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ХАБАРЛАРЫ

ИЗВЕСТИЯ

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NAS RK is pleased to announce that News of NAS RK. Series of chemistry and technologies scientific journal has been accepted for indexing in the Emerging Sources Citation Index, a new edition of Web of Science. Content in this index is under consideration by Clarivate Analytics to be accepted in the Science Citation Index Expanded, the Social Sciences Citation Index, and the Arts & Humanities Citation Index. The quality and depth of content Web of Science offers to researchers, authors, publishers, and institutions sets it apart from other research databases. The inclusion of News of NAS RK. Series of chemistry and technologies in the Emerging Sources Citation Index demonstrates our dedication to providing the most relevant and influential content of chemical sciences to our community.

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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EFFECT OF THE TERMAL TREATMENT TEMPERATURE ON THE DURABILITY AND THE CRACKING ACTIVITY OF THE CATALYSTS ON THE BASE OF MODIFIED MONTMORILLONITE

Abstract. Increase of the durability of granules of Al (2.5) NaHMM +HLaY-catalyst at crush with temperature increase of calcination of catalysts from 500 to 650^{0}C is found. It is noticed that the introduction of zeolite Y in the replaced rare-earth form leads to growth of durability of the granulated catalyst.

It is shown that preliminary calcination at 550,600^{0}C of the zeolitecontained catalysts supported on the activated Al-pillared montmorillonite in Na-and CaNa – forms, leads to significant reduction of yields of gasoline on these catalysts that demonstrates that heat treatment of the catalyst increases durability, but does not provide necessary activity of the catalyst in the fuel direction.

Keywords: catalytic cracking, termal treatment, pillared montmorillonite, gasoline, light gasoil, vacuum gasoil.

Introduction. One of the most important operational characteristics of heterogeneous catalysts is their mechanical strength with respect to compression, bump and abrasion, depending on the technology of the catalytic process [1,2]. With the continuous movement of the catalyst in the form of a fluidized bed in catalytic cracking units, the catalyst particles are hit against the equipment walls and against each other with the formation of crumb catalyst and dust, which requires constant replenishment and significantly increases the cost for the production of cracking products. For catalytic processes, an important role is played by the selection of the matrix or carrier, which provides the necessary porous structure, specific surface area, heat resistance, and mechanical strength of the catalyst. It is known that the strength characteristics of catalysts are determined by their composition and textural properties - porosity, specific surface, size of primary particles, etc. However, there are very few works in the literature devoted to the study of the relationship between strength and physicochemical properties of catalytic systems [3]. In connection with the above, the development of new effective ways to increase the mechanical strength of catalysts for oil refining based on natural clays and zeolites seems to be an actual task for modern oil refining.

In this work, Tagansky montmorillonite was used as a matrix of catalysts, on the basis of which new highly efficient cracking catalysts were synthesized by pillaring of clays [4,5]. However, the strength of catalysts based on matrices with pillared montmorillonite does not always corresponded to the requirements of their operation. To increase the strength and durability of the catalysts, pretreatment of natural montmorillonite was varied by adjusting the calcination temperature, which is accompanied by an increase in the bulk density and strength of the catalysts.

The purpose of the work is to determine the crush strength and the activity of catalysts based on Al-pillared montmorillonite and zeolite Y in the cracking of vacuum gas oil, depending on the temperature of the preliminary calcination of the catalyst.

Experimental part

In the synthesis of pillared clays, an aluminum hydroxocomplex of the proposed 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. 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[6]. The catalyst was additionally modified with zeolite Y in the substituted La-form (15%).

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 crush strength of the investigated catalysts was determined from the results of three measurements on the device “Prochnomer katalizatorov” PK-21-015, JSC BSKB «Neftekhimavtomatika» (Russian).

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 30 ml. The catalytic activity was determined in the temperature range 480-550^{0}C with a bulk feed rate of 1 hour^{-1}. Vacuum gas oil (VG) of the Pavlodar Petrochemical Plant (PPCP) with the end of boiling point of 510^{0}C was used as a raw material for cracking. During the distillation of catalyzate, the gasoline fractions $T_{b.p.}$-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^{0}C; helium is carrier gas.

Results and discussions

At present, montmorillonite is successfully used in the matrix of Russian industrial cracking catalysts [7,8]. In addition to participation, along with other components of the matrix (aluminosilicate, aluminum oxide) in the formation of the porous structure of the catalyst and the primary cracking of large hydrocarbon molecules, montmorillonite provides the mechanical strength of the catalyst, which is determined by the pretreatment method of montmorillonite, its porous structure and composition. It is known that the pillaring of clays with metal oxides with the formation of columnar structures leads to the formation of new porous materials with a high specific surface, a large volume of micro- and mesopores, and an increased thermal stability [9]. Matrix-based catalysts with Al-pillared montmorillonite were chosen as objects for developing ways to increase crushing strength due to the fact that they had the highest activity on gasoline output, but were distinguished by low strength. To increase the strength and durability of the catalysts, pretreatment of natural montmorillonite was varied by adjusting the temperature of calcination in air and introducing various additives before the intercalation stage. To select the optimum temperature for calcining catalysts, two batches of Al (2.5) NaHMM + HLaY and Al (2.5) CaNaHMM + HLaY catalysts were prepared. A preliminary analysis of the samples was carried out (Table 1), from which it is clear that NaMM activation with sulfuric acid helps remove Na^+ ions from the initial montmorillonite and reduces the sodium content from 1.4% in the original NaMM to 0.2% in activated NaHMM and remove it completely after aluminum pillaring. The elemental compositions of the initial NaMM and CaNaMM are close to each other. The difference was found only in some excess of iron in NaMM compared to CaNaMM. The introduction of HLaY into the catalyst leads to an increase in the sodium content to 0.5%, and the amount of La is 2.0%. The composition of the catalyst varies little after testing in cracking.

Table 1 - The elemental composition of composite catalysts based on Al-pillared montmorillonite before and after the cracking of vacuum gas oil on it

Sample	C	O	Na	Mg	Al	Si	Cl	Ca	Fe	La
NaMM	7.78	51.6	1.4	2.1	11.3	24.7	0.3	0.56	0.39	-
NaHMM	8.09	52.5	0.2	2.0	11.4	25.0	-	0.38	0.37	-
Al(2.5)NaHMM	11.2	54.6	-	1.2	11.9	20.8	-	-	0.25	-
Al(2.5)NaHMM+HLaY	10.5	53.7	0.5	0.8	10.8	21.5	-	-	0.21	2.03
Al(2.5)NaHMM+HLaYafter the experience	10.4	52.4	0.4	0.9	11.3	22.7	-	-	0.20	1.75
CaNaMM	7.8	52.0	0.9	1.9	12.0	24.6	-	0.61	0.25	-

The crush strength of the studied catalysts, as can be seen from the results of Table 2, depends on the composition and temperature of the preliminary calcination.It is noticed that the introduction of zeolite Y in the replaced rare-earth form leads to growth of durability of the granulated catalyst.With an increase in the temperature of calcination of Al (2.5) NaHMM + HLaY- catalyst from 500 to 650^{0}C, its strength increases sharply and at 600^{0}C reaches its maximum value and then decreases. On the spent catalyst, the strength at all calcination temperatures is slightly lower than the strength of the initial, and the maximum strength equal to 104.6 N / cm^2 was found at a calcination temperature of 550^{0}C.

Table 2 - Strength characteristics of Al (2.5) NaHMM + HLaY- catalysts depending on the temperature of calcination by compression method

	Sample	Calcination temperature, ^{0}C	Strength, N / cm^2
	Al(2.5)NaHMM	500	50.1
	Al(2.5)NaHMM+HLaY	500	80.1
		550	100.3
		600	107.2
		650	94.3
	Al(2.5)NaHMM+HLaY (after experience)	500	80.1
		550	104.6
		600	70.3
		650	77.4

Earlier, we showed that Al (2.5) NaHMM + HLaY showed high activity on the yield of gasoline during the cracking of VG PPCP. This vacuum distillate has the end of boiling point (EBP) of 534^{0}C. Fractional composition: initial boiling point(IBP) - 282^{0}C; 5% -342; 10% -360; 50% -423; 90% -494; 95% -516^{0}C. Mass fraction of sulfur is 0.103%, density at 20^{0}C-885.6 kg / m^3.

The conversion of VG at its cracking increases with increasing temperature, while the yield of gasoline drops from 51.2% at 480^{0}C to 33.6% at 550^{0}C, and the yield of light gas oil grows in these conditions by 2.7% (Table 3). The maximum yield of gasoline obtained on this catalyst at 480^{0}C. The conversion of SH and the total yield of light products under these conditions are also maximum and amount to 93.0 and 69.4%, respectively [10]. The amount of gaseous reaction products increases with increasing cracking temperature from 17.8% at 48 ° C to 26.8% at 550^0 C. The amount of coke deposited on the catalyst during the cracking process also increases with increasing process temperature.

Table 3 - Material balance of VG cracking on Al (2.5) NaHMM + HLaY– catalyst at different temperatures

Raw material	VG		
Experience temperature, ^{0}C	480	500	550
Yield of products,%			
Gas	17.8	20.0	26.8
Gasoline (IBP-205^{0}C)	51.2	43.5	33.6
Coke	5.8	6.4	7.7
Light gas oil (205 - 350^{0}C)	18.2	18.0	20.9
Heavy gas oil (>350^{0}C)	4.2	9.1	8.2
Losses	2.8	3.0	2.8
Conversion	93.0	87.9	89.0
The total content of light products	69.4	61.5	54.5

The main disadvantage of this catalyst is its very low strength, which increases during calcination at high temperatures (Table 2). To determine the effect of calcination temperature on the activity of these catalysts in cracking, a batch of VG PPCP grade A, type 2 was used. The EBP of VG was 510^{0}C, the density at 20^{0}C 907.7 kg / m^3, kinematic viscosity at 50 ° C is 22.691 mm^2 / s, sulfur content is 1.43%,the temperature of hardeningis 27^{0}C, coking ability 0.21wt.%.

Table 4 - The main technical parameters of VG PPCP, obtained in 2018

	Sample	**Test method**	**Norm**	**Actual values**
1	Fractional composition: a) up to 350^{0}C is distilled,% not more than b) 90% distilled at 0C, not higher	TURB-3002206696.004-2001	18 535	
2	Density at 20^{0}C, kg / m3	GOST 3900	870÷952	907.7
3	Kinematic viscosity at 50° C, mm^2 / s	GOST 33	5÷25	22.691
4	Mass fraction of sulfur,% mass.	ST RK ISO 8754	no more 2	1.7-1.43
5	Flash point in closed crucible, ^{0}C	GOST 6356	not less 61	145
6	Pour point, ^{0}C	GOST 20287 (method A)	not less 10	27
7	Coking ability, % mass.	GOST 19932	no more 3	0.21
8	Fe amount,% mass.	X-ray fluorescence analysis		0.05
9	Ni amount, % mass.	X-ray fluorescence analysis		0.01

The catalyst calcined at temperatures of 500, 550 and 600^{0}C was tested in the cracking of VG at different temperatures (Table 5). Analysis of the data presented in Table 4 shows that with an increase in the temperature of the experiment from 480 to 550^{0}C and calcining to 600^{0}C, the catalyst activity in the fuel direction decreases significantly. Thus, the yield of gasoline decreases from 40.5% to 27.1% with an increase in the temperature of the experiment from 480 to 500^{0}C and calcining from 500 to 550^{0}C. A decrease in the yield of gasoline and an increased (growth of ~ 2 times) the formation of gases is probably due to a change in the porous structure, acidity, and elemental composition of the catalyst with increasing temperature of calcination. This is confirmed by a further decrease in the yield of gasoline with an increase of the calcinationtemperature to 600° C (Table 5). Under these conditions, the yield of gasoline decreases to 21.4%, while the yield of light gas oil increases to 23.1% and gaseous products to 48. 3%.

Table 5 - Material balance of VG cracking on Al (2.5) NaHMM + HLaY-catalyst at different temperatures of the experiment and calcining (up to $T_{calc.} = 600^0$, regeneration at 550^{0}C)

Raw material	VG			
Experience temperature, ^{0}C	480	500	500	550
Calcinat on temperature, ^{0}C	500	550	600	600
Yield of products,%				
Gas	28.6	41.6	48.3	43.6
Gasoline (IBP-205^{0}C)	40.5	27.1	21.4	21.1
Light gas oil (205 - 350^{0}C)	20.8	11.2	23.1	25.0
Heavy gasoil (> 350^{0}C)	4.4	12.1	3.8	5.6
Coke	3.7	3.9	2.2	2.7
Losses	2.0	4.1	1.2	2.0
Amount of products	100	100	100	100

The next series of experiments was carried out using montmorillonite in CaNa-form from the quarry«Zapadny» of 12 horizons containing the following alkaline cations: $Na^+ > 35$ mg / eq, $Ca^{++} \geq 28$ mg / eq, $Mg^{++} = 24$ mg / eq, $K^+ \sim 4.0$ mg / eq. (Table 6). After activating with acid and pillaring ofmontmorillonite by aluminum the composition and textural characteristics approach to the previously used MM in the Ca- and Na-forms. The raw material was VG PPCP grade B type 2 with a density of 907.7 kg / m^3, kinematic viscosity at 50^{0}C equal to 27.05 mm^2/s, the sulfur content is 1.5 wt.%,the temperature of hardeningis 30^{0}C and coking ability is 0.14 wt.%.

Table 6- Material balance of VG cracking on Al (2.5) CaNaHMM + HLaY-catalyst at temperatures of 480, 500, 550^{0}C, calcining at 500, 550, 600^{0}C and the ratio of catalyst : raw = 1:1

Raw material	VG					
Experience temperature, ^{0}C	480	500	500	500	550	*550
Calcination temperature, ^{0}C	600	500	550	600	600	*600
Yield of products, %						
Gas	36.4	5.8	28.9	29.2	42.2	32.6
Gasoline (IBP-205^{0}C)	39.2	58.5	46.8	46.4	30.0	36.2
Light gas oil (205 - 350^{0}C)	16.8	29.1	16.2	17.2	19.2	14.8
Heavy gas oil (>350^{0}C)	3.2	2.0	3.5	2.9	3.8	4.7
Coke	2.4	2.5	2.4	1.8	2.5	8.2
Losses	2.0	2.1	2.2	2.5	2.3	3.2
Amountofproducts	100	100	100	100	100	100

* ratio of catalyst: raw = 2: 1.

A freshly prepared catalyst, calcined at 500^0 C, cracks VG at 500^{0}C to produce 58.5% of gasoline, the amount of which decreases with an increase in the preliminary calcination temperature to 550°C and 600°C to 46.8% and 46.4%, respectively (Table 6). Heat treatment of the catalyst at 600^0 C reduces the yield of cracking gasoline regardless of the process temperature itself. The yield of gasoline increases with increasing ratio of catalyst: VG from 1: 1 to 2: 1.

The results indicate that heat treatment of the catalyst increases the strength, but does not provide the necessary catalyst activity in the fuel direction. A decrease in the activity of a catalyst calcined at a high temperature is possible, due to the influence of the temperature of the calcination on the textural and acidic characteristics of the catalyst,hasinfluence on the cracking direction.

The group composition of gasoline formed during the cracking of VG on Al (2.5) NaHMM + HLaY depending on the temperature of calcination is presented in Table 6, from which it can be seen that with increasing temperature of calcination an increase in the number of isoparaffins is observed while the relative content of olefins and aromatic hydrocarbons in gasoline is reduced by 18-20%. The octane number (O.N.) of gasoline cracking by motor method (m.m) decreases with increasing temperature of preliminary calcination of catalysts from 550 to 650^{0}C by 5 units.

Table 7- Group composition of gasoline cracking VG on Al (2.5) NaHMM + HLaY at different temperatures of the calcining of the catalyst

Catalyst	Calcinati-on temp-re, ^{0}C	Hydrocarbon composition				
		Paraffin-naphthenic hydrocarbons,mass.%	Isoparaffins,mass.%	Olefins,mass.%	Aromaticsmass.%	O.N. (m.m)
Al(2.5) NaHMM+ HLaY	550	13.2	16.86	39.88	19.14	65.0
	600	10.87	28.38	24.24	21.49	63.0
	650	9.02	27.58	31.63	15.61	60.0

Conclusion

An increase in the crushstrength of granules Al (2.5) NaHMM + HLaY-catalyst was found with an increase in the temperature of calcination of the catalysts from 500 to 650^{0}C. It is noticed that the introduction of zeolite Y in the substituted rare-earth La-form also leads to an increase in the strength of the granular catalyst.

It was shown that preliminary calcination of zeolite-containing catalysts deposited on pillared Al activated montmorillonite in Na- and CaNa-forms at 550, 600^{0}C leads to a significant decrease in gasoline yield on these catalysts, which indicates that thermal treatment of the catalyst increases the strength, but does not provide the necessary catalyst activity in the fuel direction.

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ТҮРЛЕНДІРІЛГЕН МОНТМОРИЛЛОНИТ НЕГІЗІНДЕГІ КАТАЛИЗАТОРЛАР БЕРІКТІГІ МЕН КРЕКИНГТЕУ БЕЛСЕНДІЛІГІНЕ ТЕРМИЯЛЫҚ ӨҢДЕУ ТЕМПЕРАТУРАСЫНЫҢ ӘСЕРІ

Аннотация. Термиялық өңдеу температурасын 500-ден 650^0C дейін жоғарылатқанда Al(2.5)NaHMM+HLaY- катализаторы түйіршіктерінің үгітілуге қарсы беріктілігі артатыны табылды. Түйіршіктелген катализаторға араластырылған сирек жер La-формасына Y цеолитин енгізу беріктіліктің өсуіне әкелетіні байқалды.

Na- және CaNa-формалы Al-мен пилларирленіп белсендірілген монтмориллонитке енгізілген цеолитқұрамды катализаторларды 550,600^0C кезінде алдын ала термиялық өңдеу осы катализаторларда бензин шығымының төмендеуіне алып келеді, бұл катализаторды термиялық өңдеу беріктілікті арттырғанымен отын бағытында катализатордың қажетті белсенділік таныта алмайтынын көрсетеді.

Түйін сөздер: Катализдік крекинг, термиялық өңдеу, пилларирленген монтмориллонит, жанармай, жеңіл газойль, вакуумдық газойль.

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ВЛИЯНИЕ ТЕМПЕРАТУРЫ ПРОКАЛКИ НА ПРОЧНОСТЬ И КРЕКИРУЮЩУЮ АКТИВНОСТЬ КАТАЛИЗАТОРОВ НА ОСНОВЕ МОДИФИЦИРОВАННОГО МОНТМОРИЛЛОНИТА

Аннотация. Найдено увеличение прочности гранул Al(2.5)NaHMM+HLaY- катализатора на раздавливание с повышением температуры прокалки катализаторов с 500 до 650^0C. Замечено, что введение цеолита Y в замещенной редкоземельной La- форме также приводит к росту прочности гранулированного катализатора.

Показано, что предварительная прокалка при 550, 600 ^{0}C цеолитсодержащих катализаторов, нанесенных на пилларированный Al активированный монтмориллонит в Na- и CaNa –формах, приводит к существенному уменьшению выходов бензина на этих катализаторах, что свидетельствует о том, что термическая обработка катализатора повышает прочность, но не обеспечивает необходимой активности катализатора по топливному направлению.

Ключевые слова: каталитический крекинг, термическая обработка, пилларированный монтмориллонит, бензин, легкий газойль, вакуумный газойль.

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