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STRENGTH AND CRACKING PROPERTIES OF HLaY-CONTAINING COMPOSITE CATALYST ON Al-PILLARED MONTMORILLONITE IN CaNa-FORM

Absract. It was shown that additives of montmorillonite in the Na form contribute to a significant increase in the crushing strength of cracking catalyst granules while preserving their activity in gasoline yield. Comparison of the results of vacuum gasoil cracking on catalysts of the same composition, but with and without NaMM binder, showed that the introduction of NaMM increases the strength of the CaNaHMM-based catalyst and does not significantly affect the gasoline yield.

Catalysts based on MM in CaNa and Na-forms showed similar activity in the release of gasoline from vacuum gasoil, regardless of the composition of the exchange cations. It was found that due to the stages of activation and pillaring, Na is completely removed from the finished catalyst. Pillarization and introduction of zeolite provide an increase in specific surface area and total pore volume. Catalysts have a high number of acid sites. The maximum yield of gasoline equal to 44.8% and light gas oil 14.6% was obtained with Al (2.5) CaNaHMM+HLaY+NaMM with the addition of a binder and crushing strength of 60-70 N / sm^2.

Key words: catalytic cracking, binder, montmorillonite, strength, gasoline, zeolite, vacuum gas oil.

Introduction. One of the promising directions for optimizing the composition of cracking catalysts is the use of layered aluminosilicates and their modified forms as a component of the matrix of cracking catalysts [1,2]. In cracking catalysts developed in Russia, Tagan montmorillonite (natural bentonite) is used as a matrix component, which has binding properties, increasing strength and increasing the bulk density of the catalyst. New highly efficient zeolite-containing vacuum gasoil (VG) cracking catalysts with the production of gasoline were developed using columnar aluminum montmorillonites, which are characterized by an increase in the number of mesopores and an increase in thermal stability. However, the strength of such catalysts does not always meet the requirements of their operation in apparatuses with a moving and fluidized bed in the processes of cracking of crude oil.

The purpose of the work is the synthesis of HLaY zeolite-containing catalysts deposited on aluminum pillared montmorillonite in CaNa- form and to reveal the effect of a binder on the activity of catalysts in the cracking of vacuum gasoil and its acid properties.

Experimental part. To prepare cracking catalysts, montmorillonite in CaNa form was used from the Zapadnyi quarry, 12 horizons, containing the following alkaline cations: Na^{+}> 35 mg / equiv, Ca^{++} ≥28 mg / equiv, Mg^{++} = 24 mg / equiv, K + ~ 4,0 mg/equiv. As a raw material for cracking, VG from LLP Pavlodar Oil Chemistry Refinery, trade mark B, type 2 was used with a density of 907.7 kg / m^3, with a boiling end of 510^{0}C, kinematic viscosity at 50^{0}C equal to 27.05 mm^2 / s, sulfur content of 1.5 mass%, pour point 30^{0}C and coking ability of 0.14 wt.%. Montmorillonite activated with a H_2SO_4 solution and pillared Al, as well as the synthesis of zeolite Y modified with lanthanum, were carried out by known methods.

The elemental composition of the catalysts was determined by X-ray fluorescence spectroscopy (INCA - Energy 450 at SEM JSM6610LV, JOEL, Japan). The textural characteristics of the catalysts were determined from isotherms of low-temperature adsorption and desorption of nitrogen on an Accusorb

instrument (BET method). The crush strength of the catalyst granules was determined by the compression method ("Prochnomer of catalysts" PK-21-015). The acidity of the catalysts was determined by the thermal desorption of ammonia. The catalytic activity of the samples was determined on a laboratory flow-through installation, corresponding to the standard, with a fixed catalyst layer with a volume of 40 ml in the temperature range 480-550^{0}C. When the catalysate was distilled, a fraction of gasoline $T_{b.\ b.}$ - 205^{0}C and light gas oil fraction 205-350^{0}C were taken. Cracking products were analyzed by GLC with a flame ionization detector and a capillary column 100 m long; temperature 250^{0}C; carrier gas - helium (Chromos GC-1000).

Results and discussion. The influence of the exchange form of MM on the activity of the cracking catalyst while maintaining its composition and method of preparation was studied using MM in a CaNa form (a new batch of MM from horizon 12). From table 1 it is seen that the gasoline yield on this catalyst ranges from 44.8-43.6% at cracking temperatures of 480 and 500^{0}C, which almost completely coincides with the gasoline yields on catalysts of the same composition (42.0-39.5%), but based on NaHMM when cracking two different lots of VG, varying in composition.

Table 1 – Material balance of VG cracking on Al (2,5) CaNaHMM + HLaY + NaMM catalyst at various temperatures. The strength of this catalyst is 60-70N/sm^2

VG raw materials	The yield of products, mass..%	
Cracking temperature	480^{0}C	500^{0}C
Gas	28,3	28,9
Gasoline (s.b.-205^{0}C)	44,8	43,6
Light gas oil (205-350^{0}C)	14,6	13,5
Heavy gas oil (> 350^{0}C)	7,3	8,4
Coke	2,9	3,3
Losses	2,1	2,3
Product Amount	100	100

Based on the results obtained, it can be concluded that two samples of catalysts of the same composition, but using Al-pillared MM in two different exchange forms, showed similar activity in gasoline yield. In connection with the foregoing, it was of interest to compare the elemental composition, textural and acid properties of the studied catalysts using activated and pillared Tagan MM in various exchange forms in the composition of the finished catalyst. The results of elemental analysis showed, that thanks to the stages of activation and pillaration, Na is completely removed from the initial MM regardless of the exchange form. With the introduction of HLaY, the elemental composition and porous structure of two MM-based catalysts in different exchange forms is practically the same.

A comparison of the acidic properties of optimal catalysts based on montmorillonites of various horizons is given in table 2, from which it can be seen that the total content of acid centers (a.c.), and also in particular the relative and absolute amount of strong a.c. of the NaHMM-based catalyst is 1.7 times superior to the catalyst supported on activated MM in CaNa form.

Table 2 – Acidic properties of optimal cracking catalysts

Sample	Content a.c.	Acid centers			
		Weak <200^{0}C	Medium 200-300^{0}C	Strong >300^{0}C	Total acidity
Al(2,5)CaNaHMM+HLaY	%	43,52	36,48	20	100
	Mkmol NH_3/г	161,64	135,50	74,28	371,43
Al(2,5)NaHMM+HLaY	%	36,3	30,1	33,6	100
	Mkmol NH_3/г	139,6	115,4	129,2	384,5

From the results obtained, it is seen that the introduction of NaMM as a binder into the zeolite-containing cracking catalyst significantly increases the crush strength of the granules while maintaining the activity of the catalyst in terms of the yield of gasoline during VG cracking. It was shown that zeolite-containing catalysts based on MM pillared with aluminum in the Na and CaNa forms are characterized by a close elemental composition, texture and acid properties, which leads to their close activity in VG cracking with the formation of gasoline. The maximum yield of gasoline equal to 44.8% and light gas oil 14.6% was obtained on Al(2,5)CaNaHMM +HLaY+ NaMM with the addition of a binder and crushing strength is 60-70 N/ sm^2.

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CaNa- АУЫСПАЛЫ ФОРМАСЫНДАҒЫ АЛЮМИНИЙМЕН ПИЛЛАЛИРЛЕНГЕН HLaY-ҚҰРАМДЫ КОМПОЗИТТІ КАТАЛИЗАТОРДЫҢ КРЕКИНГТІК ЖӘНЕ БЕРІКТІК ҚАСИЕТТЕРІ

Аннотация. Na формасындағы монтмориллонит қоспа ретінде крекинг катализатор түйіршіктерінің сыну күшін арттыруға едәуір ықпал ететіні, сонымен қатар, олардың бензин шығымындағы белсенділігін арттыратыны көрсетілген. ВГ крекингінің нәтижелері бірдей құрамдағы катализаторларды салыстырғанда NaMM байланыстырғышсыз және NaMM енгізу катализаторлардың беріктігі арттыратындығын және бензиннің шығымына айтарлықтай әсер етпейтінін көрсетті.

CaNa және Na-формалардағы ММ негізіндегі катализаторлар катиондардың құрамына қарамастан, жоғары температуралы газдардан бензин шығаруда ұқсас белсенділік көрсетті. Белсендіру және пиллалирлеу кезеңдеріне байланысты Na дайын катализатордан толығымен шығарылатындығы анықталды. Пиллалирлеу және цеолитті енгізу беткі қабаттың жалпы көлемін және кеуектердің жалпы көлемін арттыруды қамтамасыз етеді. Ұсынылған катализаторлар қышқылдың орталық санының көптігімен ерекшеленеді: Al(2,5)CaNaHMM+NaMM-катализаторында байланыстырғышты қосқанда беріктігі 60-70Н/$см^2$, бензиннің ең жоғары шығымы 44,8% және жеңіл газойль шығымы 14,6% құрады.

Түйін сөздер: каталитикалық крекинг, байланыстырғыш, монтмориллонит, беріктік, жанар май, цеолит, вакуумды газойль.

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ПРОЧНОСТНЫЕ И КРЕКИРУЮЩИЕ СВОЙСТВА HLaY-СОДЕРЖАЩЕГО КОМПОЗИТНОГО КАТАЛИЗАТОРА НА Al- ПИЛЛАРИРОВАННОМ МОНТМОРИЛЛОНИТЕ В CaNa-ФОРМЕ

Аннотация. Показано, что добавки монтмориллонита в Na-форме способствуют существенному росту прочности гранул катализаторов крекинга на раздавливание при одновременном сохранении их активности по выходу бензина. Сравнение результатов крекинга ВГ на катализаторах одинакового состава, но со связующим NaMM и без него, показало, что введение NaMM повышает прочность катализатора на основе CaNaHMM и не оказывает существенного влияния на выход бензина.

Катализаторы на основе ММ в CaNa и Na –формах проявили близкую активность по выходу бензина из ВГ независимо от состава обменных катионов. Найдено, что благодаря стадиям активации и пилларирования Na полностью удаляется из готового катализатора. Пилларирование и введение цеолита обеспечивают рост удельной поверхности и общего объема пор. Катализаторы отличаются высоким количеством кислотных центров. Максимальный выход бензина, равный 44,8% и легкого газойля 14,6% получен на Al(2,5)CaNaHMM+HLaY+NaMM с добавкой связующего и прочностью на раздавливание 60-70 Н/см^2.

Ключевые слова: каталитический крекинг, связующая, монтмориллонит, прочность, бензин, цеолит, вакуумный газойль.

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REFERENCES

[1] Gil A., Landia L.M. (2000) Recent advances in the synthesis and catalytic applications of pillared clays (Catal. Rev. – Sci Eng.) 1: 145-212 (in Eng.).

[2] Pang X. (2007) Effects of metal modifications of Y zeolites on sulfur reduction performance in fluid catalytic cracking process (Catalysis Today) 125: 173-177 (in Eng.).

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