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ИЗВЕСТИЯ

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SELECTION OF A BINDER FOR A ZEOLITE-CONTAINING CRACKING CATALYST ON AL- PILLARED TAGAN MONTMORILLONITE

Abstract. It was shown that the strength of Al(2.5) NaHMM + HLaY + NaMM catalysts increases significantly with the introduction of NaMM. The optimal amount of NaMM additive is 10 mass%. With an increase in the calcination temperature of this catalyst, an increase in strength is observed, which reaches a maximum value (223.4 N/sm^2) at 600^{0}C. A further increase in the amount of introduced NaMM to 15 and 20 wt.% reduces the strength of the catalysts at all studied calcination temperatures. On Al (2.5) NaHMM + HLaY + NaMM catalyst, a large amount (42.5%) of gaseous hydrocarbons is formed at 500^0 C, which decreases with an increase in cracking temperature to 550^0 C. The gasoline yield at 500^{0}C is 42.0%, light gas oil 5.5%. With an increase in cracking temperature, the yield of gasoline decreases to 39.5%, and light gas oil increases to 15.8%. Under these conditions, a decrease in the yield of gaseous hydrocarbons to 28.8% is observed.

Comparison of the results of VG cracking on catalysts with and without NaMM binder showed that the introduction of NaMM does not significantly affect the yield of gasoline.

Key words: catalytic cracking, montmorillonite, strength, gasoline, zeolite, vacuum gas oil (VG).

Introduction. The matrixes of modern zeolite-containing cracking catalysts are multicomponent systems that should provide a number of requirements for the catalysts during their operation: high activity, optimal porous structure and specific surface area, thermal stability, abrasion resistance [1,2]. The high heat capacity of montmorillonite (MM) promotes heat removal from the zeolite component at the regeneration stage, which leads to increased thermal stability of the catalyst [3]. Obviously, the strength characteristics of the catalysts are determined by their composition and texture properties - porosity, specific surface area, size of primary particles. However, in the literature there are very few works devoted to the study of the relationship of strength with the physicochemical properties of catalytic systems.

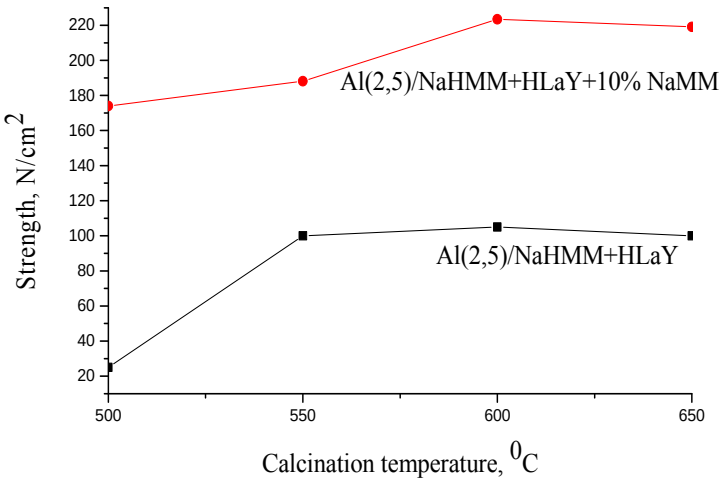
The purpose of the work is to develop new effective additives to increase the mechanical strength of cracking catalysts based on natural clays and zeolites for processing vacuum gas oils in the fuel direction and to identify the relationship of strength with the characteristics of the developed cracking catalysts.

Experimental part. 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 catalyzate 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. It was shown earlier that the use of montmorillonite in the Na-form as a matrix and a binder of zeolite-containing catalysts leads to an increase in their crushing strength. In this regard, in order to increase the strength of cracking catalysts, various amounts of the initial MM in the Na form were introduced into the zeolite-containing catalysts based on pillared MM as an additive. From figure, where the effect of NaMM additives on the strength of Al (2.5) NaHMM + HLaY is clearly shown, it is seen that the introduction of 10% NaMM increases the strength of the catalyst by 1.9–2.3 times at T_{calc} = 550–650^{0}C compared to the strength of the catalyst without NaMM.



Effect of calcination temperature on the strength of Al (2.5) NaHMM + HLaY catalysts with the addition of 10% NaMM

For the cracking tests, catalysts calcined at the optimum temperature and sufficiently strong were taken. So, Al (2.5) NaHMM + HLaY + 10% NaMM catalyst was calcined at 600^0 C, while the strength of the catalyst increased to 223.4 N/sm^2 and VG was cracked at temperatures of 500 and 550^0 ° C with determination of material balance and chromatographic analysis of the resulting gasoline fractions. The gasoline yield at 500^0 C is 42.0%, light gas oil 5.5%. With an increase in cracking temperature, the yield of gasoline decreases to 39.5%, and light gas oil increases to 15.8%. Under these conditions, a decrease in the yield of gaseous hydrocarbons to 28.8% is observed.

Material balance of VG cracking on Al (2,5) NaHMM + HLaY + 10% NaMM catalyst at various cracking temperatures

VG raw materials	The yield of products, wt.%	
Cracking temperature	500^{0}C	550^{0}C
Gas	42,5	28,8
Gasoline (b.b.-205^{0}C)	42,0	39,5
Light gas oil (205-350^{0}C)	5,5	15,8
Heavy gas oil (> 350^{0}C)	5,8	8,6
Coke	2,9	4,5
Losses	1,3	2,8
Product Amount	100	100

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АЛЮМИНИЙМЕН ПИЛЛАЛИРЛЕНГЕН ТАҒАН МОНТМОРИЛЛОНИТІ НЕГІЗІНДЕ КРЕКИНГТІҢ ЦЕОЛИТҚҰРАМДЫ КАТАЛИЗАТОРЛАРЫНА БАЙЛАНЫСТЫРҒЫШ ТАҢДАУ

Аннотация. Мақалада Al(2,5) NaHMM + HLaY + NaMM катализаторларының беріктігі NaMM енгізгенде едәуір артатыны көрсетілген. NaMM қоспасының оңтайлы мөлшері 10 масса% құрайды. Осы катализатордың қыздыру температурасының жоғарылауы негізінде берік бола түседі, ол максималды мәнге (223,4 Н/см^2) 600^{0}С жетеді. Енгізілген NaMM мөлшерінің одан әрі артуы 15 және 20 салм.% зерттелген жоғары температурадағы катализаторлардың беріктігін кемітеді. Al (2.5) NaHMM + HLaY + NaMM катализаторында 500^0 С температурада газ тәрізді көмірсутектер көп мөлшерде (42,5%) түзіледі, ол крекинг температурасының 550^0 С дейін жоғарылауы негізінде төмендейді. 500^{0}С температурада бензиннің шығымы 42,0%, жеңіл газ 5,5% құрайды. Крекинг температурасының жоғарылауы арқылы бензин шығымы 39,5% дейін төмендейді, ал жеңіл газойль 15,8%-ға дейін артады. Бұл жағдайда газ тәрізді көмірсутектер шығымы 28,8% дейін төмендейтіні байқалды.

Катализаторлардағы ВГ крекинг нәтижелерін NaMM байланыстырғышпен және онсыз салыстырғанда NaMM енгізу бензиннің түсуіне айтарлықтай әсер етпейтінін көрсетті.

Түйін сөздер: каталитикалық крекинг, монтмориллонит, беріктілік, жанар май, цеолит, вакуумды газойль (ВГ).

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ПОДБОР СВЯЗУЮЩЕГО ДЛЯ ЦЕОЛИТСОДЕРЖАЩЕГО КАТАЛИЗАТОРА КРЕКИНГА НА Al- ПИЛЛАРИРОВАННОМ ТАГАНСКОМ МОНТМОРИЛЛОНИТЕ

Аннотация. Показано, что прочность Al(2.5)NaHMM+HLaY+NaMM-катализаторов существенно повышается с введением NaMM. Оптимальное количество добавки NaMM составляет 10 мас.%. С повышением температуры прокалки этого катализатора наблюдается рост прочности, которая достигает максимального значения (223,4 Н/см^2) при 600^{0}С. Дальнейший рост количества вводимого NaMM до 15 и 20 вес.% снижает прочность катализаторов при всех изученных температурах прокалки. На Al(2.5)NaHMM+HLaY+NaMM катализаторе образуется большое количество (42,5%) газообразных углеводородов при 500^{0}С, которое уменьшается с ростом температуры крекинга до 550^{0}С. Выход бензина при 500^{0}С составляет 42,0%, легкого газойля 5,5%. С ростом температуры крекинга выход бензина снижается до 39,5%, легкого газойля растет до 15,8%. В этих условиях наблюдается уменьшение выхода газообразных углеводородов до 28,8%.

Сравнение результатов крекинга ВГ на катализаторах со связующим NaMM и без него, показал, что введение NaMM не оказывает существенного влияния на выход бензина.

Ключевые слова: каталитический крекинг, монтмориллонит, прочность, бензин, цеолит, вакуумный газойль (ВГ).

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