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## KAOLINITE MODIFIED BY ALUMINUM IN THE CRACKING OF VACUUM GASOIL AND IT'S MIXTURE WITH FUEL OIL

**Abstract.** The data of the cracking of vacuum gas oil (VG) and a mixture of VG with fuel oil (M-100) on HLaY zeolite catalyst based on acid-activated kaolinite of the Pavlodar deposit modified by aluminum are presented. The synthesis of the kaolinite matrix and the HLaY zeolite catalyst with its use, the physicochemical and acid characteristics of the catalyst and its constituent components, and the fractional and hydrocarbon compositions of vacuum gas oil are described. High mesoporosity of the H-form of the used kaolinite (86.2%), modified by aluminum of the H-form (84.1) and the HLaY catalyst (80.1%), which provide the activity of the sample in cracking of the mixture with a yield of 32.6% gasoline and 25.9% light gas oil (LG) at 450°C and in cracking of VG a yield of 38.2% gasoline and 29.4% LG at 500°C. The gasolines of cracking of LG contain an increased content of iso paraffins (up to 20.2%) and a low content of aromatic hydrocarbons (24.1%), which makes the catalyst attractive for cracking a mixture of VG with fuel oil.

**Key words:** catalytic cracking, kaolinite, vacuum gas oil, fuel oil, zeolite, modification.

### Introduction

Recently it is known that the main direction in the development of the oil refining industry is an increase in the production of motor fuels due to the involvement of heavy oil residues in the technology [1-3]. Fuel oil, which consists of about 50% of oil, is the main reserve for in-depth processing of oil raw materials. For the practical implementation of the process, it is interest to prepare catalysts using natural mineral raw materials – kaolinite and montmorillonite clays [1-7] and industrial waste - energy evils for example [2, 8].

Among the many natural clays, leading foreign companies in the preparation of microspherical industrial cracking catalysts widely use kaolin [4-7, 9], while in Russian catalysts, natural montmorillonite is preferred [10].

Kaolinites belong to the class of layered silicates [4, 5, 11, 12] with continuous layers of silicon-oxygen tetrahedrons: 1 layer of octahedra and 1 layer of tetrahedrons. The bags are firmly adjacent to each other, as a result of which water molecules and metal cations cannot enter the interpackage space of minerals. Kaolinite is a hard aluminosilicate. It does not swell in a mixture with water, has a low cationic capacity. There are no noticeable isomorphous substitutions of aluminum with atoms of other metals. Changes in the structural and other physicochemical characteristics of kaolinites in catalytic and adsorption processes can be achieved by acid and alkaline activation of clays [12-15].

An important property of kaolinite clay catalysts is their ability to remain active in the presence of heavy metals [16], which is of considerable interest for cracking of residual crude oil. Large reserves of kaolinites in Kazakhstan [17] determine the attention to the study of the adsorption and catalytic properties of modified kaolinites.

Previously [18-19] we studied the activity of HCeY - zeolite catalysts on aluminum-modified kaolinites of the Ermakov and Sarymsak deposits in cracking of heavy vacuum gas oil and adsorption

water purification from heavy metal cations on sorbents based on these clays [20-21]. It has been shown that cracking activity and adsorption capacity in water treatment depend on the chemical composition of the initial kaolinites. The catalyst based on Ermakov kaolinite showed great activity in the cracking. And an adsorbent based on the Sarymsak kaolinite – in the water treatment.

The aim of the work was synthesis of matrix based on aluminum modified Pavlodar kaolinite, HLaY zeolite, the preparation of HLaY zeolite-containing catalyst and the determination of the activity of the synthesized catalyst in cracking of vacuum gas oil and its mixture with fuel oil.

### Experimental part

For preparation of the catalyst, the kaolinite clay of the Pavlodar deposit RK was subjected to grinding and “elutriation”. Clay was activated by acid with a 20% sulfuric acid solution according to the standard procedure for 6 hours in a boiling water bath. After activation, the clay was washed from  $\text{SO}_4^{2-}$  ions, sequentially dried at room temperature (day), at 150°C (2 hours) and calcined for 2 hours at 500°C. Subsequent modification of kaolinite by aluminum was carried out by slow introduction of synthesized according to the method [19] hydroxocomplex with concentration of aluminum of 2.5 mmol  $\text{Al}^{3+}$  / g kaolinite. Calcination at 500 ° C is accompanied by the decomposition of the hydroxocomplex to alumina. The matrix of the prepared catalyst is designated as Al (2.5) HPK.

For preparation of the catalyst we used HY zeolite in the rare earth form — HLaY, which was obtained from NaY zeolite by ion exchange with  $\text{NH}_4\text{Cl}$  followed by the exchange of  $\text{NH}_4$  ion to lanthanum. The content of HLaY zeolite in the catalyst is 15%. The elemental composition of the catalyst samples and their components was determined by X-ray fluorescence analysis on a “Niton XRF Analyzers” instrument manufactured by “Thermo Scientific” and using X-ray fluorescence spectroscopy in an energy dispersive microanalysis system “INCA-ENERGY 450” mounted on a JSM6610LV JEOL scanning electron microscope, Japan. The average value of three measurements was used.

The catalysts were characterized by BET, X-ray phase analysis performed on a DRON 4 \* 0.7 device with  $\text{CuK}\alpha$  radiation, and TPD (temperature-programmed desorption) of ammonia.

The activity of the synthesized catalysts in cracking was determined with using of vacuum gas oil of Pavlodar Petrochemical Plant (PPCP) with e.b. 532°C and mixture of vacuum gas oil (70%) with fuel oil (30%).

The products of cracking and raw feed were analyzed chromatographically. For analysis of gasoline and the gas phase of cracking, Chromos GH-100 chromatograph with a 100 m capillary column with a stationary phase HP-1 (ASTM D 6729-04) was used. The carrier gas is helium. The analysis of vacuum gas oil components was carried out on an Auto System XL SIMIDS chromatograph with a Perkin Elmer SIMIDS -100% column (polymethylsiloxane), 30 m long with a helium flow of 40  $\text{cm}^3/\text{min}$  (ASTM D2887).

### Results and discussions

Fractional and hydrocarbon composition of VG are presented in tables 1 and 2, and the chromatogram of the initial VG in figure 1.

Table 1 - the Fractional composition of the VG PPCP

| The percentage of distillate, % | Distillation temperature by weight, °C | The percentage of distillate, % | Distillation temperature by weight, °C |
|---------------------------------|--|---------------------------------|--|
| 5                               | 258                                    | 55                              | 407.5                                  |
| 10                              | 290.1                                  | 60                              | 415.7                                  |
| 15                              | 312.0                                  | 65                              | 422.9                                  |
| 20                              | 323.1                                  | 70                              | 430.7                                  |
| 25                              | 338.6                                  | 75                              | 440.1                                  |
| 30                              | 383.6                                  | 80                              | 450.1                                  |
| 35                              | 365.7                                  | 85                              | 461.6                                  |
| 40                              | 377.4                                  | 90                              | 474.7                                  |
| 45                              | 388.4                                  | 95                              | 498.2                                  |
| 50                              | 398.5                                  | 100                             | 532.0                                  |

Table 2 - Hydrocarbon Composition of the VG PPCP

| Класс углеводородов         | Content, % weight. |
|-----------------------------|--------------------|
| Paraffin hydrocarbons       | 66.2               |
| Isoparaffin hydrocarbons    | 13.2               |
| Aromatic HC                 | 6.0                |
| Olefins                     | 0.4                |
| Naphthenes                  | 3.4                |
| Oxygen containing compounds | 2.9                |
| Unidentified compounds      | 7.9                |
| Total                       | 100                |

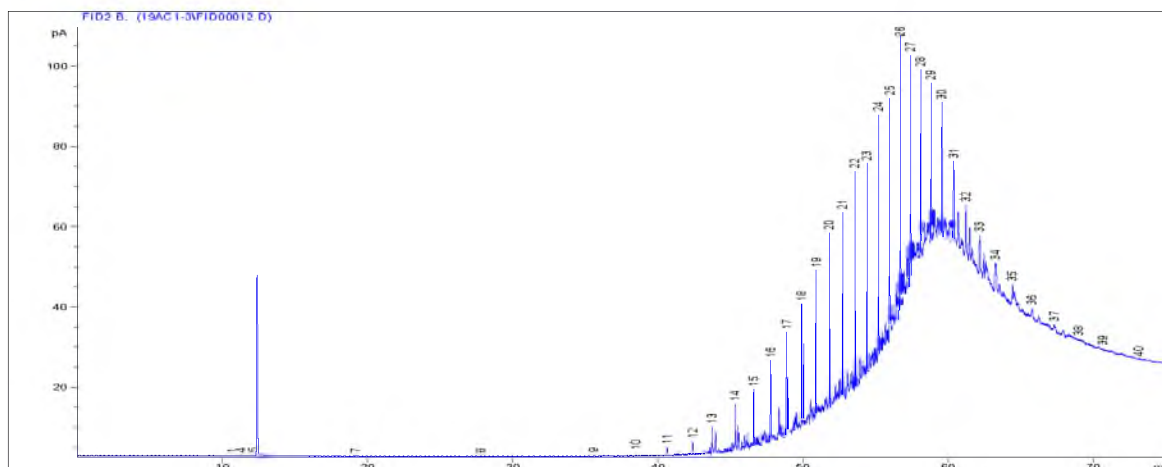


Figure 1 - Chromatogram of PPCP vacuum gas oil with e.b. 532°C

According to the data of X-ray fluorescence spectroscopy, the composition of the used fuel oil M-100 PPCP includes 2.5% sulfur, 0.07% vanadium and 0.02% nickel.

The chemical composition of the used Pavlodar kaolinite PK, its H-form (HPK), aluminum modified Al(2.5)HPK and HLaY zeolite catalyst are shown in table 3.

Table 3 - The chemical composition of K, HK, Al(2.5)HPK and HLaY-zeolite catalyst

| Sample            | Content, weight % |      |                                |                  |                  |      |                  |                                |                                |
|-------------------|-------------------|------|--------------------------------|------------------|------------------|------|------------------|--------------------------------|--------------------------------|
|                   | Na <sub>2</sub> O | MgO  | Al <sub>2</sub> O <sub>3</sub> | K <sub>2</sub> O | SiO <sub>2</sub> | CaO  | TiO <sub>2</sub> | Fe <sub>2</sub> O <sub>3</sub> | La <sub>2</sub> O <sub>3</sub> |
| K                 | 0.18              | 0.08 | 34.86                          | 0.1              | 59.52            | 0.15 | 1.25             | 3.83                           | -                              |
| HK                | 0.03              | 0.03 | 32.81                          | 0.08             | 63.11            | 0    | 1.38             | 2.57                           | -                              |
| Al(2.5)HPK        | 0.12              | 0.12 | 35.00                          | 0.14             | 59.8             | 0.14 | 1.2              | 4.5                            | -                              |
| Al(2.5)HPK + HLaY | 0.10              | 0.10 | 35.9                           | 0.08             | 57.67            | 0.11 | 0.85             | 3.44                           | 1.70                           |

An analysis of the data in the table shows that acid activation leads to a decrease of the Al<sub>2</sub>O<sub>3</sub> content (by ≈3%), which was compensated by the introduction of an aluminum hydroxocomplex. The initial kaolinite contains a small amount of 0.18% Na<sub>2</sub>O and its amount decreases during the processing of the catalyst. The iron content in the initial sample is 3.83%, in the aluminum-modified sample - 4.50% and in the HLaY zeolite-containing catalyst - 3.44%. The amount of La<sub>2</sub>O<sub>3</sub> in the catalyst is 1.7%.

The textural characteristics of Al(2.5)HPK matrix and Al(2.5)HPK + HLaY samples are illustrated in table 4.

Table 4 - Characterization of aluminum-modified kaolinite sample and HLaY-catalyst by BET

| Catalyst        | S <sub>ss</sub> , m <sup>2</sup> /g | Total volume of pores, sm <sup>3</sup> /g | R, nm   | Relative content, % |                  |
|-----------------|-------------------------------------|---|---------|---------------------|------------------|
|                 |                                     |   |         | Micropores <2 nm    | Mesopores 2-8 nm |
| Al(2.5)HPK      | 28.8                                | 0.09                                      | 2.0-8.0 | 16.0                | 84.0             |
| Al(2.5)HPK+HLaY | 131.8                               | 0.15                                      | 2.0-8.0 | 19.9                | 80.1             |

When the H-form of Pavlodar kaolinite is modified by aluminum, the specific surface increases from 28.8 m<sup>2</sup>/g to 131.8 and the number of mesopores, on the contrary, decreases to 80.1%.

X-ray diffraction diffractograms of the HK matrix and HLaY zeolite catalyst on aluminum-modified kaolinite are shown in figure 2. Reflex 2.02 is assigned to the lanthanum present on the surface.

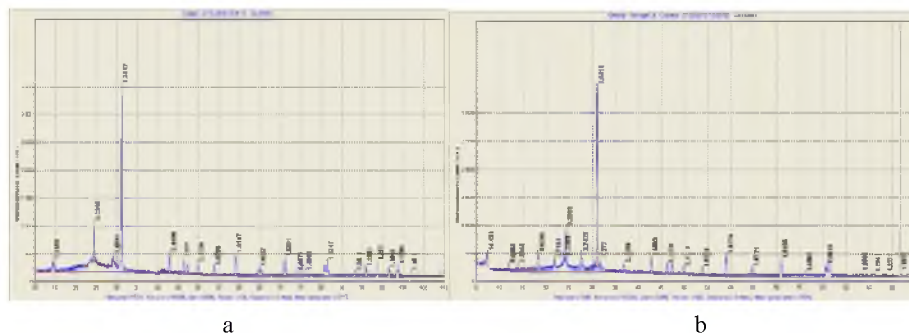


Figure 2 - The diffractograms of HPK (a) и Al(2.5)HPK +HLaY (b)

The activity of aluminosilicate contacts in cracking, as it is known, it is primarily associated with their acidity. The acid characteristics of the initial, acid-activated and aluminum-modified kaolinite, as well as the HLaY catalyst based on it are shown in table 5.

Table 5 - Acid characteristics of kaolinites of the studied samples

| Sample              | Content of a.c.           | Weak a.c.<br>< 200°C | Medium a.c.<br>200-300°C | Strong a.c.<br>>350°C | Total acidity |
|---------------------|---------------------------|----------------------|--------------------------|-----------------------|---------------|
| NK                  | %                         | 47.8                 | 45.2                     | 7.0                   | 100           |
|                     | mcmole NH <sub>3</sub> /g | 20.9                 | 19.8                     | 3.0                   | 43.8          |
| HPK                 | %                         | 38.9                 | 38.7                     | 22.3                  | 100           |
|                     | mcmole NH <sub>3</sub> /g | 45.1                 | 44.9                     | 10.0                  | 115.9         |
| Al(2.5)HPK          | %                         | 24.3                 | 51.7                     | 24.0                  | 100           |
|                     | mcmole NH <sub>3</sub> /g | 29.2                 | 62.0                     | 28.8                  | 120.0         |
| Al(2.5)HPK+<br>HLaY | %                         | 23.0                 | 47                       | 30.0                  | 100           |
|                     | mcmole NH <sub>3</sub> /g | 30.2                 | 61.7                     | 39.4                  | 131.3         |

The lowest acidity (43.8 mcmole/g) and the number of strong acid centers (a.c.) - 7% is the difference between the initial PK sample. Activation by acid and modification with aluminum lead to an increase of the total acidity and the number of strong a.c. The highest acidity (131.3 mcmole/g) and the number of strong a.c. -30% Al(2.5)HPK + HLaY

Data on the activity of the catalyst Al(2.5)HPK + HLaY in the cracking of VG and its mixture with fuel oil are shown in table 6.

Table 6 - Cracking VG and mixtures of VG with fuel oil on Al(2.5)HPK+HLaY

| The yield of cracking products, % weight | VG    |       |       | VG+ Fuel oil |       |
|--|-------|-------|-------|--------------|-------|
|  | 450°C | 500°C | 550°C | 450°C        | 500°C |
| Gas                                      | 4.0   | 9.4   | 11.2  | 7.5          | 10.0  |
| Gasoline                                 | 22.1  | 38.2  | 18.5  | 32.6         | 24.3  |
| Coke                                     | 7.1   | 8.0   | 8.1   | 10.4         | 9.1   |
| Light gas oil                            | 40.0  | 29.4  | 25.0  | 25.9         | 23.2  |
| Heavy gas oil                            | 24.8  | 27.8  | 37.2  | 21.3         | 30.9  |
| Losses                                   | 2.0   | 2.2   | 2.1   | 2.3          | 2.5   |
| Conversion                               | 73.2  | 85.0  | 62.8  | 73.4         | 64.6  |
| Sum of light products                    | 62.1  | 67.6  | 43.5  | 58.6         | 46.5  |
| Octane number                            | 85    | 85    | 85    | 85           | 85    |
| Total                                    | 100   | 100   | 100   | 100          | 100   |

In VG cracking on a synthesized catalyst (table 6), the optimum temperature is 500°C. At this temperature, the yield of gasoline was 38.2%, the amount of light gas oil - 29.4%, the yield of light products - 67.6% and the conversion of raw materials - 85%. The decrease of the cracking temperature to 450°C and increasing to 550°C leads to a decrease in gasoline yields. In the cracking of a mixture of VG with fuel oil, the best results were obtained at 450°C: gasoline yield - 32.6%, light gas oil - 25.9%, the amount of light products - 58.6%. The gasoline yield during cracking of a mixture of VG with fuel oil is lower at 500°C, and at 450 ° C higher compared with VG cracking. When the mixture is cracked, coke formation is more intense than in the VG cracking: 10.4% at 450°C. The rather high activity of the synthesized catalyst is probably determined by the high content of strong acid centers and increased mesoporosity of catalyst.

The hydrocarbon compositions of the gasoline cracking gasoline and a mixture of gasoline with fuel oil are shown in table 7.

Table 7 - The hydrocarbon composition of VG cracking gasoline and a mixture of VG + fuel oil on aluminum-modified kaolinite

| Catalyst        | Raw         | T <sup>o</sup> ,C | Paraffins | Iso paraffins | Aromatic PC | Naphthenes | Ole fins | Σ   |
|-----------------|-------------|-------------------|-----------|---------------|-------------|------------|----------|-----|
| Al(2.5)HPK+HLaY | VG          | 450               | 6.9       | 22.9          | 2,3         | 15.0       | 32.9     | 100 |
|                 | VG          | 500               | 5.7       | 20.4          | 2.5         | 14.4       | 34.9     | 100 |
|                 | VG+Fuel oil | 450               | 7.1       | 19.9          | 20.8        | 18.1       | 34.1     | 100 |
|                 | VG+Fuel oil | 500               | 6.0       | 20.2          | 23.0        | 18.3       | 32.5     | 100 |

In the composition of cracking gasolines the attention is drawn to the low content of aromatic hydrocarbons, which even in the cracking of a mixture of vacuum gas oil and fuel oil does not exceed 23% at 500°C with the benzene content (1.3 and 1.5% wt). The gasoline obtained on the HLaY catalyst based on aluminum-modified kaolinite in the cracking of VG and a mixture of VG with fuel oil, can be recommended for practical use in reducing of the amount of olefins in gasoline by hydro processing.

The hydrocarbon composition of the VG cracking gases and the mixture of VG with fuel oil on the sample are illustrated in table 8.

Table 8 - Hydrocarbon composition of gases of VG cracking and mixtures thereof with fuel oil on Al (2.5) HPK + HLaY

| Hydrocarbons                            | VG    |       | VG+Fuel oil |       |
|---|-------|-------|-------------|-------|
|   | 500°C | 450°C | 450°C       | 500°C |
| Methane                                 | 14.0  | 18.9  | 19.5        | 21.2  |
| Ethane                                  | 10.3  | 12.7  | 13.0        | 14.1  |
| Ethylene                                | 15.0  | 13.7  | 19.5        | 19.1  |
| Propane                                 | 9.8   | 9.0   | 4.5         | 6.4   |
| Propylene                               | 22.7  | 20.1  | 13.3        | 19.6  |
| Iso butane                              | 4.3   | 3.3   | 2.3         | 3.0   |
| Butane                                  | 1.2   | 0.8   | 0.8         | 1.4   |
| Butylene                                | 12.5  | 10.8  | 3.2         | 7.8   |
| ΣC <sub>5</sub> +C <sub>5</sub> +       | 7.4   | 23.9  | 10.7        | 10.2  |
| ΣC <sub>2</sub> -C <sub>3</sub> alkenes | 37.7  | 33.8  | 32.8        | 38.7  |
| ΣC <sub>2</sub> -C <sub>4</sub> alkenes | 50.2  | 44.6  | 36.0        | 46.5  |

The compositions of the gaseous phase in the cracking of VG gases and the mixture of VG with fuel oil gases on an aluminum-modified kaolinite sample are quite close. VG cracking takes place with the release of significant quantities of dry gas (methane + ethane). At 450 and 500°C these values are 24.3 and 31.6%. The yield of C<sub>2</sub> - C<sub>4</sub> alkenes at these temperatures is 50.2 and 44.6%. the most yield of propylene - 22.7% and butylene - 12.5% is formed during of the cracking of VG. When cracking of mixture of fuel oil with VG, less formation of propylene and butylenes was noted. The total amount of C<sub>2</sub>-C<sub>4</sub> alkenes in VG cracking is 36.0 and 46.5% at 450 and 500°C. In the composition of the cracking gases of the mixture of VG with fuel oil the content of dry gas 32.5 and 35.3% at 450 and 500 ° C and a significant (up to 46.5%) amount of C<sub>2</sub>-C<sub>4</sub> alkenes is more than in the case of VG cracking.

## Conclusion

The results of a study of the cracking of a mixture of VG with fuel oil and VG showed that the HLaY zeolite-containing catalyst based on aluminum-modified acid-activated Pavlodar kaolinite shows a rather high activity in the formation of light oil products of 32.6% gasoline and 25.9% LG at 450°C with a raw conversion of 73.4%. The more active (38.2% gasoline and 29.4% LG) catalyst is in VG cracking. A distinctive feature of cracking gasolines on an HLaY catalyst modified with aluminum kaolinite is an increased content of isoparaffins (22.9% in cracking of VG at 450°C and 20.2% in cracking of a mixture of fuel oil with VG at 500°C) and a reduced amount of aromatic hydrocarbons not exceeding 2.5% in cracking of VG and 23.0% - in the cracking of a mixture of VG with fuel oil. The content of benzene is 1.3 - 1.5% wt. for every kind of raw. The increased content of olefinic hydrocarbons in the gasoline (32.5 - 34.9%) indicates the need for practical use of hydrotreating of the resulting gasoline.

An assumption was made about the effect of acidity and the mesoporous structure of the synthesized catalyst on the efficiency of work in the fuel direction to produce gasoline and light gas oil.

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## ВАКУУМДЫҚ ГАЗОЙЛЬ ЖӘНЕ ОНЫҢ МАЗУТПЕН ҚОСПАСЫНЫҢ КРЕКИНГІНДЕГІ АЛЮМИНИЙМЕН ТҮРЛЕРНДІРІЛГЕН КАОЛИНИТ

**Аннотация.** Алюминиймен түрлендіріліп, қышқылдық белсендірілген Павлодар кен орнының каолиниті негізіндегі HLaY-цеолитті катализаторындағы вакуумдық газойль (ВГ) және ВГ мазутпен (М-100) қоспанының крекингі бойынша мәліметтер келтірілген. Кіріспе бөлімінде каолинитті саз-балшықтар пайдаланылған катализаторлардағы крекингтің ерекшеліктері айтылған. Саз-балшықты қышқылды өңдеуден өткізіп, артынан SO<sub>4</sub>-иондарынан жылыстататын каолинитті матрицаның синтезі, сирек кездесетін аралас формадағы HY-цеолитінің және HLaY-цеолитті катализаторларының синтездері сипатталған. Цеолит құрамы 15%мас құрады. Катализаторлар мен оны құраушы компоненттері БЭТ, рентгенфазалық анализ және аммиактың термобағдарламалық десорбциясы әдістері арқылы сипатталған. Үлгілердің элементтік құрамы анықталды. Хроматографиялық әдіспен анықталған вакуумдық газойльдың фракциялық және көмірсутектік құрамы, крекинг бензині мен газ фазасының көмірсутектік құрамы келтірілген.

Қышқылдық өңдеу кезіндегі алюминий оксиді құрамының төмендеуі 2.5ммоль Al<sup>3+</sup>/г/каолинит концентрлі алюминий гидрокомплексін енгізіп, қыздырғанда Al<sub>2</sub>O<sub>3</sub> дейін ыдырау арқылы орнына келтірілді.

Алюминиймен түрлендірілген H-формалы каолиниттің меншікті бетінің мөлшері HLaY цеолитін енгізгенде 28.8 -ден 131.8 м<sup>2</sup>/г дейін үлкейеді. Каолинит қолданылған H-форма (86.2%), алюминиймен түрлендірілген H-форма (84.1%) және HLaY-катализатор (80.1%) жоғары мезокеуектілік көрсетті, шамасы сол шикізатты белсендіріп мен катализатордың белсенділігін арттыратын сияқты.

ВГ мен мазут қоспасының крекингінде 450°C кезінде бензин шығымы (32.6%) ВГ крекингінен көбірек (22.1%) шығады, ал 500°C кезінде ВГ крекингінде бензин шығымының нәтижесі жоғары (38.2%) болады. Жеңіл газойль ВГ крекингінде ең жоғары нәтиже (450°C кезінде 40.0%) көрсетеді. 450 және 500°C кезінде ВГ крекингінің түсті өнімдері (62.0 және 67.6%) қоспадан қарағанда (58.5 және 47.5%) жоғары болды. ВГ крекингінде шикізаттың ең үлкен конверсиясы байқалады.

Каолинитті қышқылмен өңдеу, алюминиймен түрлендіру және HLaY цеолитті енгізу жалпы қышқылдық пен күшті және орта қышқылдығының артуына әкеледі, Al(2.5)НПК+HLaY катализаторы үшін сәйкесінше 131.3 мкмоль NH<sub>3</sub>/г, 30 және 47%.

ВГ мен ВГ мазутпен қоспасы крекингінің бензиндері изо-парафиндер құрамының жоғарылауымен ерекшеленеді (ВГ үшін 450°C кезінде 22.9% және қоспа үшін 500°C кезінде 20.2%). 450°C кезіндегі ВГ бензинінің ароматты көмірсутектер құрамы 2.3-2.5%, ал қоспада 20.8% болды. Каолинитқұрамды катализаторындағы ВГ мен ВГ мазутты қоспасының крекинг бензиндері 1.3-1.5% аспайтын бензол құрамының аз болуымен және қанықпаған көмірсутектердің көп болуымен ерекшеленеді. Крекинг

бензинінің құрамындағы изо-парафиндер құрамының (20.2% дейін) артуы және ароматты көмірсутектер құрамының (24.1%) төмендеуі ВГ мазутпен қоспасының крекингі үшін катализаторды тартымды етеді.

Қышқылдық пен мезокеуекті құрылымның Бензин мен жеңіл газойль алынатын отындық бағыт бойынша жұмыстар тиімділігіне әсері туралы ұсыныстар айтылды.

**Түйін сөздер:** катализдік крекинг, каолинит, вакуумдық газойль, мазут, цеолит, түрлендіру.

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### МОДИФИЦИРОВАННЫЙ АЛЮМИНИЕМ КАОЛИНИТ В КРЕКИНГЕ ВАКУУМНОГО ГАЗОЙЛЯ И ЕГО СМЕСИ С МАЗУТОМ

**Аннотация.** Приведены данные по крекингу вакуумного газойля (ВГ) и смеси ВГ с мазутом (М-100) на HLaY-цеолитном катализаторе на основе модифицированного алюминием кислотно-активированного каолинита Павлодарского месторождения. В разделе «Введение» отмечены особенности крекинга на катализаторах с использованием каолининовых глин. Описаны синтез каолининовой матрицы, включающий кислотную обработку глины с последующим отмыванием от SO<sub>4</sub>-ионов, HY –цеолита в замещенной редкоземельной форме и HLaY-цеолитного катализатора. Содежание цеолита составляло 15%мас. Катализаторы и составляющие его компоненты охарактеризованы методами БЭТ, рентгенофазового анализа и термопрограммированной десорбции аммиака. Определен элементный состав образцов. Приведен фракционный и углеводородный составы вакуумного газойля, углеводородные составы бензинов крекинга и газовой фаз, определенные. хроматографическим методом.

Уменьшение содержания оксида алюминия при кислотной активации компенсировали введением гидроксиокомплекса алюминия с концентрацией 2.5ммоль Al<sup>3+</sup>/г каолинита с последующим разложением до Al<sub>2</sub>O<sub>3</sub> при прокаливании.

Величина удельной поверхности модифицированной алюминием H- формы каолинита при введении цеолита HLaY увеличивается от 28.8 до 131.8 м<sup>2</sup>/г. Показана высокая мезопористость H-формы использованного каолинита (86.2%), модифицированной алюминием H-формы (84.1%), и HLaY-катализатора (80.1%), которая, по-видимому, влияет на активацию сырья и активность катализатора.

Показано, что при 450<sup>0</sup>С в крекинге смеси ВГ с мазутом выход бензина (32.6%) больше, чем при крекинге ВГ (22.1%), а при 500<sup>0</sup>С лучшие результаты по выходу бензина (38.2%) получены для ВГ. Больше всего легкого газойля (40.0% при 450<sup>0</sup>С) образуется при крекинге ВГ. Выход светлых продуктов при 450 и 500<sup>0</sup>С для ВГ (62.0 и 67.6%) превышает этот показатель для смеси (58.5 и 47.5%). В крекинге ВГ отмечена и самая большая (85%) конверсия сырья..

Активирование каолинита кислотой, модифицирование алюминием и введение цеолита HLaY приводят к росту общей кислотности и увеличению числа сильных и средних кислотных центров, которые для катализатора Al(2.5)НПК+HLaY составляют 131.3 мкмоль NH<sub>3</sub>/г, 30 и 47%, соответственно.

Бензины крекинга ВГ и смеси ВГ с мазутом отличаются повышенным содержанием изо-парафинов (22.9% при 450<sup>0</sup>С для ВГ и 20.2% при 500<sup>0</sup>С для смеси).. Содержание ароматических углеводородов в бензине из ВГ 2.3-2.5% и 20.8% из смеси при 450<sup>0</sup>С. Бензины крекинга ВГ и смеси ВГ с мазутом, полученные на каолинит-содержащем катализаторе, отличаются малым содержанием бензола, не превышающем 1.3-1.5%, и высоким содержанием непредельных углеводородов. Это, по-видимому, определяет необходимость дополнительной гидроочистки бензинов, получаемых на модифицированных алюминием каолинит-содержащих катализаторах, при практическом использовании. Повышенное содержание изо-парафинов (до 20.2%) и пониженное содержание ароматических углеводородов (24.1%) делают катализатор привлекательным для крекинга смеси ВГ с мазутом

Высказано предположение о влиянии кислотности и мезопористой структуры синтезированного катализатора на эффективность работы по топливному направлению с получением бензина и легкого газойля

**Ключевые слова:** каталитический крекинг, каолинит, вакуумный газойль, мазут, цеолит, модифицирование.

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