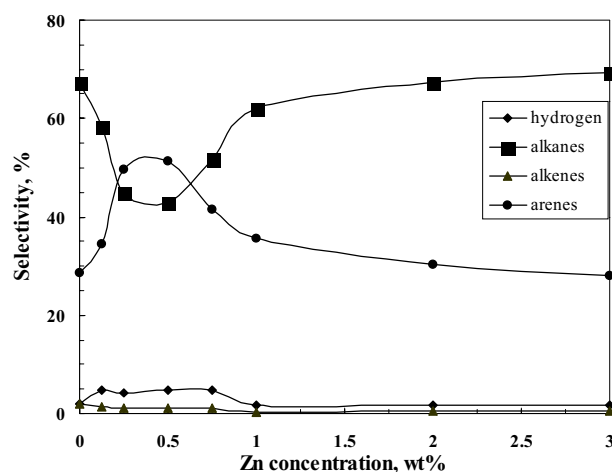


Fig. 1. Relationship between the selectivity of the formation of the products of C_2 - C_4 alkanes conversion and Zn NSP concentration in ZSM ($T=550^\circ\text{C}$, $W=100\text{ h}^{-1}$).

kanes is converted almost completely. On an unmodified zeolite the conversion degree reaches 99% at 600°C only. At 500-550°C the content of aromatic hydrocarbons increases, the concentration of C_1 - C_2 alkanes in the reaction products decreases. The increase in the volumetric flow rate by 2 times leads to a small decrease in the conversion degree, whereas the selectivity of aromatic hydrocarbon formation increases by more than 3%. The selectivity of hydrogen and C_2 - C_3 olefins formation also increases. When Zn NSP concentration in a zeolite increases to 0.25 wt%, the catalyst activity in the reaction of low alkanes aromatization further increases. Thus, the selectivity of arenes formation on C-2 catalyst at 550°C and 100 h^{-1} was 49.7% at the conversion degree of

99%, whereas on C sample these characteristics were 28.5 and 96%, respectively. Zn NSP concentration in a zeolite brought to 0.5 wt% led to a still more significant increase in the aromatizing catalyst activity, the selectivity of arenes formation was 51.3% at 550°C, that is almost by 2 times higher than on the initial catalysts. At the same time decreases the formation of by-products (C₁-C₂ alkanes). The increase in the volumetric flow rate to 200 and 300 h⁻¹ leads to a smooth decrease in the conversion degree and the selectivity of arenes formation and to the increase in the selectivity of C₁-C₂ alkanes and C₂-C₃ olefins formation. It should be also noted that despite of the increase in the volumetric charge on the catalyst by 2-3 times its aromatizing activity remains high and the selectivity of arenes formation exceeds 40%.

Zn NSP concentration brought to 0.75 wt% has led to the decrease in the selectivity of aromatic hydrocarbons formation as compared to C-3 catalyst by 8.6% at 550°C and 100 h⁻¹, although total catalyst activity retains high (the conversion degree is 98%). At the further increase in Zn NSP concentration in a zeolite by 0.25 wt%, i.e. when its content is brought to 1 wt%, a more significant decrease in the selectivity of aromatic hydrocarbon formation and the increase in the formation of by-products occur. On the increase in Zn NSP concentration in ZSM-5 the general tendency of decrease in the selectivity of arenes formation and increase in C₁-C₂ alkanes formation retains. The catalysts containing 1, 2, and 3 wt% of Zn NSP exhibit a high aromatizing activity at the initial process temperatures, i.e. at 450-500°C. There is observed a formation of a rather large quantity of aromatic hydrocarbons. When the temperature rises to 550°C, there is no rise in arenes yield on these catalysts, by the contrast a large amount of by-products is formed. It should be noted that on C-6 and C-7 catalysts practically the same amount of aromatic hydrocarbons is formed as on the initial catalyst.

Thus, the results obtained evidence that the increase in Zn NSP content in ZSM-5 to 1 wt% and higher leads to a sufficient decrease in the catalyst activity in the reaction of C₂-C₄ low alkanes aromatization and to the increase in its activity in cracking. The optimum Zn NSP concentration in a zeolite is 0.5 wt% because on C-3 catalyst the largest quantity of aromatic hydrocarbons is formed (51.3%).

Table 3 shows the data on the influence of Zn NSP concentration in a zeolite and the nature of the modifier on the yield of the desired product and the composition of gaseous and liquid products of C₂-C₄

low alkanes conversion at 550°C and 100 h⁻¹. The yield of aromatic hydrocarbons sufficiently increases at the zeolite modification by Zn. Thus, on an unmodified ZSM-5 the yield was 27.4%, whereas on C-1 catalyst it was already 34.1 wt%. The yield reaches 49-50% on zeolites containing 0.25 and 0.50 wt%. The increase in Zn NSP concentration in ZSM-5 to 0.75 wt% and higher leads to the decrease in the yield of the catalysate that contains less C₆-C₈ aromatic hydrocarbons, the fraction of C₉₊ hydrocarbons being drastically increased. With the increase in Zn NSP content in a zeolite from 1.0 to 3.0 wt% the gaseous products contain more methane and less ethane and hydrogen, olefins content practically does not change. An insignificant content of C₂-C₃ olefins evidences that they are intermediate products that actively enter further interactions leading to the production of aromatic hydrocarbons. Thus, by analyzing the data on the influence of Zn NSP concentration in a zeolite on the composition of the conversion products of the mixture of C₂-C₄ low alkanes, it is possible to note that with the increase in the concentration the contents of benzene, toluene, xylenes in the reaction products change distinctly and pass through the extremum, the concentration of higher molecular aromatic compounds passes through minimum. The maximum quantity of benzene - toluene - xylenes fraction (BTX-fraction - 82.7%) is in the liquid product obtained on C-3 catalyst.

As seen from the data of the Table 3, quantitative compositions of the products obtained on the catalysts with different kinds of Zn differ greatly. Thus, the largest quantity of BTX-fraction is formed on C-3 and C-11, in this case the compositions of the liquid products obtained are close. So is the composition of the catalysts obtained on C-8 and C-9 samples. Hydrogen, ethylene and propylene contents in gaseous products obtained on different Zn-containing catalysts vary insignificantly, whereas methane and ethane contents differ greatly: a larger amount of methane and that smaller of ethane are formed on C-3 and C-10 catalysts than on C-8, C-9 and C-11 catalysts. The differences revealed in the composition of gaseous and liquid products formed on the catalysts under study are conditioned by different rates of the occurrence of individual process stages, i.e. the properties of a catalyst depend on the method for the introduction of the modifying metal, its physicochemical properties and the electron state of the catalyst.

On the basis of the experimental data obtained from the study of acidic and catalytic properties of the

Table 3
Composition of the products of C₂-C₄ low alkanes conversion on a zeolite catalyst containing different amounts of Zn NSP, and on the conventional catalysts
(T_{reaction}=550 °C, W=100 h⁻¹)

Catalyst	Catalysate yield (wt%)	Composition of liquid hydrocarbons (wt%)				Composition of gaseous products (wt%)						
		benzene	toluene	C ₈ aromatics	C ₉₊ aromatics	H ₂	CH ₄	C ₂ H ₄	C ₂ H ₆	C ₃ H ₆	C ₃ H ₈	
C	27.4	22.3	31.4	11.3	35.0	2.6	57.0	2.3	32.1	0.4	5.5	
C-1	34.1	24.5	33.5	11.7	30.3	7.7	62.5	2.0	26.2	0.1	1.5	
C-2	49.2	27.2	37.8	11.8	23.2	8.5	60.6	2.0	26.7	0.2	2.0	
C-3	50.8	31.9	39.4	11.4	17.3	9.8	60.1	2.0	25.9	0.2	2.0	
C-4	41.9	25.8	34.6	15.0	24.6	9.0	60.4	1.5	25.5	0.2	3.4	
C-5	35.7	16.7	30.7	9.5	43.1	2.8	63.1	0.6	33.4	-	-	
C-6	30.2	12.6	22.5	8.6	56.3	2.6	72.2	0.7	24.5	-	-	
C-7	28.2	9.5	16.3	7.1	67.0	2.4	85.7	1.0	11.0	-	-	
C-8	42.4	29.7	30.4	9.4	30.5	10.1	53.5	1.4	31.4	0.1	3.5	
C-9	29.4	28.6	33.0	7.8	30.6	8.6	55.8	1.7	32.3	0.1	1.4	
C-10	43.3	25.2	34.2	9.0	31.6	8.3	59.3	2.5	28.0	0.1	1.8	
C-11	44.4	31.1	36.7	12.2	20.0	9.2	49.3	2.3	31.7	0.4	7.1	

samples prepared it is possible to establish the role of the specific acidic sites in the acceleration of individual stages of the process of low alkanes aromatization. Thus, the activity of the initial H-ZSM-5 is determined by the presence of strong Brönsted sites where take place the cracking of saturated hydrocarbons and further transformations of olefins formed (oligomerization, hydrogen redistribution etc.). For Zn/HZSM-5, the dehydrogenation of initial paraffins and aromatization of unsaturated compounds occurs over strong Lewis sites containing Zn²⁺ cations. That is why, to obtain an effective catalyst of C₂-C₄ low alkanes aromatization, an optimum proportion of strong Lewis and Brönsted acidic sites is necessary. The fraction of strong Lewis sites being determined by Zn NSP concentration in HZSM-5, to reach an optimum proportion of acidic sites of different types, this concentration should be 0.5 wt%, as shown above.

As seen from the data of Table 4, the activity of conventionally produced C-8, C-9 and C-10 catalysts compares well with the activity of C-3 catalyst. The degree of conversion of the initial feedstock retains high (98-99% at 550°C and 100 h⁻¹). Nevertheless, the selectivity of aromatic hydrocarbon formation on C-8, C-9 and C-10 catalysts is sufficiently lower than on C-3 catalyst. A zeolite where zinc was introduced by ion exchange followed by the impregnation (43.7%) has the highest selectivity towards aromatic hydrocarbons. The formation of by-products (C₁-C₂ alkanes) increases on the catalysts produced using conventional methods that evidences a significant reaction rate of cracking and hydrogenation of intermediate compounds formed.

The application of C-11 catalyst allows producing aromatic hydrocarbons from saturated C₂-C₄ hydrocarbons at 450°C and 100 h⁻¹. With the increase in the reaction temperature a significant increase in the conversion degree and selectivity of arenes formation occurs. At 550°C and 100 h⁻¹ these values are 96 и 46.3%, respectively. The activity of C-11 catalyst is lower than that of C, C-8, C-9 and C-10 catalysts, its selectivity for aromatic hydrocarbon formation is somewhat higher. Nevertheless, its total and aromatizing activities are lower than those of C-3 catalyst are.

Fig. 2 shows the results of the study of the influence of the operating period of Zn-containing catalysts on their catalytic properties. Since unmodified ZSM-5 reveals the highest activity in the reaction of low alkanes aromatization at 600°C, the determination of its stable operation period was carried out at this tem-

perature. On Zn-containing zeolites the initial gaseous feedstock is converted almost completely at 550°C, that is why the period of their time between regenerations was determined at that temperature.

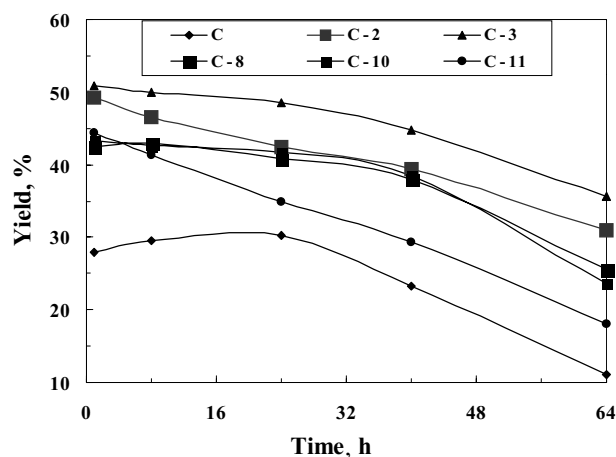


Fig. 2. Relationship between the yield of aromatic hydrocarbons and the operation time of ZSM-5 (T=600°C) and Zn-containing zeolites (T=550°C, W=100 h⁻¹).

The initial H-ZSM-5 retains its catalytic activity constant for about 24 hours, then the decrease in the conversion degree and in the selectivity of the formation of aromatic hydrocarbons is observed. At the same time the increase in the selectivity of low olefins formation occurs, and the selectivity of alkanes formation changes insignificantly.

Zn NSP introduction into a zeolite leads, along with a significant increase in the catalyst aromatizing activity, to the rise in its operating period. Zeolites containing Zn NSP or conventional catalysts have a stable operating period for 40 hours. A commercial catalyst has a stable operating period of 8 hours, then a drastic decrease both in the conversion degree of the initial feedstock and in the yield of aromatic hydrocarbons are observed. At the same time the concentration of C₂-C₃ olefins rises being connected with the deceleration in the reaction rate of hydrogen redistribution.

Conventional catalysts (C-8 and C-10) are characterized by very close indices of activity and stability in the process of low alkanes aromatization. A zeolite containing 0.5% Zn NSP possesses the highest operation stability among the samples studied. We also should note a high catalytic operation stability of C-2 sample. In 40 hours of continuous operation the conversion degree and selectivity of aromatic hydrocarbon formation on C-3 decrease only by 5 and 3.8% respectively, in 64 hours - by 19 and 6.7%. On

Table 4
Characteristics of the products of the conversion of C₂-C₄ low alkanes mixture on ZSM-5 and Zn/ZSM-5

Catalyst	W (h ⁻¹)	T _{reaction} (°C)	X (%)	S ₁ (%)	S ₂ (%)	S ₃ (%)	S ₄ (%)	A (%)
C	100	450	60	1.4	76.6	7.4	14.7	8.8
	100	500	86	1.8	75.5	3.3	19.4	16.7
	100	550	96	2.0	67.4	2.1	28.5	27.4
	100	600	99	2.2	68.1	1.4	28.3	28.0
	200	600	92	1.8	66.1	2.4	29.7	27.3
C-3	100	450	61	3.9	78.5	3.2	14.5	8.8
	100	500	88	4.3	59.2	1.7	34.8	30.6
	100	550	99	4.8	42.9	1.1	51.3	50.8
	200	550	95	6.6	44.7	3.3	45.4	43.1
C-8	100	450	62	2.0	80.0	2.9	15.1	9.4
	100	500	90	3.6	62.2	0.9	33.3	30.0
	100	550	98	5.9	50.0	0.9	43.3	42.4
	200	550	97	6.2	49.6	1.5	42.7	41.4
C-9	100	450	59	3.9	85.5	3.0	7,6	4,5
	100	500	89	4.4	57.5	1.6	36.5	32.5
	100	550	99	6.2	62.8	1.3	29.7	29.4
	200	550	98	7.3	59.7	1.7	31.3	30.7
C-10	100	450	61	2.3	70.6	4.5	22.6	13.8
	100	500	88	2.5	54.8	2.7	40.0	35.2
	100	550	99	4.7	50.0	1.6	43.7	43.3
	200	550	99	4.8	50.0	2.2	43.0	42.6
C-11	100	450	51	3.1	67.5	5.0	24.4	12.4
	100	500	78	3.4	60.3	4.5	31.8	24.8
	100	550	96	5.3	46.8	1.6	46.3	44.4
	200	550	97	6.0	45.4	2.2	46.4	45.0

Note. W is the volumetric rate; X is the conversion degree; S₁, S₂, S₃ and S₄ are the selectivities of the formation of hydrogen, C₁-C₂ alkanes, C₂-C₃ alkenes and aromatic hydrocarbons, respectively; A is the yield of aromatic hydrocarbons.

conventional catalysts the decrease in these indices in 64 hours of operation is 25-28% and 8.2-10.7%. In addition, the yield of aromatic hydrocarbons formed on C-3 sample during all the operating period is significantly higher than on other catalysts.

Thus, from the above it appears that C-3 catalyst is the most effective in C₂-C₄ low alkanes aromatization. Its activity, selectivity and stability are significantly higher than those of traditional catalysts and

commercial samples. The selectivity of aromatic hydrocarbon formation on C-3 exceeds 50%, the conversion degree being 99% at the reaction temperature of 550°C and the volumetric feedstock flow rate being 100 h⁻¹. The time between regenerations is more than 60 hours, but the catalyst keeps a rather high catalytic activity towards the desired products after this period of time, which allows continuing the process if necessary. To establish the optimum duration

of the reaction cycle of a catalyst after which there would be no problems connected with the restoration of its catalytic activity by oxidative regeneration it is very important to study the process of coke formation and the nature of coke deposits.

In accordance with the data of differential thermal analysis for all the samples studied, the presence of overlapping exothermal effects within 460-920°C with pronounced extreme points within 620-640°C and less pronounced extremes points in the high-temperature region was established. This evidences the presence of a wide range of coke deposits (Fig.3).

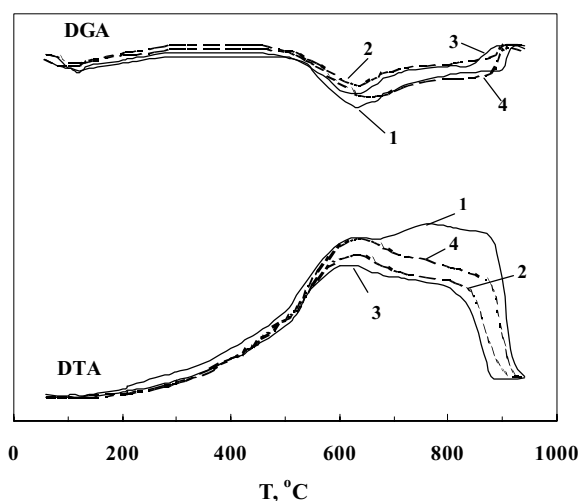


Fig. 3. DTA and DGA curves for coke deposits of C (1), C-2 (2), C-3 (3) and C-10 (4) catalysts.

The largest amount of coke is contained on the sample C (19.3%) that is explained by an intensive coke-formation reaction. Smearing of peaks and higher burn-out temperatures of coke deposits are observed on DTA curve for the catalyst C as compared to Zn-containing catalysts that points to their higher polycondensation degree. That is why the regeneration of this catalyst will be extremely difficult. Zn-containing catalysts have a lower quantity of coke deposits, the compaction products formed are less condensed that is confirmed by a lower temperature of the end of the coke burning.

The least coke amount is on C-3 catalyst (11.1%), this catalyst is characterized by the presence of an exothermal peak in the region from 460 to 680°C with a clear maximum at 620°C and the II form in the shape of a small shoulder before 860°C. In 64 hours of the operation of C-2 and C-10 catalysts larger amounts of coke were formed (11.7 and 14.3%, respectively), the form II and the end of the coke burnout are shifted

to a higher-temperature region, especially for C-10 catalyst.

Thus, the data on differential thermal analysis show that the introduction of Zn NSP into a zeolite leads to the decrease in the intensity of coke formation and production of less condensed coke deposits that make possible a relatively easy oxidative regeneration. The data obtained agree well with the results of the tests of the catalytic stability of Zn-containing catalysts. For example, C-3 catalyst reveals the highest activity in the process of C₂-C₄ low alkanes aromatization that is due to the decrease in the reaction rate of coke formation on this catalyst.

Conclusions

By mechanical mixing produced were zeolite catalysts containing different amounts of the electroexplosion nanosized Zn powder and conventional Zn as well the zeolites where Zn was introduced from Zn nitrate solution by ion exchange followed by impregnation. Zn introduction into a zeolite leads to the formation of strong aproton acidic Zn²⁺-containing sites characterized by a high energy of ammonia retention. The zeolites with Zn NSP introduced possess higher catalytic activity and stability in the aromatization of C₂-C₄ low alkanes as compared to conventional zinc-containing catalysts. A catalyst containing 0.5 wt% Zn NSP produced by mechanical mixing of Zn powder and ZSM-5 zeolite is the most effective for this process.

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