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Influence of sulphide Cu (I) promoting additives concentration on acid and catalytic properties of high-silica zeolites in straight-run gasoline conversion

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Abstract. In present article the influence of Cu_2S promoting additives concentration on acid and catalytic properties of high silica MFI-type zeolites is investigated in the process of conversion of straight-run gasoline fractions of gas condensate into high octane components of motor fuels. It was shown that zeolite modified with 1 % of Cu_2S nanoscaled powder possesses the highest acid centers concentration and highest catalytic activity.

1. Introduction

Research and development of high-yield advanced stock processing is an challenge of oil and gas chemistry. Within catalytic thermal processes antiknock can sufficiently improve the properties of straight-run gasoline fractions of oil and gas condensates.

One of the modern trends of rational nature management is a conversion of light hydrocarbons into high octane motor fuels component by means of zeolite-containing catalysts [1-3]. MFI-type zeolite is widely used in zeolite-based catalytic processes. It was stated that zeolite can be used to catalyze lots of acid-base hydrocarbons conversion reactions [4-10]. Due to the unique structure that facilitates its molecular-sieve selectivity zeolite sorbs only size-defined substances. Also, zeolite possesses unique acid properties and is related to supersacids. All its features facilitate the application of zeolite in petrochemical industry. Moreover, zeolite is more active catalyst than convenient catalytic systems. In present article we compared acid properties and catalytic activity of MFI-type zeolite and zeolite modified with Cu_2S .

2. Experimental procedure

High-silica zeolites (HSZ) were produced by hydrothermal synthesis from alkaline aluminosilica gels at 175–185 °C in the course of 2–4 days [11]. After the crystallization was complete, the resulting zeolites were washed with water, dried at 110°C, and calcined at 600°C for 6 h. The HSZ were converted to the hydrogen active form by treatment with a 25% NH_4Cl solution at 90 °C for 2 h, with subsequent drying at 110 °C and calcination at 600 °C for 6 h (the content of Na_2O in decationized zeolites was less than 0.01%). The HSZ catalysts obtained were identified by IR spectroscopy (Nicolet 5700 IR Fourier spectrometer) and X-ray phase analysis (DRON-3 X-ray installation, Mo anode, Ni filter). According to X-ray phase analysis data, all the HSZ samples obtained belong to zeolites of the MFI type.

A certain amount of Cu_2S nanoscaled powder was added to the origin zeolite. Mechanochemical activation was carried out with vibratory ball mill KM-1 for 12 hours at 25 °C. Nanoscaled particles of



Cu₂S were obtained within very high-temperature synthesis. The described method was applied for the synthesis of HSZ modified by 0.5, 1 and 3 % (mass) of Cu₂S.

The acid properties of HSZ were studied in a thermal-desorption installation on the basis of ammonia adsorption in a flow of carrier-gas helium in the temperature range 50–650 °C at a linear heating rate of 10 deg min⁻¹. To eliminate diffusion hindrances and the effect of the physical form of ammonia adsorption on, HSZ ammonia was adsorbed at a high flow rate of the carrier-gas (110 cm³ min⁻¹) at 100 °C in the course of 1 h. After that, the reactor with a sample under study was cooled to 50 °C and ammonia was desorbed, with a katharometer serving as detector. Helium of A brand (99.995 vol %) and ammonia of pure grade were used in the experiments. The concentration of acid centers (μmol per gram of catalyst) in the samples under study was determined from the amount of ammonia contained in desorption peaks (forms), with the determination accuracy of adsorbed ammonia by gas chromatography being ±2.5%.

Transformations of the straight-run gasoline fraction with a boiling onset point of 170 °C from the gas condensate were studied on zeolite-containing catalysts on a flow-through catalytic installation with a fixed catalyst bed (reactor volume 10 cm³) in the temperature range 350–425 °C at a volumetric flow rate of the raw material of 2 h⁻¹, atmospheric pressure, and experiment duration of 1 h at each fixed process temperature.

The gas condensate from the Myl'dzhinskoe deposit has the following fraction composition: boiling onset point 31 °C, 82 vol % of the condensate boils away at 200 °C, end boiling point 297 °C, loss and residue 10 vol %. As regards the group hydrocarbon composition, the straight-run gasoline fraction with a boiling onset point of 170 °C from the gas condensate has the following composition (wt %): n-alkanes 22.7, isoalkanes 33.2, naphthenes 39.9, and arenes 4.2. The octane number of the straight-run gasoline fraction with boiling onset point of 170 °C from the gas condensate of the Myl'dzhinskoe deposit is 60 points by the research method (RM) scale.

Gaseous hydrocarbons were analyzed on a stainless steel column (length 3 m, inner diameter 3 mm) packed with 5% NaOH on Al₂O₃, and liquid hydrocarbons, on a quartz glass capillary column (100 m × 0.25 mm × 0.25 μm) with a supported fixed ZB-1 phase. Gaseous and liquid products formed in conversion of straight-run gasoline fractions of the gas condensate were quantitatively analyzed by gas chromatography on a hardware-software complex based on a Khromatek-Kristall 5000 v. 1 gas chromatograph, with Khromatek-Analitik processing software. The research octane numbers were calculated by using the Khromatek-Analitik processing software from results of a gas-chromatographic analysis of the hydrocarbon composition of the starting raw material and liquid products formed in conversion of straight-run gasoline on the zeolite-containing catalysts under study. The error of the gas-chromatographic determination of gaseous and liquid hydrocarbons is ±2.5%.

3. Experiments and results

3.1. Influence of Cu₂S promoting additives on acid properties of zeolite-containing catalysts

Acid properties of catalysts were estimated by means of temperature-programmed ammonia desorption. Temperature desorption profiles of all catalysts have two peaks. Low-temperature peak (120–250 °C) of initial zeolite with T_{max} = 185 °C is mainly related with ammonia desorption from weak acid centers (form I) that are coordinative unsaturated aluminium ions. High temperature peak (300–550 °C) with T_{max} = 400 °C is mainly related with ammonia desorption from strong acid centers (form II) that are hydrogen ions of hydroxylic bridge groups. From the data presented in table 1 it can be seen that initial high-silica zeolite possesses 383 μmol/g of weak acid centers and 128 μmol/g of strong acid centers. Within Cu₂S modification the increase of total acid centers concentration takes place due to the increase in weak acid centers concentration while the concentration of strong acid centers remains approximately the same. It should be noted that samples modified by 0.5 % and 1 % of sulphide Cu(I) nanoscale powder possess the highest acid centers concentration (weak acid centers concentration is respectively 415 μmol/g and 410 μmol/g). Also, Cu₂S additions lead to the rise of ammonia desorption temperature. For example, for weak acid centers it increases at 5–12 °C and at 10–20 °C for strong centers.

Table 1. Acid properties of zeolite-based catalysts

Catalyst	T _{max} , °C		a.c.c, μmol/g		
	I	II	I	II	common
HSZ	185	400	382	128	510
0.5 % Cu ₂ S / 99.5 % HSZ	197	425	415	130	545
1 % Cu ₂ S / 99 % HSZ	196	420	410	130	540
3 % Cu ₂ S / 97 % HSZ	190	410	390	130	520

3.2. Influence of Cu₂S promoting addition on catalytic properties of zeolite-containing catalysts

The investigation of temperature influence shown that with its rise from 350 to 425 °C and with space feed rate 2 h⁻¹ high octane gasoline yield for all investigated samples decreases since the degree of initial stock hydrocarbons conversion increases. The results of the corresponding investigations are presented in table 2.

Firstly the yield of gas products, primarily due to C₃-C₄ paraffines, increases from 9.7 % (350 °C) to 33.7 % (425 °C). The yield of C₆-C₉ liquid aromatic hydrocarbons increases from 9.3 % to 24.8 %. Toluol and xylol take the main part of aromatics. With the increasing temperature the yield of benzene and C₅₊ oleffines increases from 0.4 % and 1.6 % (350 °C) to 1.5 and 2.9 % (425 °C), respectively. But the yield of naphthenic, n- and isoparaffinic C₅₊ hydrocarbons decreases with the increasing temperature (table 2). Gas products are mainly presented by propane and butane.

The dependence of obtained liquid products octane number on temperature is presented in figure 1 (a).

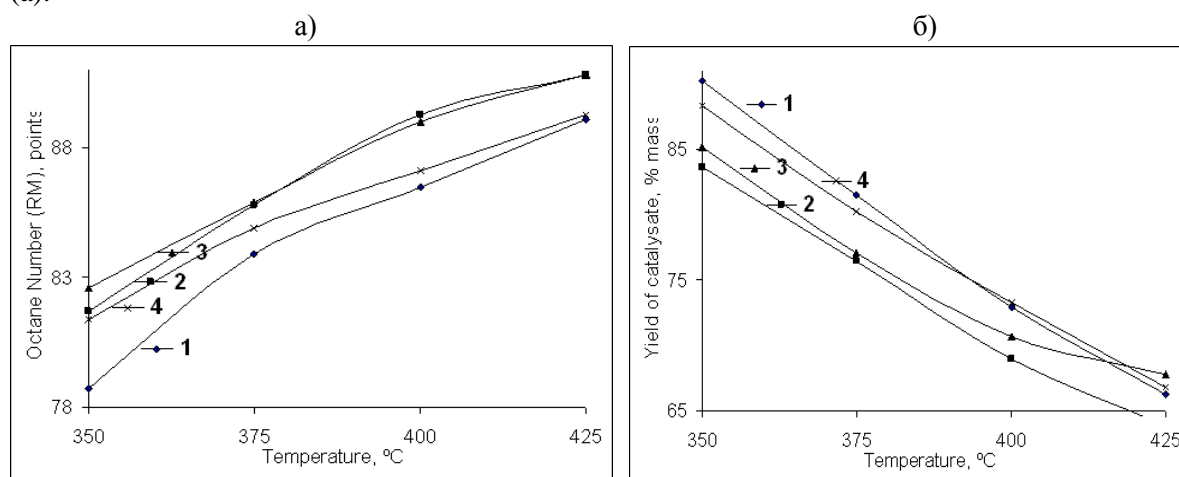


Figure 1. The influence of straight run gasoline conversion temperature with zeolite-containing catalyst on the obtained catalysate octane number (a) and catalysate yield (b). 1 — HSZ, 2 — 0.5 % Cu₂S / 99.5 % HSZ, 3 — 1 % Cu₂S / 99 % HSZ, 4 — 3 % Cu₂S / 97 % HSZ

Table 2. The composition of straight run catalytic gas condensate gasoline conversion products: 1 — HSZ, 2 — 0.5 % Cu₂S / 99.5 % HSZ, 3 — 1 % Cu₂S / 99 % HSZ, 4 — 3 % Cu₂S / 97 % HSZ

	Catalyst											
	375	400	425	375	400	425	375	400	425	375	400	425
Temperature, °C												
Gas phase, % mass	18.5	27.1	33.7	22.9	29.3	32.2	19.7	26.7	33.2	23.5	31.0	36.2
Liquid phase, % mass	81.5	72.9	66.3	77.1	70.7	67.8	80.3	73.3	66.8	76.5	69.0	63.8
Gas phase composition, % mass												
Methane	0.2	0.4	0.6	0.2	0.4	0.7	0.2	0.4	0.6	0.2	0.4	0.7
Ethane	1.1	1.5	2.3	1.1	1.6	2.5	1.1	1.6	2.3	1.1	1.6	2.5
Ethylene	1.5	1.7	2.4	1.0	1.4	2.1	1.4	1.7	2.1	1.1	1.5	1.9
Propane	50.6	50.5	50.1	52.7	52.2	52.4	52.0	51.9	52.0	51.8	52.2	52.8
Propylene	3.8	4.2	5.7	2.7	3.6	4.8	3.6	4.3	4.9	2.5	3.5	4.1
Isobutane	22.1	21.5	19.5	22.2	21.2	19.1	21.2	20.4	19.2	22.5	21.2	19.5
N-butane	17.7	17.1	15.3	18.0	17.0	15.1	17.6	16.7	15.6	18.5	16.9	15.4
Isobutene	2.9	3.1	4.0	2.1	2.7	3.2	2.8	3.1	3.3	2.2	2.7	3.0
Liquid phase composition, % mass												
Aromatic	16.5	20.9	24.8	19.4	24.7	28.9	18.1	21.5	26.6	19.5	24.7	28.9
Benzene	0.7	1.1	1.5	0.8	1.4	1.7	0.8	1.2	1.6	0.9	1.4	1.7
Isoparaffines	38.3	38.2	37.0	37.9	37.1	36.0	38.0	37.6	35.4	38.3	37.1	36.0
Naphthenes	27.4	24.9	23.1	28.1	24.9	21.9	26.7	24.6	23.4	25.7	23.3	21.6
Paraffines	15.3	13.3	12.2	11.6	11.0	10.7	14.9	13.6	11.9	14.3	12.7	11.3
Olefines	2.6	2.7	2.9	2.2	2.3	2.5	2.3	2.6	2.8	2.2	2.2	2.2
Octane number (research method)	83.9	86.5	89.1	85.8	89.3	90.3	85.9	89.0	90.8	84.9	87.1	89.3

With this figure we can conclude that the promoting addition of copper sulphide increases the octane number of obtained catalysate in comparison with the catalysate obtained with the origin HSZ. The highest octane number was obtained with samples 2 (0.5 % Cu₂S / 99.5 % HSZ) and 3 (1 % Cu₂S / 99 % HSZ). It varies from 82 (350 °C) to 91 (425 °C) points of RM.

The influence of temperature of straight-run gasoline conversion with zeolite-containing catalyst on catalysate yield is shown in figure 1 (b). Also, we can see that the highest gas product yield takes place with the origin zeolite. Promoting additions increase the activity of raw hydrocarbons conversion. This facilitates the increasing of liquid catalysate yield if compare to the origin zeolite. It should be pointed out that at all process temperature the sample with 1 % of Cu₂S and 99 % of HSZ performs better yield than the sample with 0.5 % of Cu₂S and 99.5 % of HSZ. So the yield of catalysate increases at 2–4 %.

4. Conclusion

Acid properties of initial high-silica zeolite and zeolite-containing catalysts modified with nanoscale Cu_2S powder were investigated. Introduction of 0.5 % mass and 1 % mass of Cu_2S promoting addition facilitated the increase of weak centers concentration at 9 %.

Catalytic properties of zeolite-containing catalysts in straight-run gasoline fractions conversion into high octane components of motor fuels were investigated. It is stated that the yield of aromatic hydrocarbons increases with increasing temperature for all investigated catalysts. Also, increasing temperature leads to the decrease of main product yield due to the increase in degree of stock conversion. High octane catalysate mostly consists of isoparaffins, arenes and naphthens. Gas products mostly consist of propane and butane.

From all the proposed catalysts the most active samples contain 0.5 % Cu_2S / 99.5 % HSZ and 1 % Cu_2S / 99 % HSZ. These catalysts facilitate the obtaining of products with maximum octane numbers: 82 points at 350 °C and 91 points at 425 °C (research method). However, in the temperature range 350–425 °C catalysate yield with the sample, modified with 1 % of nanoscaled powder of Cu_2S , is higher than the one obtained with the sample, modified with 0.5 % of nanoscaled powder, at 2–4 %, respectively. Thus, it was shown that the sample containing 1 % Cu_2S / 99 % HSZ performs the best activity and desired reaction product ratio.

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