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Effect of the Nature and Amount of Binders for Activity of Ni/ZSM-5 Catalyst during Transformation of the Straight-Run Gasoline Fraction of Oil

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Abstract

The Ni/ZSM-5 samples were prepared by dry mechanical stirring of ZSM-5 zeolite with Ni nanopowder with 50 nm average particle size in terms of 0.5 mass %. Based on them, zeolite-containing catalysts with pseudoboehmite and hydrargillite containing 10, 20, 30 and 40 mass % of Al_2O_3 were obtained. Acid characteristics of the resulting samples were studied by the technique of temperature-programmed desorption of ammonia. The strength and concentration of catalyst acid sites were determined. Acidity decreased with increasing binder amount in zeolite, as established. Catalytic activity of nickel-containing samples with binder was studied during transformation of the straight-run gasoline fraction of oil. A part of pseudoboehmite used as binder to prepare catalysts could be replaced with its precursor, *i.e.* hydrargillite, as demonstrated. The yield of the liquid product, in the composition of which the aromatic hydrocarbon fraction decreased and the proportion of isoalkanes increased, rose at an increase of the binder content in the catalyst and carrying out transformation of the straight-run gasoline fraction of oil under high hydrogen pressure conditions.

Keywords: ZSM-5 zeolite, nickel nanopowder, binder, pseudoboehmite, hydrargillite, acidity, activity, straight-run gasoline fraction of oil, processing

INTRODUCTION

Binder characterized by the presence of active sites of this or that nature has significant effects on catalytically active metal components introduced into zeolite catalyst. The most efficient binder that combines high activity, selectivity, and mechanic strength of oil processing catalysts is γ-alumina. The advantage of aluminium oxide compared to other carriers (activated coal, aluminosilicates, silicates, Mg, Ti, and other metal oxides, and zeolites), in addition to cheapness and availability, consists in specific interaction with the modifying metal and stabilization of its high-dispersion active phase in catalyst surface [1].

So called active alumina used in the production of catalysts represents low-temperature unstable modification of γ-Al_2O_3 formed during thermal decomposition of aluminium hydroxides. All modifications of aluminium hydroxides and oxides are associated with each other by single alumino-oxygen system that has two extreme stable crystalline states, such as aluminium trihydroxides (γ-$Al(OH)_3$), or hydrargillite (GG), and α-Al_2O_3, *i.e.* corundum. Pseudoboehmite (PB), γ-AlOOH, in which GG turns into at 150–200 °C temperatures, is an intermediate, and alumina (γ-Al_2O_3) is formed at 150–200 °C temperatures [2]. It is possible to obtain carriers with various parameters of porous structure and mechanical strength when varying techniques for preparation of alumina [3, 4].

Hydrargillite is formed in processing of bauxites and after its calcination, transforms into alumina that is initial raw materials to obtain aluminum. World GG production is estimated in millions of tons per year. Hydrargillite is a single-phase sample, it is spherical aggregates of crystals with an average size of 80 microns, the specific surface is less than 5 m^2/g. Thermal treatment of GG at 300 °C increases the specific surface to 300 m^2/g, the formation of nanoscale pores and channels due to destruction of the structure of the initial GG during dehydration is also recorded. The reaction proceeds *via* the formation of the intermediate phase of PB in all cases [5].

Pseudoboehmite is aluminium hydroxide with the structure of boehmite, characterized by a low degree of crystallinity, has a developed surface and a high cohesive ability. Unlike GG, it is readily moulded, while macrocrystalline GG can be pressed only under very high pressure that destroys its crystalline structure. Alumina has a higher ability to adhesion than crystalline aluminium hydroxides but significantly lower compared to PB. In turn, among all modifications of aluminium oxides including amorphous (alumogel); γ-Al_2O_3 shows the highest ability to cohesion. This fact is driven by its crystalline structure formed by the densest cubic packing of oxygen atoms in the voids of which aluminum atoms are located. Due to this, a strong interatomic bond is formed due to intermolecular interactions at the expense of van der Waals forces within one phase representing the main condition of cohesion. Chemical bonds are formed between different crystals of the resulting alumina when calcining pseudoboehmite. Thus, from the physicochemical standpoint, all aluminium hydroxides are equivalent, however, pseudoboehmite that is alumina precursor is the most preferable hydroxide as binder [1].

Hydrargillite is mainly used in synthesis of aluminium oxide carriers for paraffin dehydrogenation catalysts and hydrodesulphurization [1]. Pseudoboehmite, as an alumina precursor finds wide applications as binders in oil processing catalysts, particularly those obtained on the basis of high-silica zeolites [7]. Being a component of the zeolite-containing catalyst, pseudoboehmite not only improves strength characteristics, but also affecting its acidity, increases the isomerizing ability of the catalyst in transformation of the straight-run gasoline fraction of oil.

Modification of ZSM-5 zeolite by nanosized nickel powder (NNP) contributes to not only an increase in the yield of liquid products with high contents of isoalkanes when transforming light hydrocarbon raw materials but also more stable catalyst performance compared to the initial sample, as established by us earlier [8]. This is related to the presence of nickel-containing active centres that take part in hydrogenation and dehydrogenation reactions. Atmospheric pollution with fuel combustion products that do not correspond to the modern environmental requirements is a global problem. To deal with the latter it is necessary to decrease the content of aromatic hydrocarbons in the composition of car gasolines, especially benzenes, herewith, their octane number should remain high. Therefore, isomerization of light hydrocarbon raw materials obtained from oil and gas condensate containing considerable amounts of normal alkanes is of great interest for the oil-processing industry, and the improvement and development of more efficient catalysts of this process is relevant.

EXPERIMENTAL

ZSM-5 high-silica zeolite with the silicate module of 40 was obtained by the hydrothermal synthesis method. Zeolite modification with nickel nanopowder obtained by gas-phase method in terms of 0.5 mass % of nickel oxide was carried out by the method of dry mechanical mixing in KM-1 vibrating mill for 2 h followed by pressing of the resulting mixture into tablets, crushing, and selecting a fraction of 0.5–1.0 mm for tests. Average particle size of NNP species was 50 nm.

To prepare catalysts with binder the plastic mass was obtained *via* mixing of zeolite, PB, and/or GG and water, and nitric acid (0.1–0.15 mol/mol of Al_2O_3) was added for plastification. Binder content in the zeolite-containing catalyst in terms of Al_2O_3 was varied from 10 to 40 mass %. The resulting mass was subjected to extrusion moulding. Catalyst granules with 2 mm diameter and 5–6 mm length were dried in air for 24 h and in a drying oven at 100 °C and then calcined at 550 °C for 6 h.

Acid properties of the resulting samples were studied by the technique of temperature-programmed desorption of ammonia. The method allows determining the distribution of acid sites by strength and their amounts. Its chromatographic option consists in the fact that a sample with substance-probe (ammonia) species pre-adsorbed therein is heated at 10 °C/min rate in a helium flow. The concentration of acid sites corresponds to desorbed ammonium amounts, and their strength – to temperature maxima in desorption curves.

Activity of zeolite-containing catalysts was studied during transformation of the straight-run gasoline fraction (IBP – 155 °C) of oil of the following composition, mass %: *n*-alkanes 254.6, isoalkanes 31.6, cycloalkanes 35.8, arenes 8.0; the octane number by the research method (RM) was 70 points. Octane numbers of the initial raw materials and resulting catalysts were determined via IR by calculation technique based on chromatographic data. Catalysts testing was carried out using a flow setup in 300–360 °C temperature range at volume feed rate of raw materials of 2 h–1 and atmospheric pressure.

Activity of the Ni/ZSM-5/10 % PB sample was also studied at hydrogen pressure of 2.0 MPa; catalyst volume/hydrogen volume ratio was 1/400. Prior to testing, activation of this catalyst was carried out for 3 h at 420 °C temperature and 2.0 MPa hydrogen pressure (the ratio of catalyst volume/hydrogen volume was 1/100).

Experiment duration at each temperature was 1 h. Catalyst activity did not change during this time, judging by comparable analyses results of samples of reaction products that were taken every 20 min of catalyst operation. Sampling of gaseous and liquid reaction products for analysis was performed at each process temperature. The composition of initial raw materials and their transformation products was analyzed by GLC method using a Chromatek-Kristall 5000.2 chromatograph. To determine liquid phase composition BP-1 PONA capillary column (100 m × 0.25 mm × 0.5 μm) was used, and to define gas phase composition – capillary GS-Gas Pro (60 m × 0.32 mm) and packed Carbosieve S-II (4 m × 2 mm 60/80 mesh) columns.

RESULTS AND DISCUSSION

Table 1 gives research results of acid characteristics of the Ni/ZSM-5 catalyst and samples obtained on its grounds with the

TABLE 1

Acid properties of zeolite-containing catalyst and binder

Catalysts	T_{max}, °C		Concentration of acid cites, μmol/L		
	T_I	T_{II}	C_I	C_{II}	C_Σ
Ni/ZSM-5	205	420	728	256	984
Ni/ZSM-5/10%PB	200	385	710	252	962
Ni/ZSM-5/20%PB	195	380	655	238	893
Ni/ZSM-5/30%PB	185	365	571	233	804
Ni/ZSM-5/40%PB	170	360	486	148	634
PB	155	350	228	219	447
Ni/ZSM-5/10%PB–10%GG	195	375	592	193	785
Ni/ZSM-5/20%PB–20%GG	170	355	473	144	617
PB–GG (1:1)	145	350	219	134	353

Note. T_I, T_{II} are temperatures of maxima of low and high temperature peaks at thermodesorption curves; C_I, C_{II} and C_Σ are concentration of weak and strong acid sites and their sum, respectively.

addition of different binder amounts. All samples have two types of acid sites: low-temperature with ammonia desorption range from 100 to 300 °C and high-temperature, ammonia from which is desorbed in the range ranging from 300 to 600 °C. The highest content of acid sites with the maximum strength is typical for the Ni/ZSM-5 catalyst. Catalyst acidity decreases when adding PB to the nickel-containing zeolite, the former also having two acid sites but with a substantially lower concentration and strength. It is impossible to obtain a catalyst with the required mechanical strength of its granules in case of the addition of only GG to the Ni/ZSM-5 sample, therefore, a mixture of PB and GG in the 1 : 1 ratio was added to zeolite. The strength and concentration of acid sites of the GG sample is lower than those for PB, which is attested by a decrease in acidity of their mixture compared to initial PB. This is most significantly displayed in a decrease of high-temperature acid sites, herewith, the strength and concentration of low-temperature acid sites also somewhat decreases. In accordance with this, acidity of Ni-containing zeolite catalysts with the addition of a mixture of GG and PB in terms of 20 and 40 mass % of Al_2O_3 content is somewhat lower than acidity of appropriate catalysts with the addition of only PB. The observable changes in acid properties of samples are probably related to a decrease in the amount of initial nickel-containing zeolite characterized by high acidity and with an increase in the fraction of a binder with lower acidity in the catalyst.

Table 2 gives data on the effect of process temperature on the composition of liquid transformation products of the straight-run gasoline fraction of oil over nickel-containing zeolite samples with the addition of different binder amounts.

It can be seen that a catalysate that contains almost equal amounts of cyclo- (34.3 mass %) and isoalkanes (33.9 mass %) are formed over the Ni/ZSM-5 sample at reaction temperature of 300 °C, which is comparable with their concentration in initial raw materials – 35.8 and 31.6 mass %, respectively. Thus, the catalyst at this temperature shows a distinct molecular-sieve effect that consists in transformation of mainly the most low-octane components of the gasoline fraction, such as *n*-alkanes: their content in the catalysate was 18.1 mass % compared to 24.6 mass % in straight-run gasoline. The octane number increases by 14 points resulting from an increase in the content of aromatic hydrocarbons in the catalysate from 8.0 to 12.6 and a decrease in the concentration of *n*-alkanes. The intensification of isomerization and aromatization processes proceeds with an increase in process temperature to 320 °C, and the formation of aromatic hydrocarbons begin to prevail at 340 and 360 °C. Alkene content in catalysates is minor and generally does not exceed 1 mass %, which attests the stability of the resulting gasolines. The octane number of catalysates increases from 84 at 300 °C to 94 points at 360 °C, and their yields at these temperatures are 76 and 52 %, respectively.

The addition of pseudoboehmite to the Ni/ZSM-5 in terms of 10 % of Al_2O_3 content in the catalyst (Ni/ZSM-5/10%PB) leads to the formation of catalysates in the 300–340 °C range. The content of iso- and cycloalkanes increases in them, the fraction of aromatic hydrocarbons, *n*-alkanes and alkenes reduces, and also the yield of a catalysate, the octane number of which decreases by 1–3 points, rises.

These trends are most apparent with an increase in the proportion of alumina in the nickel-containing zeolite catalyst. Thus, the yield of aromatic hydrocarbons decreases at 300 and 360 °C, respectively, by 2.2 and 6.8 mass % and alkenes – by 0.6 and 0.1 mass %, however, the yield of isoalkanes and liquid products increases by 2.5 and 10.3 mass % and 16 and 19 %, respectively. Thus, the addition of PB to the nickel-containing catalyst allows significantly increasing the yield of the target product; the fraction of isoalkanes increases and the proportion of aromatic hydrocarbons and alkenes decreases therein.

Upon addition of the identical amounts of PB and GG to the Ni/ZSM-5 sample, its acidity decreases compared to adding the same amount of PB (see Table 1). As a consequence, catalyst activity decreases (see Table 2). Thus, catalysate yield for the Ni/ZSM-5/20%PB sample at 300 °C is 86 %, its octane number is 81 points, and these indicators at 360 °C are 57 % and 93 points, respectively. Catalyst yields increase by 1–5 % in the whole temperature range during processing of straight-run gasoline over the Ni/

TABLE 2

Effect of process temperature for composition of liquid transformation products of the straight-run gasoline fraction of oil over zeolite-containing catalysts

Products, mass %	Process temperature, °C			
	300	320	340	360
Ni/ZSM-5				
n-Alkanes	18.1	14.3	9.3	6.4
Isoalkanes	33.9	34.9	32.6	27.7
Aromatic hydrocarbons	12.6	18.4	27.2	39.9
Cycloalkanes	34.3	31.6	30.1	25.4
Alkenes	1.1	0.8	0.8	0.6
Catalysate yield	76	74	62	52
Octane number	84	87	89	94
Ni/ZSM-5/10 % PB				
n-Alkanes	15.7	11.8	10.0	4.6
Isoalkanes	36.8	35.9	34.3	27.9
Aromatic hydrocarbons	12.5	13.1	23.8	39.5
Cycloalkanes	34.5	39.1	31.5	27.8
Alkenes	0.5	0.1	0.4	0.2
Catalysate yield	80	76	65	54
Octane number	83	84	88	93
Ni/ZSM-5/20 % PB				
n-Alkanes	16.2	13.2	10.6	8.3
Isoalkanes	36.2	35.8	35.1	30.8
Aromatic hydrocarbons	11.5	12.2	23.6	35.4
Cycloalkanes	35.6	38.4	30.2	25.2
Alkenes	0.5	0.4	0.5	0.3
Catalysate yield	86	80	70	57
Octane number	81	82	84	93
Ni/ZSM-5/30 % PB				
n-Alkanes	16.6	15.5	11.7	8.6
Isoalkanes	37.3	35.9	33.3	33.6
Aromatic hydrocarbons	10.6	12.2	23.1	34.3
Cycloalkanes	34.9	36.1	31.5	23.2
Alkenes	0.6	0.3	0.4	0.3
Catalysate yield	88	82	76	60
Octane number	78	82	84	87
Ni/ZSM-5/40 % PB				
n-Alkanes	14.1	16.0	11.8	4.0
Isoalkanes	36.4	36.5	34.8	38.0
Aromatic hydrocarbons	10.4	11.8	21.6	33.1
Cycloalkanes	38.3	34.9	31.3	24.4
Alkenes	0.5	0.8	0.5	0.5
Catalysate yield	92	85	83	71
Octane number	81	82	83	85
Ni/ZSM-5/10 % PB-10 % GG				
n-Alkanes	16.9	16.1	12.4	6.7
Isoalkanes	36.7	36.8	35.8	32.8
Aromatic hydrocarbons	8.4	9.2	16.9	28.7
Cycloalkanes	37.2	36.9	34.2	31.4
Alkenes	0.8	1.0	0.7	0.4
Catalysate yield	87	82	75	60
Octane number	78	81	86	91
Ni/ZSM-5/20 % PB-20 % GG				
n-Alkanes	17.0	14.8	17.1	14.0
Isoalkanes	36.7	37.0	34.8	36.5
Aromatic hydrocarbons	8.5	10.0	13.3	13.8
Cycloalkanes	37.0	37.5	33.9	35.0
Alkenes	0.8	0.7	0.9	0.7
Catalysate yield	97	96	88	82
Octane number	79	81	82	84
Ni/ZSM-5/10 % PB (P = 2.0 MPa)				
n-Alkanes	13.7	11.3	11.8	8.0
Isoalkanes	38.8	39.5	38.8	36.7
Aromatic hydrocarbons	11.6	12.6	24.2	27.5
Cycloalkanes	35.8	36.5	25.1	27.0
Alkenes	0.1	0.1	0.1	0.8
Catalysate yield	83	80	78	74
Octane number	85	86	87	89

ZSM-5/10 % PB-10 % GG catalyst. Herewith; its octane number decreases by 1–5 points mainly due to a reduction in aromatic hydrocarbon fraction by 3.1–6.7 mass %. The addition of PB and its mixture with GG in an amount of 40 mass % as binder to the Ni/ZSM-5 sample leads to even more significant changes in their properties. Thus, 92 % of the liquid product with an octane number of 81 points containing 10.4 mass % of aromatic hydrocarbons and

36.4 mass % of isoalkanes is formed over the Ni/ZSM-5/40 % PB catalyst at initial process temperature of 300 °C. Temperature increase to 360 °C leads to a reduction in catalyst yields to 71 % and an increase in its octane number to 85 points due to concentration increase of aromatic hydrocarbons and isoalkanes therein to 33.1 and 38.0 mass %, respectively. At 300 °C, there is a high catalysate yield with a lower octane number and content of aromatic hydrocarbons therein for the Ni/ZSM-5/20 % PB-20 % GG sample compared to the liquid product obtained over the Ni/ZSM-5/20 % PB sample. Herewith, the concentration of isoalkanes differs slightly. Higher amounts of the liquid product is formed over a catalyst that contains a mixture of PB and GG than when using a catalyst containing 40 mass % PB, and the concentration of aromatic hydrocarbons therein decreases by 19.3 mass %. Thus, the use of a mixture of PB and GG as binder allows reducing the aromatization activity of the Ni/ZSM-5 catalyst and increasing liquid product yields compared to the use of only PB as binder. It is important to note that the concentration of high-octane components (isoalkanes) does not decrease herewith.

Studies were carried out on transformation of the straight-run gasoline fraction of oil for the Ni/ZSM-5/10 % PB sample subjected to pre-activation at 2.0 MPa hydrogen atmosphere. It can be seen that the differences are minor at the initial temperature of the process of 300 °C when comparing hydrocarbon composition of products and the yield of catalysates obtained over the initial and activated Ni/ZSM-5/10 % PB catalysts at atmospheric and high pressure, respectively (see Table 2). Benzene yield increases by 3 % and its octane number – by 2 points; the yield of isoalkanes increases by 2 mass %, and the yield of arenes decreases by 0.9 mass % under high pressure conditions. These trends remain during increasing process temperature, however, the differences in appropriate indicators are more significant. Liquid product yield increases by 20 % at 360 °C, and the content of isoalkanes – by 8.8 mass %. Herewith, the concentration of aromatic hydrocarbons decreases by 12 mass %, and catalysate octane number – by 4 points. Thus, the effect of catalyst pre-treatment and pressure is most significantly reflected on process indicators at 340–360 °C temperature. Table 3 presents results obtained at 320 °C to assess the effect of the amount and nature of the binder added to the Ni/ZSM-5 catalyst on the composition of gaseous and liquid transformation products of the straight-run gasoline fraction of oil.

The maximum amount of gaseous products are formed over a sample with the addition of 10 mass % of PB and comprises 24 %, and the lowest one – over the Ni/ZSM-5/20 % PB/20 % GG catalyst (4 %). There is a clear correlation between the amount of the gas formed during transformation of straight-run gasoline and the amounts of binder in the nickel-containing zeolite catalyst: its acidity and, consequently, cracking ability are reduced with increasing the concentration of Al_2O_3 in the sample, which reduces gas formation. There is no significant change in the yield and composition of the resulting catalysates compared to a sample tested at atmospheric pressure when carrying out the process at 300 and 320 °C under high pressure conditions. A significant change in the composition and amount of gases formed at these temperatures also does not happen.

Gaseous products formed over all samples under study contain *n*-alkanes, alkenes, isoalkanes and cycloalkanes, and also hydrogen in the amount of 0.3–0.8 mass %. It is worth noting that hydrocarbons with the number of carbon atoms of more than 5 in gaseous products of transformation of straight-run gasoline are present in minor amounts; their total content does not exceed 1.5 mass % (not given in Table 3).

Propane (~50 mass %) and *n*-butane (~20 mass %) prevail in the composition of gaseous products; methane and ethane concentrations do not exceed 2 mass %. The amount of isobutene is significantly higher than isopentane contents. An increase in binder content in the catalyst and conducting the process at elevated pressure leads to a decrease in the yield of *n*-alkanes and an increase in the formation of isoalkanes. The highest concentration of alkenes in the gaseous products accounts for propylene, the amount of which is twice higher compared to that with ethylene and butenes.

The unsaturated hydrocarbon fraction increases in the composition of gases formed on it with rising of the binder contents, which attests slowing down a proton transfer reaction. The amount of olefins decreases mainly resulting from an increase in hydrogenation reaction rate constant during carrying out the process in the presence of hydrogen.

Molecular hydrogen almost does not react with organic matter at temperatures lower than 480 °C. The reaction is likely only in the surface of the catalyst that also sorbs both hydrogen and organic species easing their contact. Platinum, palladium, rhodium, ruthenium, and nickel are the most efficient among metals that allow carrying out hydrogenation of unsaturated compounds with hydrogen at atmospheric pressure and relatively low temperatures. Although many details of process mechanism and stereochemistry are yet unclear and currently being studied using modern analysis techniques the Horiuti–Polanyi mechanism (1934) is generally used, when describing the process. Alkene and hydrogen sorption occurs

TABLE 3

Effect of binder content in the catalyst for composition and yield of composition products of straight-run gasoline fraction of oil (T = 320 °C, V = 2 h^{-1})

Products	Yield, mass %						
	Binder content in catalyst						
	10 % PB	20 % PB	30 % PB	40 % PB	20 % PB-GG	40 % PB-GG	10 % PB (2.0 MPa)
Gaseous							
n-Alkanes C_1–C_5	79.5	72.8	71.7	70.4	68.5	66.3	76.1
Alkenes C_2–C_4	0.7	1.6	3.3	3.8	4.5	5.1	0.2
Isoalkanes C_4–C_5	18.6	23.5	24.0	24.7	25.4	27.4	22.3
Liquid							
n-Alkanes C_4–C_{14}:	11.8	13.2	15.5	16.0	16.1	14.8	11.3
C_4	1.0	3.3	3.0	3.6	2.6	2.2	2.7
C_5	3.1	4.0	4.5	4.4	4.2	3.6	4.3
C_6	3.1	3.2	2.9	3.1	3.7	3.3	1.7
C_7	1.9	2.2	2.3	1.9	2.6	2.5	0.3
C_8	1.9	1.9	2.2	1.7	2.2	2.2	1.7
Isoalkanes C_4–C_{13}:	35.9	35.8	35.9	36.5	36.8	37.0	39.5
C_4	0.5	2.2	0.7	2.2	2.6	1.3	1.1
C_5	2.6	4.2	2.4	4.4	3.8	3.3	4.5
C_6	5.7	6.0	5.1	6.0	6.1	5.5	7.0
C_7	6.0	5.8	6.2	5.8	6.3	6.0	5.9
C_8	6.6	6.2	7.1	6.2	7.0	7.2	5.8
C_9	9.8	8.7	10.7	8.7	9.4	10.5	11.5
C_{10}	3.8	2.9	3.3	2.9	2.6	3.0	3.3
Cyclo C_5–C_{12}:	39.1	38.4	36.1	34.9	36.9	37.5	36.5
C_6	5.3	5.4	5.1	5.0	5.7	5.2	3.1
C_7	11.8	11.5	11.5	10.9	12.2	11.9	10.2
C_8	12.9	11.8	12.2	12.1	12.1	12.7	14.4
C_9	8.2	6.2	6.6	6.2	6.1	7.0	7.9
Arenes C_6–C_{13}:	13.1	12.2	12.2	11.8	9.2	10.0	12.6
C_6	0.3	0.4	0.3	0.4	0.3	0.4	0.4
C_7	1.8	2.0	1.8	1.9	1.4	1.4	2.0
C_8	6.4	5.3	5.5	5.5	4.4	4.8	5.6
C_9	3.2	2.1	2.1	2.3	1.9	2.0	2.5
C_{10}	0.8	0.9	1.0	1.0	0.8	0.8	1.3

over catalysts in the first step; a hydrogen atom migrates to the β-carbon atom of the double bond in the second step and reductive elimination of the product happens in the third step. There is some temporal gap, in which hydrogen metabolism, *cis*-*trans*-isomerization or double bond migration may occur between the addition of the first and second hydrogen atoms. Side processes may become accelerated at insufficient saturation of the catalyst with hydrogen. Alkene hydrogenation rate decreases with increasing the number of substituents at double bonds. The ratio between the rates set for pure hydrocarbons does is not the same during hydrogenation of their mixtures and proceeds much faster, which is explained by large chemiosorption coefficient. The process of hydrogenation of alkenes over nickel nanoparticles is described in more detail in paper [9].

Table 3 gives structural-group composition of the main liquid products of transformation of straight-run gasoline over samples under study. Normal alkanes are presented by hydrocarbons with chain length from 4 to 14 carbon atoms with the prevalence of C_4–C_8 hydrocarbons. *n*-Alkanes with the following distribution are formed over the Ni/ZSM-5/10 % PB sample: C_5=C_6>C_7=C_8>C_4, and with an increase of PB content in the catalyst from 20 to 40 mass %, it varies: C_5>C_4>C_6>C_7>C_8. *n*-Alkanes characterized by the distribution of C_5>C_6>C_7>C_4>C_8 are formed over Ni/ZSM-5/10 % PB-10 % GG and Ni/ZSM-5/10 % PB-20 % GG catalysts, and C_5>C_4>C_6=C_8>C_7 species are generated over the Ni/ZSM-5/10 % PB sample (at hydrogen pressure). Reaction products contain C_4–C_{13} isoalkanes. At the same time, iso-hydrocarbons with the number of carbon atoms of over 10 are present in a low amount i.e. less than 1.0 mass % due to steric limitations related to the use of zeolite of pentasil type. Regardless of catalyst composition, more C_9 isoalkanes are contained in all the resulting gasolines, later, C_9>C_8>C_7>C_6>C_{10}>C_5>C_4 isoalkanes appear in the descending order. Isoalkanes with a somewhat different distribution (C_9>C_6>C_7>C_8>C_5>C_{10}>C_4) are formed over the Ni/ZSM-5/10 % PB sample tested under high hydrogen pressure conditions. Catalysates contain cycloalkanes with the number of carbon atoms from 5 to 12, however, species with the number of carbon atoms from 6 to 9 prevail among them. In catalysates obtained over all samples under study, cycloalkanes are distributed, as follows: C_8>C_7>C_9>C_6, moreover, C_7 and C_8 cycloalkanes are contained in almost equal amounts and far more than C_6 and C_9 cyclic saturated hydrocarbons. Aromatic derivatives of this type in liquid products are presented by C_6–C_{13} hydrocarbons with the prevalence of C_6–C_{10} alkanes. They are distributed as follows: C_8>C_9>C_7>C_{10}>C_6. Thus, by varying binder content in zeolite catalyst or conditions of conducting transformation of straight-run gasoline, not only the yield but also hydrocarbon composition of the resulting liquid product can be significantly changed.

CONCLUSION

A part of pseudoboehmite used as binder to prepare zeolite-containing oil processing catalysts can be replaced for its precursor, i.e. hydrargillite. By varying pseudoboehmite/hydrargillite ratio or conditions of carrying out transformation of straight-run gasoline, not only the yield but also hydrocarbon composition of the resulting liquid product can be significantly changed. An increase of binder content in the Ni/ZSM-5 catalyst, and also carrying out the process at high pressure lead to a decrease in the formation of aromatic hydrocarbons during transformation of the straight-run gasoline fraction of oil and to an increase in catalysate yield, in the composition of which there is a rise in high-octane components (isoalkanes).

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