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Д.В.Сокольский атындағы «Жанармай,
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ХАБАРЛАРЫ

ИЗВЕСТИЯ

НАЦИОНАЛЬНОЙ АКАДЕМИИ НАУК
РЕСПУБЛИКИ КАЗАХСТАН
АО «Институт топлива, катализа и
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Қазақстан Республикасы Ұлттық ғылым академиясы "ҚР ҰҒА Хабарлары. Химия және технология сериясы" ғылыми журналының Web of Science-тің жаңаланған нұсқасы Emerging Sources Citation Index-те индекстелуге қабылданғанын хабарлайды. Бұл индекстелу барысында Clarivate Analytics компаниясы журналды одан әрі the Science Citation Index Expanded, the Social Sciences Citation Index және the Arts & Humanities Citation Index-ке қабылдау мәселесін қарастыруда. Webof Science зерттеушілер, авторлар, баспашылар мен мекемелерге контент тереңдігі мен сапасын ұсынады. ҚР ҰҒА Хабарлары. Химия және технология сериясы Emerging Sources Citation Index-ке енуі біздің қоғамдастық үшін ең өзекті және беделді химиялық ғылымдар бойынша контентке адалдығымызды білдіреді.

НАН РК сообщает, что научный журнал «Известия НАН РК. Серия химии и технологий» был принят для индексирования в Emerging Sources Citation Index, обновленной версии Web of Science. Содержание в этом индексировании находится в стадии рассмотрения компанией Clarivate Analytics для дальнейшего принятия журнала в the Science Citation Index Expanded, the Social Sciences Citation Index и the Arts & Humanities Citation Index. Web of Science предлагает качество и глубину контента для исследователей, авторов, издателей и учреждений. Включение Известия НАН РК в Emerging Sources Citation Index демонстрирует нашу приверженность к наиболее актуальному и влиятельному контенту по химическим наукам для нашего сообщества.

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каб. 310, тел. 291-62-80, факс 291-57-22, e-mail:orgcat@nursat.kz
Адрес типографии: ИП «Аруна», г. Алматы, ул. Муратбаева, 75

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A.K. Akurpekova, N.A. Zakarina, O. Dalelhanuly, D.A. Zhumadullaev

JCS D.V. Sokolsky Institute of Fuel Catalysis and Electrochemistry, Almaty, Kazakhstan
akurpekova@mail.ru, zakarina_nelly@rambler.ru, orken_kz777@mail.ru, dauletmmm@mail.ru

CATALYTIC CRAKING OF A VACUUM GASOLINE ON HLaY - A ZEOLITE CATALYST ON A NONACTIVATED ALUMINUM MILLED

Abstract. A comparison of the phase, elemental composition of CaNa-montmorillonite (MM) with the properties of MM in the Na-form was made, and it was found that the initial CaNaMM and NaMM, as well as the catalysts based on them, are close to each other in elemental and phase compositions. The textural properties of montmorillonites are determined and it is shown that the specific surface area, pore volume and number of micropores of the initial CaNaMM is slightly higher than that of NaMM. The specific surface during aluminum pillaring grows 2.2 times, while in the case of NaMM, the growth is 1.5 times.

Using the TPD NH_3 method it was shown that the catalyst based on CaNaMM exceeds the catalyst based on NaMM in total acidity, the number of medium and strong acid sites (Table 3). It was shown that a zeolite-containing catalyst with a matrix of Al-pillared MM in the CaNa-form exhibits high activity in the cracking of vacuum gas oil (VG) with the production of 60% light gas oil. The high thermal stability of the cracking catalyst on the base of MM in the CaNa-form and its high mechanical strength have been established.

Keywords: catalytic cracking, zeolite, pillar montmorillonite, light gas oil, gasoline, gas, vacuum gas oil.

Introduction. The oil refining and petrochemical industry plays an important, and in some cases the most important role in the economy of any country [1-4]. In this regard, worldwide attention is paid to the deepening of oil refining, expanding the range, improving the quality of commodity fuels, especially environmental properties [5,6]. The tightening of environmental requirements for car engines around the world leads to a gradual transition from gasoline to diesel engines. Thus, in Europe, gasoline consumption decreased by 22%, and diesel fuel consumption increased by 19% [7]. Increased demand leads to the search for new sources of diesel fuel. One of such sources is potentially catalytic cracking, in which, in addition to gasoline and light hydrocarbon gases, a distillate fraction is produced - light catalytic cracking gas oil (LGCC) with a boiling range of 200-350^{0}C. LGCCs are used as a component of diesel fuel when compounding with a straight-run diesel fraction of up to 30%. The share of LGCC in commercial diesel fuel is limited to a high content of aromatic hydrocarbons, sulfur, low cetane number and high density [8]. Due to the growing demand for diesel fuel and the constant improvement of technology and catalysts, the catalytic cracking process can now be considered as a way to produce not only gasoline, but also high-quality diesel fuel [9]. In modern plants using industrial cracking catalysts by cracking vacuum gas oil, it ranges from 10–15% with a rather low cetane number (25–30 points) [9–11]; on advanced ball catalysts, increased yield of light gas oil (37,6-38,2%)was observed [12], and on granulated, for example, a series of "Adamant" light gasoil yield even higher (42,6-45,4%) [13].

Zeolites used in the composition of catalysts should have high activity and selectivity in the cracking of petroleum fractions, stability under high-temperature effects in air and water vapor, and the necessary dimensions of the entrance windows in the structure cavity [14-16]. Zeolites of the X and Y types in the rare-earth exchange form or in the ultra stable form are most relevant to such requirements, and therefore they find their primary use in the synthesis of cracking catalysts [17, 18].

For the preparation of the matrix of cracking catalysts, it was proposed to use a new class of materials based on natural bentonites, modification of which by pillaring allows increasing the specific surface, their thermal stability and significantly increasing the volume of micro- and mesopores [19,20]. In chemical modification of layered aluminosilicates with an expanding lattice, it becomes possible to regulate the acid-base properties of the surface and fix transition metal compounds on it, which was the basis for using these materials as catalysts in hydrocarbon conversion reactions: cracking, isomerization, alkylation, etc. [22, 23].

Based on zeolite Y in a lanthanum-substituted form (HLaY) deposited on an aluminum pillar montmorillonite in the Na-form (AlNaMM), a composite catalyst for cracking heavy vacuum gas oil has been developed to produce light gas oil with a yield of 55-67% depending on the volume of the catalyst. An increase in the yield of light gas oil was found (up to 72%) after steam treatment of the catalyst [24]. The composition of the catalyst for the production of light gas oil during the cracking of VG is protected by the innovative patent of the Republic of Kazakhstan [25]. In connection with the use of zeolite HLaY on Al-pillar MM in Na-form in the composition of the catalyst for producing light gas oil, it was of interest to reveal the dependence of the cracking properties of this catalyst on the composition of MM, its physicochemical properties, as well as on the composition and properties of vacuum gas oil.

The purpose of the work is the synthesis of HLaY zeolite-containing catalysts deposited on Al-pillared montmorillonite in CaNa- form and revealing the influence of the composition of the initial MM, its exchange form and physicochemical characteristics on the yield of light gas oil during cracking of vacuum gas oil of make B with increased sulfur content.

Experimental part

Tagan montmorillonite (Kazakhstan) from the Zapadny open pit, 12 horizons containing the following alkaline cations were used as raw materials for the preparation of the catalyst: Na^+> 35 mg / eq, Ca^{++} ≥28 mg / eq, Mg^{++} = 24 mg / eq, K^+ ~ 4.0 mg / eq. The aluminum hydroxocomplex of the supposed composition $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$ abbreviated (Al_{13}^{7+}) with a four-coordinated aluminum atom, was used as a fixing agent in pillaring. The method of obtaining oligomeric (Al_{13}^{7+}) consists in hydrolysis of an aqueous $AlCl_3$ solution with an aqueous solution of NaOH with a ratio of $OH^- / Al^{3+} = 2.5$ and a final pH = 4.1 under conditions of vigorous stirring. The procedure for the synthesis of aluminum montmorillonite (AlNaHMM) is described in [19-22]. The catalyst was additionally modified with zeolite Y in the substituted La-form (15%), molded into granules, dried for 24 hours at room temperature, then calcined at 150°C (2 hours) and 500°C (2 hours).

Elemental analysis of the catalyst samples was carried out by the method of energy dispersive - X-ray fluorescence spectroscopy on the energy dispersive microanalysis system INCA - Energy 450, installed on a JSM6610LV scanning electron microscope, JOEL, Japan.

The textural characteristics of the catalysts were determined by the isotherms of low-temperature adsorption and desorption of nitrogen on an Accusorb device (BET method).

XRD samples of catalysts were carried out using a DRON-4 * 0.7 X-ray diffractometer; with CoK_α and CuK_α radiation. The diffractometric reflexes of the catalyst samples were compared with ICPDS powder standards.

The catalytic activity of the samples was determined in a laboratory flow-type installation corresponding to the standard, with a fixed catalyst bed in an amount of 40 ml. The catalytic activity was determined in the temperature range 500-550^{0}C. Vacuum gasoil (VG) of make B, type 2 of Pavlodar Petrochemical Plant (PPCP) was used as a raw material for cracking with the following characteristics: the density 907.7 kg / m^3, kinematic viscosity at 500°C equal to 27.05 mm^2 / s, sulfur content 1.5 mass.%, harden point 30^{0}C and coking ability 0.14 wt.%, with the end of boiling 510^{0}C. During the distillation of catalyzate, the gasoline fractions $T_{b.b.}$-205^{0}C and light gas oil 205-350^{0}C were collected. The analysis of the hydrocarbon composition of gasoline cracking was performed on a chromatograph “Chromos-1000” with a flame ionization detector and a capillary column 100 m long; temperature is 250°C; the carrier gas is helium.

Results and its discussion

The physicochemical characteristics of the Tagan montmorillonite in the Na-form, which was used previously, and in the CaNa-form, as well as HLaY-zeolite catalysts with their use are shown in Table 1-3.

Table 1 shows the data on the elemental composition of calcium-sodium and sodium forms of the Tagan montmorillonite and catalysts based on them. The table includes the average of 3 measurements in weight%.

Table 1 - The elemental composition of composite catalysts based
on Al-pillared montmorillonite in CaNa-and Na-forms

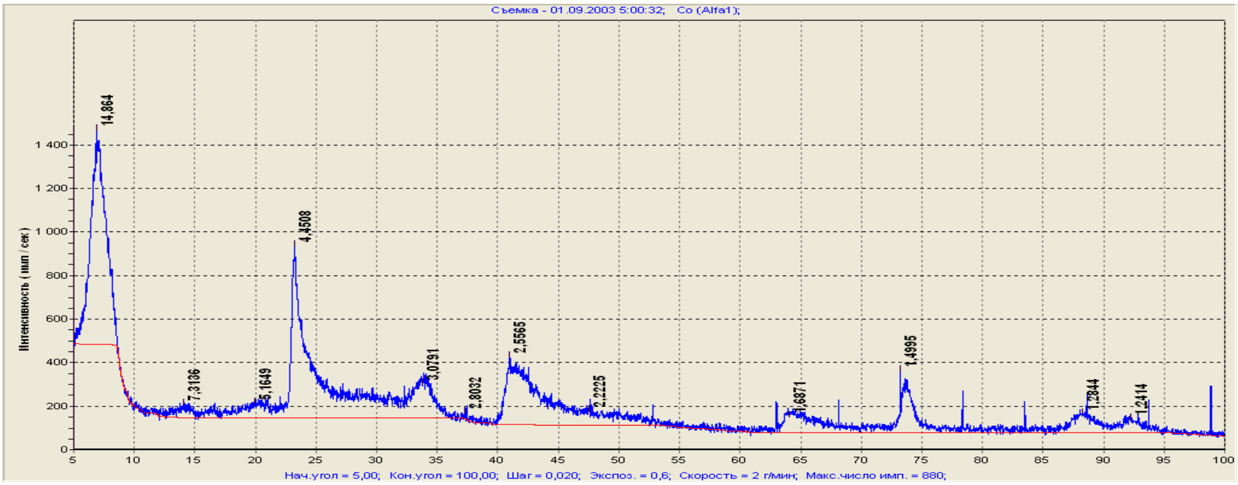
Sample	O	Na	Mg	Al	Si	Ca	Fe	La
CaNaMM	54,6	1,0	2,1	13,4	27,9	0,7	0,3	
Al(2.5)CaNaMM	56,4		1,6	16,7	25,0		0,3	
Al(2.5)CaNaMM+HLaY	53,8	0,2	1,1	19,8	23,2		0,2	1,7
NaMM	51,6	1.4	2,1	11,3	24,7	0.56	0.39	
Al(2.5)NaMM	54,63	-	1,19	11,87	20,83	-	0,25	-
Al(2.5)NaMM+HLaY	53,66	0,48	0,79	10,80	21,53		0,21	2.03

From the analysis of the data in Table 1, it follows that pillaring of Al leads to the complete replacement of sodium and calcium from both types of MM and a decrease in the relative amounts of magnesium and silicon. The aluminum content after pillaring increased, which confirms the formation of aluminum-oxide columns. With the introduction of HLaY, the amount of La in the CaNaMM-based catalyst is 1.7% and 0.2% of Na appears, while the amount of La and Na in Al (2.5) NaMM + HLaY is significantly higher (2.03 and 0.48%). It should be noted a higher content of Fe in the initial NaMM (0.39%) compared to CaNaMM (0.3%). In the process of pillaring and introducing zeolite, a decrease in the amount of Fe is observed, more significant in the case of a catalyst based on NaMM. In the prepared catalysts based on two different MM, the amount of Fe is approximately the same.

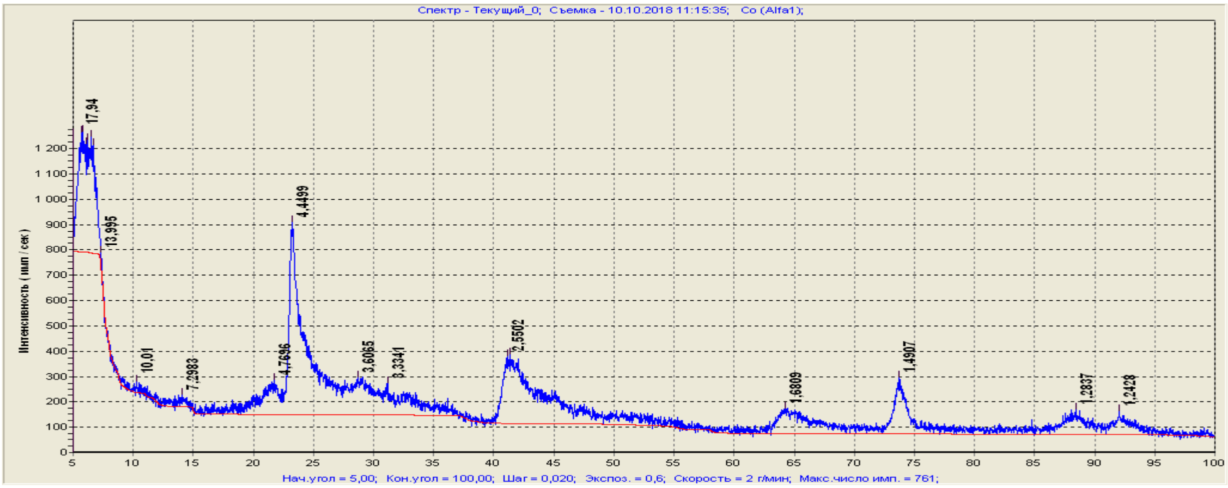
According to the X-ray phase analysis (XRD) in the initial samples of CaNaMM next phases were identified with reflexes: MM-11.0; 4.46; 3.23; 2.50; 1.67; 1.50; 1.28; quartz-4.27; 3.34; 2.45; 2.23; 2.12; 1.98; 1.81; 1.54; HLaY-14,6; kaolinite-7.2.

It can be seen from Figure 1 that when pillary CaNaMM, the first basal reflex increases from d_1 = 14.8Å to 17.9Å. The introduction of zeolite leads to a slight decrease in the first basal reflex to d_1 = 16.3Å and the appearance of reflex 14.6. A comparison with the Al (2.5) NaMM + HLaY- catalyst shows that in this case the separation of the MM layers in the finished catalyst is much less than –11.0 Å, and the reflex 14.6 also appears when HLaY is introduced [23].

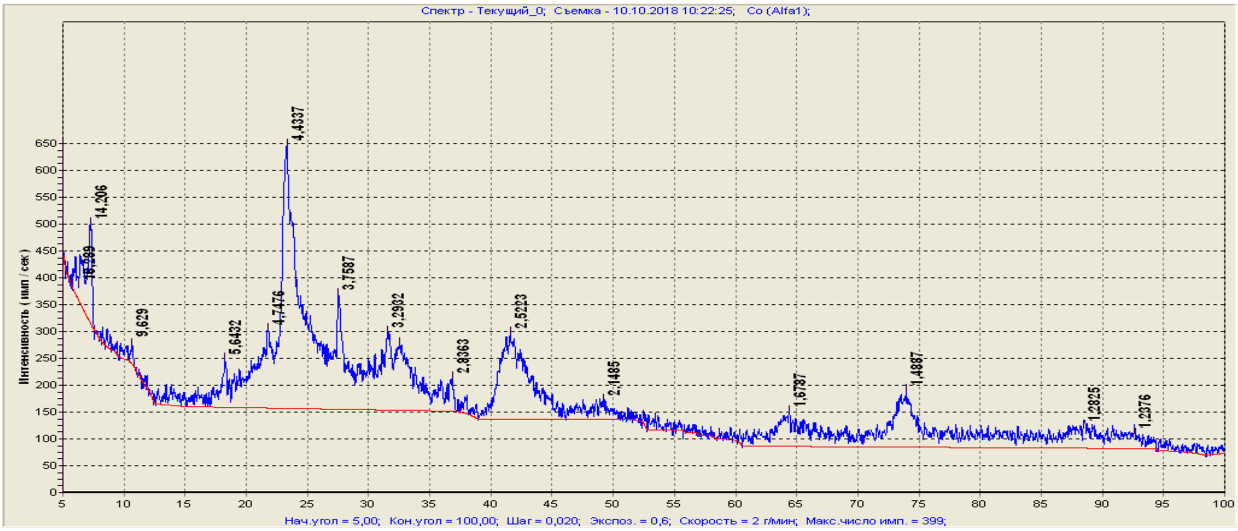
The textural properties of the initial MM in CaNa- and Na-forms and the catalysts based on them are presented in Table 2. The specific surface area of CaNaMM grows when pillaring Al from 86.4 cm^3/g to 190.5 cm^3/g, and with the introduction of HLaY there is a further increase in the specific surface to 308.6 cm^3/g. The total pore volume also increases with pillaring, which is accompanied by an increase in the number of micropores and a decrease in the number of mesopores. It is of interest to compare the textural properties of the original form of CaNaMM with the properties of montmorillonite in the Na-form, which we used earlier to prepare the catalyst. From table 2 it can be seen that the specific surface area, pore volume and number of micropores in the initial CaNaMM are slightly higher than in NaMM. The specific surface during aluminum pillaring grows 2.2 times, while in the case of NaMM, the growth is 1.5 times. For both carriers, an increase in the number of micropores is observed in pillaring: in the case of CaNaMM, by 1.5 times, and for NaMM, by 2.9 times. The introduction of zeolite leads to a further increase in the number of micropores, while in the case of NaMM, modifying with HLaY zeolite reduces the number of micropores in the catalyst. A comparison of the cracking catalysts based on MM in the CaNa- and Na-forms shows that Al(2.5)CaNaMM+HLaY has a much more developed surface and a greater number of micropores than the catalyst based on NaMM.



CaNaMM



Al(2,5)CaNaMM



Al(2.5)CaNaMM+HLaY

Figure 1 - Diffractograms of the original CaNaMM, pillared Al (2.5) CaNaMM and modified with zeolite Al (2.5) CaNaMM + HLaY

Table 2 - Comparative textural characteristics of the original calcium-sodium and sodium forms of the Tagan montmorillonite and catalysts based on them

Sample	S, m^2/g	Total pore volume, sm^3 / g	R, Å	Relative amount,%	
				Micropores, (0-20Å)	Mesopores, (20-80Å)
CaNaMM	86,4	0,083	10,0-73,0	30,0	70,0
Al(2.5)CaNaMM	190,5	0,182	10,0-75,0	44,1	55,9
Al(2.5)CaNaMM+HLaY	308,6	0,167	11,0-72,0	57,4	42,6
NaMM	80,9	0,081	11,5-75,0	26,7	73,3
Al(2.5)NaMM	123,4	0,176	10,0-90,0	78,5	21,5
Al(2.5)NaMM+HLaY	124,2	0,107	10,0-65,0	50,0	50,0

Comparison of acidic properties of cracking catalysts based on MM in various exchange forms showed that the catalyst based on CaNaMM exceeds the catalyst based on NaMM (Table 3) in total acidity, the number of medium and strong acid sites. The distribution of acid sites in strength is almost completely preserved on the catalyst after testing in the cracking reaction. According to the relative amount of acid sites of different strength, the catalysts using MM of different composition are close to each other.

Table 3 - Acidity of zeolite-containing Al (2.5) CaNaMM + HLaY-catalyst before and after the experiment according to TPD ammonia

Sample	Content a.c.	Acid Centers			
		Weak<200^{0}C	Medium 200-300^{0}C	Strong >300^{0}C	Total acidity
Al(2,5)CaNaMM+ HLaY(before)	%	29,67	35,58	34,75	100
	μmol NH$_3$/g	87,36	104,76	102,31	294,43
Al(2,5)CaNaMM+ HLaY (after)	%	26,31	36,14	37,55	100
	μmol NH$_3$/g	77,72	106,76	110,92	295,4
Al(2,5)NaMM+ HLaY	%	45,0	30,0	25,0	100
	μmol NH$_3$/g	112,5	75,0	62,5	250,0

The data on the VG cracking on Al (2.5) CaNaMM + HLaY- catalyst is shown in Figure 2.

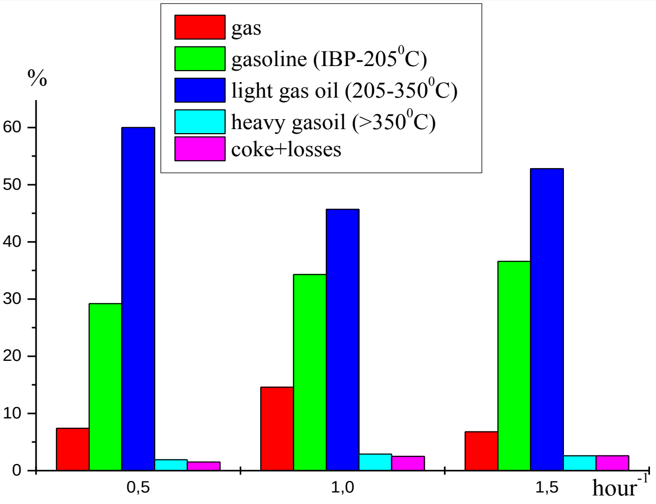


Figure 2 – Data of the VG cracking on Al (2.5) CaNaMM + HLaY-catalyst by varying the space velocity at the T = 500^{0}C

From the results of the material balance of the cracking of VG, it can be seen that on Al(2.5)CaNaMM+HLaY-catalyst, with the space velocity of 0.5hour $^{-1}$ the maximum yield of light gas oil equal to 60.0% was obtained at a cracking temperature of 500^{0}C. With an increase of the space velocity, the yield of light gas oil decreases, the amount of produced gas and gasoline increases. The tested catalyst is characterized by the formation of a large amount of light gas oil in the process of cracking VG.

An increase of the cracking temperature from 500°C to 550°C leads to a slight decrease in the yield of light gas oil from 60.0% at 500^{o}C to 58.8% at 550° C. Comparative data on the activity of Al(2.5)CaNaMM+HLaY catalysts in the cracking of VG at a temperature of 500-550^{0}C are presented in table 3.

Table 4 – Material balance of VG cracking
on Al (2.5) CaNaMM + HLaY- catalyst at various temperatures

Products	The yield of products, wt.%	
Temperature	500^{0}C	550^{0}C
Gas	7,4	8,4
Gasoline (b.b.-205^{0}C)	29,2	29,6
Light gas oil (205 - 350^{0}C)	60,0	58,8
Heavy gas oil (>350^{0}C)	1,9	1,8
Coke+Losses	1,5	1,4
Amount of products	100	100

Thus, for Al (2.5) CaNaMM + HLaY catalyst, optimal conditions were selected for producing light gas oil by cracking VG with a yield of at least 60%: the cracking temperature is 500^{0}C, the feed space velocity is 0.5 hour^{-1}. Cetan number of gas oil is 63, sulfur content 1.91 wt.%. The crush strength of this catalyst granule is 166.3 N / sm^2. The strength of NaMM based catalyst granules is higher and amounts to 216-230 N / sm^2 [24].

To determine the thermal stability of Al (2.5) CaNaMM + HLaY catalyst, it was subjected to thermovapor treatment at the temperature 750^{0}C during 6 hours with 100% vapor.. Table 4 presents comparative data on the effect of thermovapor treatment of the synthesized catalyst on the activity in the cracking of the VG at the temperature 500^{0}C.

Table 5 - Material balance of VG cracking on Al (2.5) CaNaHMM + HLaY at 500^{0}C before
and after thermovapor treatment (tv/t) at the feed space velocity 0.5 hour $^{-1}$

The yield of products, wt.%	Before (tv/t)	After(tv/t)
Gas	7,4	7,3
Gasoline (b.b.-205^{0}C)	29,2	27,7
Light gas oil (205 - 350^{0}C)	60,0	60,9
Heavy gas oil (>350^{0}C)	1,9	2,5
Coke+Losses	1,4	1,6
Amount of products	100	100

As follows from the data of table 5, the yield of light gas oil after termovapor treatment increases to 60.9%, the yield of gasoline, on the contrary, decreases by 1.5%, and the yield of heavy gas oil increases by 0.6% compared to the results before tv/t. Comparison with the results obtained earlier on the catalyst using NaMM [23,24] showed that before tv/t the catalyst based on CaNaMM shows higher activity and the yield of light gas oil and gasoline-60.0 and 29.2% (see table .4) probably due to higher specific surface area and acidity (see Tables 2 and 3). The yield of light gas oil and gasoline on Al(2.5)NaMM + HLaY at 500^0 C is 55.0 and 17%, respectively (Table 6). However, after tv/t, the yield of light gas oil increases to 72%, and the yield of gasoline decreases to 7.9 %. According to the results on Al (2.5) CaNaMM + HLaY, the yield of light gas oil after tv /t increases only by 1-2%, while the yield of gasoline remains at a fairly high level (27.7%).

Table 6 - Cracking VG PPCP on Al (2.5) NaMM + HLaY before and after tv/t (reactor 50 ml) [23,24]

Cracking products	Yield,% wt.			
	before vapor treatment		after vapor treatment	
	500°C	550°C	500°C	550°C
Gas	2.0	19.3	3.0	5.0
Gasoline	17.0	20.5	7.9	25.5
Coke	7.8	2.3	9.8	10.0
Light gas oil (205 - 350^{0}C)	55.0	45.3	72.0	52.1
Heavy gas oil (>350^{0}C)	15.0	10.0	5.5	5.4
Losses	2.2	2.2	2.0	2.0
Conversion	82.8	87.4	92.7	92.6
Amount of products	72.0	75.8	79.9	77.6

Thus, the obtained results showed that the developed highly active and stable catalyst for the cracking of vacuum gas oil with obtaining 60.0% of light gas oil retains its activity when using MM with various exchange cations and exhibits high thermal stability during cracking VG with sulfur content up to 1.5 mass .%. The catalyst can be recommended for practical use.

Conclusion

A comparison of the phase, elemental composition of CaNa-montmorillonite with the properties of montmorillonite in the Na form was made and it was found that the initial CaNaMM and NaMM, as well as the catalysts based on them, are close to each other in elemental and phase compositions. The textural properties of montmorillonites are determined and it is shown that the specific surface area, pore volume and number of micropores of the initial CaNaMM is slightly higher than that of NaMM. The specific surface during aluminum pillaring grows 2.2 times, while in the case of NaMM, the growth is 1.5 times.

Using the method of TPD NH3, it was shown that the catalyst based on CaNaMM exceeds the catalyst based on NaMM in total acidity, the number of medium and strong acid sites (Table 3). It was shown that a zeolite-containing catalyst with a matrix of Al- pillared MM in the CaNa-form exhibits high activity in the cracking of VG with obtaining 60% light gas oil. The high thermal stability of the cracking catalyst on the base CaNaMM and its high mechanical strength have been established.

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А.К.Акурпекова, Н.А.Закарина, Ө.Дәлелханұлы, Д.А. Жумадуллаев

Д.В. Сокольский атындағы жанармай, катализ және электрохимия институты АҚ, Алматы қ.,Казақстан

БЕЛСЕНДІРІЛМЕЙ АЛЮМИНИЙМЕН ПИЛЛАРИРЛЕНГЕН МОНТМОРИЛЛОНИТТЕГІ HLaY – ЦЕОЛИТТІ КАТАЛИЗАТОРЫНДАҒЫ ВАКУУМДЫҚ ГАЗОЙЛЬДІҢ КАТАЛИТИКАЛЫҚ КРЕКИНГІ

Аннотация. CaNa-монтмориллониттің фазалық, элементтік құрамы Na- формалы монтмориллонит қасиеттерімен салыстырылды және бастапқы CaNaMM және NaMM, сонымен қатар солар негізіндегі катализаторлар элементтік және фазалық құрамы бойынша өзара ұқсас болатыны анықталды. Монтмориллониттердің текстуралық қасиеттері анықталып, бастапқы CaNaMM меншікті беті, кеуектер көлемі, микрокеуектер саны NaMM қарағанда бірнеше артық екені көрсетілді. Меншікті беті алюминиймен пилларирлегенде 2,2 есе өседі, ал NaMM бұндай жағдайда 1,5 есе артады.

NH_3 ТПД әдісімен CaNaMM негізіндегі катализатор жалпы қышқылдық, орта және күшті қышқылды орталықтар саны бойынша NaMM негізіндегі катализатордан асып түсетіні көрсетілді (3-кесте). Al пилларирленген CaNa-формалық монтмориллонит матрицалы цеолитқұрамды катализатор ВГ крекингінде 60% жеңіл газойль түзіп жоғары белсенділік танытады. CaNa-формалы ММ негізіндегі крекинг катализаторының жоғары термиялық тұрақтылығы мен оның жоғары механикалық беріктігі анықталды.

Түйін сөздер: каталитикалық крекинг, цеолит, пилларирленген монтмориллонит, жеңіл газойль, жанармай, газ, вакуумдық газойль

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А.К.Акурпекова, Н.А.Закарина, О.Далелханулы, Д.А.Жумадуллаев

АО Институт топлива, катализа и электрохимии им.Д. В.Сокольского,
г. Алматы, Казахстан

КАТАЛИТИЧЕСКИЙ КРЕКИНГ ВАКУУМНОГО ГАЗОЙЛЯ НА HLaY – ЦЕОЛИТНОМ КАТАЛИЗАТОРЕ НА НЕАКТИВИРОВАННОМ ПИЛЛАРИРОВАННОМ АЛЮМИНИЕМ МОНТМОРИЛЛОНИТЕ

Аннотация. Проведено сопоставление фазового, элементного состава CaNa-монтмориллонита со свойствами монтмориллонита в Na- форме и найдено, что исходные CaNaMM и NaMM, а также катализаторы на их основе близки между собой по элементному и фазовому составам. Определены текстурные свойства монтмориллонитов и показано,что что удельная поверхность, объем пор и количество микропор у исходного CaNaMM несколько выше, чем у NaMM. Удельная поверхность при пилларировании алюминием растет в 2,2 раза, в то время как в случае NaMM рост составляет 1,5 раза.

Методом ТПД NH_3 показано, что по суммарной кислотности, количеству средних и сильных кислотных центров катализатор на основе CaNaMM превосходит катализатор на основе NaMM (табл.3). Показано, что цеолитсодержащий катализатор с матрицей из пилларированного Al монтмориллонита в CaNa-форме проявляет высокую активность в крекинге ВГ с получением 60% легкого газойля. Установлена высокая термическая стабильность катализатора крекинга на основе ММ в CaNa-форме и его высокая механическая прочность.

Ключевые слова: каталитический крекинг, цеолит, пилларированный монтмориллонит, легкий газойль, бензин, газ, вакуумный газойль.

Information about authors:

Akurpekova A.K. - Candidate of Chemical Sciences, the Senior Researcher of laboratory of oil processing catalysts of JCS “D.V. Sokolsky Institute of fuel, catalysis and electrochemistry”, Almaty, Kazakhstan. Tel. +77476737782, e-mail: akurpekova@mail.ru, https:orcid.org/0000-0002-8021-4644

Zakarina N. A. – Doctor of Chemical Sciences, Professor, Head of the laboratory of oil processing catalysts of JCS “D.V. Sokolsky Institute of fuel, catalysis and electrochemistry”,Almaty, Kazakhstan. Tel. +77014018953, e-mail: nelly_zakarina@rambler.ru, https:orcid.org/0000-0002-5895-8110.

Dalelkhauly O. - researcher of laboratory of oil processing catalysts of JCS “D.V. Sokolsky Institute of fuel, catalysis and electrochemistry”, Almaty, Kazakhstan. Tel. +77071983717, e-mail: orken_kz777@mail.ru, https:orcid.org/ /0000-0001-5856-3488

Zhumadullaev D.A. - researcher of laboratory of oil processing catalysts of JCS “D.V. Sokolsky Institute of fuel, catalysis and electrochemistry”, Almaty, Kazakhstan. Tel. +77016577763, e-mail: dauletmmm@mail.ru, https://orcid.org/0000-0001-6245-6802

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