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«Жанармай, катализ және электрохимия институты» АҚ

ХАБАРЛАРЫ

ИЗВЕСТИЯ

НАЦИОНАЛЬНОЙ АКАДЕМИИ НАУК
РЕСПУБЛИКИ КАЗАХСТАН
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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 Үлттық гылым академиясы «ҚР ¥ҒА Хабарлары. Химия және технология сериясы» ғылыми журналының Web of Science-тің жаңаланған нұсқасы Emerging Sources Citation Index-те индекстелуге қабылданғанын хабарлайды. Бүл 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 үсынады. ҚР ¥ҒА Хабарлары. Химия және технология сериясы Emerging Sources Citation Index-ке енуі біздің қогамдастық үшін ең өзекті және беделді химиялық ғылымдар бойынша контентке адалдығымызды білдіреді.

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DEVELOPMENT OF EFFECTIVE CATALYSTS FOR PROCESSING C_3-C_4 HYDROCARBONS

Abstract. The aim of the article is to study the effect of preparation and activation methods of a modified zeolite-containing catalyst on the activity and stability of catalytic properties displayed by it during the conversion of C_3-C_4 hydrocarbons. During the experiment, the industrial cracking catalyst OMNIKAT, which is a zeolite in the sodium form, was used as the initial one. Zinc, gallium, and REE (rare earth elements) were sequentially applied to decationized samples of this catalyst by ion exchange, impregnation, and dry mechanical mixing, and the effect of these methods on the catalytic properties of the zeolite-containing catalyst was observed. As a result of a comparative analysis of the regularities of aromatization of C_3-C_4 hydrocarbons, it was found that the mechanical mixing method is the most preferable, since it provides the best process performance.

In order to improve the activity and stability of the catalysts, thermocouple and thermal activations were carried out during the preparation process. Further, differences were revealed for the thermocouple and thermal activation of the modified catalyst and their effect on the activity and selectivity of the zinc-gallium-zeolite-containing catalyst with respect to ArH (aromatic hydrocarbons) in the process of conversion of C_3-C_4 hydrocarbons. The choice of these particular operations was dictated by the fact that preliminary thermal and thermal vapor treatment of the catalyst practically does not require significant capital expenditures, i.e., economically most acceptable.

Regularities of reaction-regeneration cycles were established. Thus, the optimal technological parameters for the regeneration of catalytic compositions are: temperature - 600°C, atmospheric pressure, oxidizer - air feed rate - 2 h^{-1}, which lead to the restoration of the activity and selectivity of the spent catalyst to the fresh level. Studies of the of oxidative regeneration process a zinc-gallium-zeolite-containing catalyst have shown that while maintaining a clearly regulated regeneration regime, the activity of the latter is restored.

The main task of the research was the development of effective catalysts for the conversion of C_3-C_4 hydrocarbons. Therefore, in the first place, we compared the conversion rates and selectivity for ArH. The proposed catalyst is characterized by good operational properties (high activity and long service life), providing 59.2% by weight of the target product yield at 98.8% conversion of C_3-C_4 hydrocarbons.

Key words: refinery gases, C_3-C_4 hydrocarbons, zeolite-containing catalyst, modifiers, reaction-regeneration cycles.

Introduction. The steady increase in the consumption of fuels motor and the associated deepening of oil refining requires the steady development of secondary, destructive processes, which are accompanied by a significant release of by-product — refinery gases. Basically, they are represented saturated and unsaturated hydrocarbons of the C_3-C_4 fraction mixture. The total yield of these hydrocarbons at oil refineries (refineries) is on average 4-8% of the mass of the volume of processed oil [1-4].

According to statistics, in the balance of production and consumption of hydrocarbon gases for chemical synthesis, about 30% of the total amount of obtained gaseous hydrocarbon raw materials is used, while the rest is spent on non-chemical needs [5].

Materials and methods. Studies aimed at the selection of highly active catalytic systems for processing refinery gases into a concentrate of aromatic hydrocarbons (ArH) or gasoline components are carried out in many countries of the world [6,7]. In the works of Academician Kh. M. Minachev, at the end of the last century, the possibility of the use of synthetic zeolites as catalysts for the processing of hydrocarbon components of natural, associated and oil refinery gases, as well as gas condensate into high-octane motor fuel and ArH [8]. The totality of data in the field of zeolite catalysis for the subsequent period made it possible to fully confirm these predictions [9-12].

In connection with the tendency to gradually replace obsolete catalysts with more efficient ones, the idea arose of studying the possibility of using the industrial zeolite-containing cracking catalyst

OMNIKAT in the process of converting C_3-C_4 hydrocarbons.

As a result of earlier studies, it was established that it is promising to carry out the process of conversion of C_3-C_4 hydrocarbons in the presence of a modified zeolite-containing system based on the industrial OMNIKAT catalyst. In works [13-15], the data obtained as a result of the screening of potential promoters (Zn, Ga, Cd, REE oxides) of the conversion of C_3-C_4 hydrocarbons are given, according to which the greatest positive effect takes place upon modification of a zeolite-containing catalyst with zinc, gallium and REE oxides in the form of an industrial concentrate (IG), which confirms the well-known tendency [16,17].

The aim of this study is to study the effect of the method of preparation and activation of a modified zeolite-containing catalyst on the activity and stability of catalytic properties exhibited by it during the conversion of C3-C4 hydrocarbons.

Experimental part. The C_3-C_4 hydrocarbon fraction taken for the study had the following composition (wt.%): Ethane - 2%; ethylene - 3%; propane - 7%; propylene - 25%; butane - 3%; iso-butane - 23%; butylene's - 32%.

During the experiment, an industrial cracking catalyst OMNIKAT was used as a starting catalyst, which is a zeolite in the sodium form, on decationized samples of which zinc, gallium and REE are successively applied by the method of ion exchange, impregnation by water absorption of dry mechanical mixing (in a ball vibrating mill for 1h). The samples contained 20% (wt.) Of the binder - aluminum oxide.

Before the experiments, the catalysts were activated in a stream of air at the reaction temperature for 2-3 hours.

The process is carried out on a flow-through unit at atmospheric pressure in the temperature range of 450-600°C and a volumetric feed rate of 180 h^{-1}.

The gaseous and liquid phases analyze by gas chromatography.

Results and discussion. Zeolite multicomponent catalyst 1% Zn_2 + - 3% Ga_3-–3% IG-H-OMNIKAT was synthesized in three ways: by ion exchange, impregnation and dry mechanical mixing.

Since the main task of the research was the development of effective catalysts for the conversion of C_3-C_4 hydrocarbons, first of all, the indicators of conversion and selectivity for ArH were compared. Comparison of the data showed (Table 1) that when modifying additives were introduced into the zeolite by the ion exchange method and by the impregnation method, in the first 5 hours of operation, the raw material conversion and catalyst selectivity with respect to the target products are characterized by similar values. An increase in the duration of the experiment to 15 h leads to a decrease in aromatization, an increase in cracking activity, and a rapid deactivation of the catalyst (an increase in the yield of gaseous products and coke).

It also follows from the data in the table that the dynamics of SP (seal products) accumulation, regardless of the method of introducing modifiers, has a similar character: an increasing in the inter-regeneration run leads to an increasing in the degree of coking of the samples. At the same time, it is important to note that samples obtained by mechanical mixing have the least tendency to coke formation. At the same time, two sharp jumps are observed associated with insignificant formation of carbon deposits on the catalyst surface (at the initial stages up to 2 h) and intense (duration of operation more than 10 h), probably associated with the gradual accumulation of surface and intracanal coke deposits on active centers of zeolite.

Table 1

Influence of the modifier input method on process indicators conversion of hydrocarbons C_3-C_4

Duration of the experiment, h	Conversion, % wt	Selectivity for ArH, % wt.	Liquid catalyst composition, % wt.				Coke yield, % wt.
			AlH	benzene	toluene	Σ xylenes	
Ion exchange method							
1	93,8	40,5	1,6	47,1	40,0	11,3	0,8
5	94,0	44,7	0,8	49,3	38,2	11,7	0,9
10	92,6	38,4	0,7	42,8	32,0	14,5	1,6
15	86,1	38,1	1,1	34,7	36,8	27,4	2,1
Impregnation method							
1	94,0	42,1	4,5	25,1	42,6	18,1	1,2
5	94,0	44,8	3,9	29,7	46,2	15,8	1,3
10	92,8	41,6	2,1	36,5	47,1	13,0	1,5
15	90,4	40,8	4,0	34,4	48,7	16,7	2,0

Dry mechanical mixing method							
1	97,5	53,3	0,2	25,5	43,6	26,4	0,4
5	98,5	53,5	0,3	28,6	42,9	24,6	0,7
10	98,0	53,2	0,4	29,2	40,7	28,0	1,2
15	95,6	50,2	0,2	31,4	39,4	25,2	1,6

Catalyst: 1% Zn_2 + + 3% Ga_3 + 3% REE-H-OMNIKAT; W = 180 h-1; T = 550°C)

As a result of a comparative analysis of the regularities of aromatization of C_3-C_4 hydrocarbons, it was found that the method of mechanical mixing is the most preferable, since it provides the best process indicators (the yield of ArH and selectivity is higher than on samples prepared by traditional methods). And the close values of the conversion of C_3-C_4 hydrocarbons, the yield of ArH, and the selectivity for catalysts prepared by the impregnation and mixing method, presumably indicate that both methods lead to the formation of active centers close in nature in the structure of the zeolite, which carry out aromatization hydrocarbons C_3-C_4. However, higher performance in the case of mechanical mixing is probably associated with the conditions of catalyst synthesis in a vibration mill, which promotes greater dispersion of components, breakdown of silicates into micro blocks, and the formation of micro strains and point defects. It is possible that the conditions for the mechanical activation of the zeolite-containing catalyst generally contribute to the accumulation of energy, which makes it possible to reduce the activation energy of the subsequent chemical transformation of C_3-C_4 hydrocarbons and improve the steric conditions for the process [18].

In addition, to the data in Table 1, it can be seen that the modification of the zeolite by dry mechanical mixing allows to obtain more stable catalytic systems, and the selectivity of ArH formation, corresponding to more than 50%, retains it throughout the entire period of the process.

It is also known from the literature that in order to improve the activity and stability of catalysts, the latter are often subjected to additional operations during preparation, in particular, heat treatment in various media: freon, halogen-containing gases, hydrogen, steam, etc. [18].

Proceeding from this, it is of considerable interest to study the effect of preliminary thermal and thermocouple treatment on the activity and selectivity of a zinc-gallium-zeolite-containing catalyst with respect to ArH in the process of the conversion of C_3-C_4 hydrocarbons (Fig. 1). The choice of these particular operations was dictated by the fact that preliminary thermal and thermal vapor treatment of the catalyst practically does not require significant capital expenditures, i.e., economically most acceptable.

The data presented in Fig. 1 indicate that the preliminary thermocouple treatment of the modified zeolite-containing catalyst did not increase its activity. According to our hypothesis, the decrease in the activity of the catalyst in this case is associated with the adsorption of water on the active sites of the zeolite, which proceeds simultaneously through two mechanisms: coordination and dissociation of water molecules.

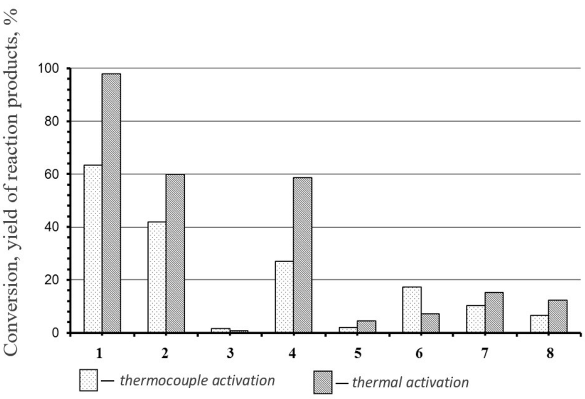

Fig. 1. Influence of the activation method on the conversion of C_3-C_4 hydrocarbons (1), selectivity with respect to ArH (2), yield of coke (3), ArH (4), hydrogen (5), methane (6), C_2 (7), and C_3 + (8). (1Zn-3Ga-3IG-H-OMNIKAT; T = 550°C)

The subsequent adsorption of raw materials leads to the formation of complex surface complexes that form a diffusion front for the penetration of molecules into the pores and leading to structural changes in the catalyst. These changes can lead to disturbances in the contacts "zinc-gallium-REE" and "acidic" centers responsible for the aromatizing activity of the catalyst. Where as the high-temperature calcination of the catalyst was accompanied by an increase in its activity.

However, it should be noted that thermal activation depended in a complex way on the calcination temperature (Fig.2). For example, if the thermal activation of the catalyst at 500 and 600°C did not lead to a significant change in its catalytic properties, then an increase in temperature to 700°C was accompanied by an increase in the yield of ArH by 1.1 wt.%. At a calcination temperature of 700°C, the maximum degree of conversion of the raw material (98.8%) and selectivity with respect to ArH (58.4%) were also observed. A further increase in the calcination temperature to 800°C was accompanied by a decrease in conversion by 16 wt.%, and aromatizing activity by 8.5 wt.%. The activity of the catalyst when the catalyst is calcined at 900°C differs even more sharply from the initial sample: the conversion decreased by half, and the yield and selectivity for ArH decreased to 7.2 and 16.1 wt.%, respectively. The decrease in the activity of the calcined catalyst at temperatures above 700°C is possibly due to local overheating and destruction of the zeolite lattice under the influence of temperature.

At the same time, when choosing the conditions for heat treatment, one should take into account the effect of the duration of calcination. Thus, a 3-hour treatment at temperatures up to 700°C had a positive effect on the activity of the catalyst, however, an increase in the time of exposure to temperature led to a decrease in the yield of ArH.

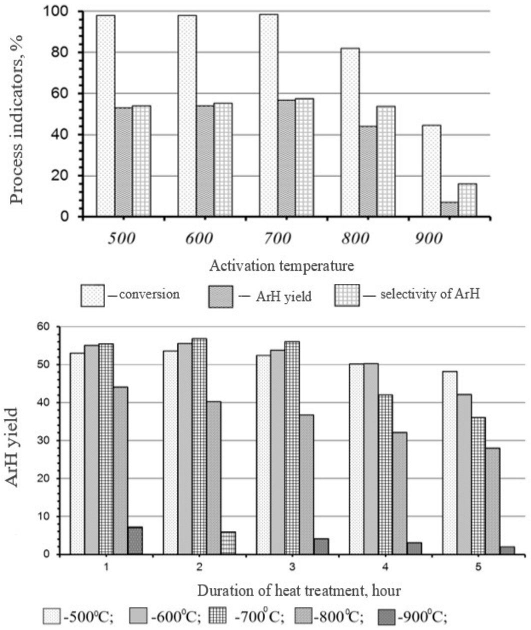

Fig. 2. Influence of temperature and duration of treatment of 1Zn-3Ga-3IG-H-OMNIKAT catalyst on indicators of the process of conversion of hydrocarbons C_3-C_4

The data obtained on the duration of the temperature treatment indicates that the optimal duration of the calcination of zeolites is 2 hours. Probably, it is this processing mode that contributes to the formation of the optimal ratio of active sites of various types due to dihydroxylation of the catalyst surface.

Figure 3 shows histograms showing the results of the duration effect of the process on the catalytic activity and stability of the modified zinc-gallium-zeolite-containing catalyst during the conversion of hydrocarbons C_3-C_4. As can be seen from the data presented, the synthesized zeolite-containing catalyst provides a high yield of a catalyst that is stable in terms of the component composition over a long period of operation (Fig. 3, a).

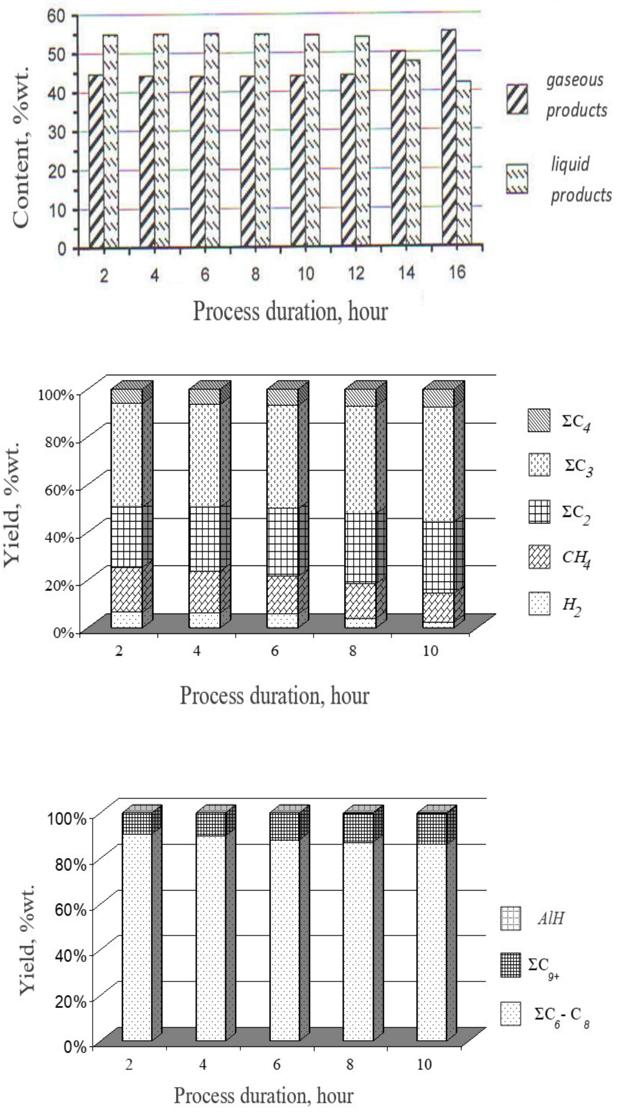

Fig. 3. Influence of the duration of the process on the distribution (a) and the composition of the gaseous (b) and liquid (c) phase

Since one of the main criteria associated with the possibility of introducing active catalysts into industry is the stability of their operation, several series of experiments were carried out for the regeneration properties of the modified zeolite-containing catalyst (Fig. 4).

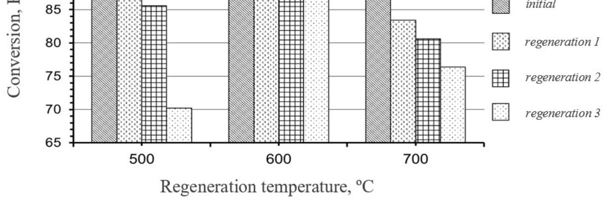

Fig. 4. Dependence of PBF conversion on the regeneration temperature

The study of the reproducibility of the activity of the studied catalysts was based on a comprehensive analysis of the regeneration cycles of samples taken from the system after 10 hours of operation. Specific air consumption was 200 volumes per 1 volume of catalyst in 1 hour. Oxidative regeneration was carried out in a flow of dry air at temperatures of 500-700°C.

The data on the catalyst regeneration characteristics presented in Figs. 4 and 5 indicate that, in the course of 2 regeneration cycles at 600°C, the active centers of the zeolite-containing catalyst restore activity close to the initial one, which makes it possible to extend the overall service life of the catalysts. However, regeneration at 500 and 700°C is accompanied by a decrease in the activity of the zeolite-containing catalyst (conversion of C_3-C_4 hydrocarbons) immediately after the 1st cycle by more than 15%, and at 500°C by 6 wt.%.

Thus, the temperature regime of regeneration at the level of 600°C is optimal from the point of view of the possibility of restoring the catalyst activity. Probably, this temperature regime contributes to the complete burn-out of coke without changes in the crystal structure of the zeolite-containing catalyst.

A decrease in the aromatizing activity of the catalyst with an increase in the number of regenerative cycles over 2 is obviously due to the fact that with an increase in the duration of operation, the coke formed on the surface is characterized by a high degree of polycondensation (Fig.5). In such conditions, to completely remove it, it is necessary to use a higher temperature (> 600°C) and a longer duration of regeneration

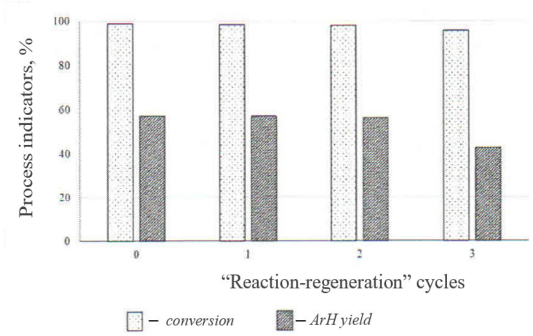

Fig. 5. Dependence of PBF conversion and ArH yield on the number of reaction-regenerative cycles

An increase in temperature, as well as the time of the process, leads to the transition of the oxidation process to the external diffusion region, which is determined by the rate of oxygen diffusion from the bulk to the surface of the granules. Under these conditions, the process of SP burnout occurs against the background of an abrupt increase in temperature and surface sintering, and the segregation of active centers.

Long-term (more than 3 cycles) further operation leads to a decrease in the total catalytic activity, probably associated with irreversible surface changes, which is in good agreement with the data available in the literature [19, 20].

Conclusion.

As a result of the studies carried out, it was found that the introduction of 1% zinc, 3% gallium and 3% rare earth elements (REE) as modifying additives in the composition of a zeolite-containing cracking catalyst using mechanochemical technology and subsequent high-temperature treatment, makes it possible to obtain highly active and a selective catalyst for the conversion of C_3-C_4 hydrocarbons to ArH.

The proposed catalyst is characterized by good operational properties (high activity and long service life), providing 59.2% by weight of the target product yield at 98.8% conversion of C_3-C_4 hydrocarbons.

The regularities of the reaction-regeneration cycles have been established. Thus, the optimal technological parameters for the regeneration of catalytic compositions are: temperature - 600°C, atmospheric pressure, oxidizer - air feed rate - 2 h^{-1}, which lead to the restoration of the activity and selectivity indicators of the spent catalyst to the fresh level. Studies of the process of oxidative regeneration of a zinc-gallium-zeolite-containing catalyst have established that while maintaining a clearly regulated regeneration regime, the activity of the latter is restored.

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КӨМІРСУТЕКТЕРДІ C_3-C_4 ҚАЙТА ӨҢДЕУДІҢ ЖОҒАРЫ ТИІМДІ КАТАЛИЗАТОРЛАРЫН ЗЕРТТЕУ ЖӘНЕ ӘЗІРЛЕУ

Аннотация. Мақаланың мақсаты құрамында өзгертілген құрамында цеолит бар катализаторды дайындау және іске қосу әдістерінің C_3-C_4 көмірсутектерін түрлендіру процесінде каталитикалық қасиеттердің белсенділігі мен тұрақтылығына әсерін зерттеу болып табылады. Тәжірибе кезінде натрий түріндегі цеолит болып табылатын OMNIKAT өндірістік крекинг катализаторы қолданылды. Мырыш, галлий және РЗЭ осы катализатордың деконирленген үлгілеріне ион алмасу, сіңдіру және құрғақ механикалық араластыру арқылы дәйекті түрде енгізілді және бұл әдістердің құрамында цеолит бар катализатордың каталитикалық қасиеттеріне әсері байқалды. Көмірсутектерді C_3-C_4 хош иістендіру заңдылықтарын салыстырмалы талдау нәтижесінде механикалық араластыру әдісі ең қолайлы екендігі анықталды, өйткені ол процестің ең жақсы өнімділігін қамтамасыз етеді.

Катализаторлардың белсенділігі мен тұрақтылығын жақсарту мақсатында дайындық процесінде термопара және жылу активациялары жүргізілді. Бұдан әрі модификацияланған катализатордың термопарасы мен термиялық активтенуі және олардың құрамында мырыш-галлий-цеолит бар катализатордың көмірсутектерді C_3-C_4 конверсиялау процесіндегі АрУ-ға қатысты белсенділігі мен селективтілігіне әсері үшін айырмашылықтар анықталды. Осы нақты операцияларды таңдау катализаторды алдын ала термо және термо-буымен өңдеу іс жүзінде айтарлықтай күрделі шығындарды қажет етпейтіндігімен, яғни экономикалық жағынан ең қолайлы болып табылатындығымен түсіндірілді.

Реакция-регенерация циклдарының заңдылықтары анықталды. Осылайша, каталитикалық композициялардың регенерациясының оңтайлы технологиялық параметрлері: температура 600˚С, атмосфералық қысым, тотықтырғыш-ауаның берілу жылдамдығы -2сағат, бұл белсенділікті қалпына келтіруге және жұмсалған катализатордың жаңа деңгейге дейін селективтілігіне әкеледі. Құрамында мырыш-галлий-цеолит бар катализатордың тотығу регенерациясы процесіне жүргізілген зерттеулер нақты регенерация режимін сақтай отырып, соңғысының белсенділігі қалпына келетінін көрсетті.

Зерттеудің негізгі міндеті көмірсутектерді C_3-C_4 конверсиялаудың тиімді катализаторларын жасау болды. Сондықтан, ең алдымен, біз АрУ үшін түрлендіру мен таңдамалылықты салыстырдық. Ұсынылған катализатор жақсы пайдалану қасиеттерімен сипатталады (жоғары белсенділік және ұзақ қызмет ету мерзімі), көмірсутектерді C_3-C_4 98,8% конверсиялау кезінде өнімнің мақсатты шығымының 59,2% -ын қамтамасыз етеді.

Түйін сөздер: тазартқыш газдар, C_3-C_4 көмірсутектер, құрамында цеолит бар катализатор, модификаторлар, реакциялық-регенерациялық циклдар.

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РАЗРАБОТКА ЭФФЕКТИВНЫХ КАТАЛИЗАТОРОВ ПЕРЕРАБОТКИ УГЛЕВОДОРОДОВ C_3-C_4.

Аннотация. Целью статьи является изучение влияния методов приготовления и активации модифицированного цеолитсодержащего катализатора на проявляемую им активность и стабильность каталитических свойств в процессе превращения углеводородов C_3-C_4. При проведении эксперимента в качестве исходного был использован промышленный катализатор крекинга ОМНИКАТ, представляющий собой цеолит в натриевой форме. На декатионированные образцы данного катализатора последовательно наносили цинк, галлий и РЗЭ методами ионного обмена, пропитки и методом сухого механического смешения и наблюдали влияние этих методов на каталитические свойства цеолитсодержащего катализатора. В результате сравнительного анализа закономерностей ароматизации углеводородов C_3-C_4 было установлено, что метод механического смешения является наиболее предпочтительным, так как он обеспечивает наилучшие показатели процесса.

С целью улучшения активности и стабильности катализаторов в процессе приготовления проводились термопаровые и термические активации. Далее были выявлены различия для термопаровой и термической активации модифицированного катализатора и их влияние на активность и селективность цинкгаллийцеолитсодержащего катализатора по АрУ в процессе превращения углеводородов C_3-C_4. Выбор конкретно этих операций был продиктован тем, что предварительная термо- и термопарообработка катализатора практически не требуют значительных капитальных затрат, т.е. экономически наиболее приемлемы.

Были установлены закономерности реакционно-регенерационных циклов. Так, оптимальными технологическими параметрами для регенерации каталитических композиций являются: температура – 600ºС, атмосферное давление, скорость подачи окислителя – воздуха – 2 $ч^{-1}$, которые приводят к восстановлению показателей активности и селективности отработанного катализатора до уровня свежего. Исследованиями процесса окислительной регенерации цинкгаллийцеолитсодержащего катализатора было установлено, что при сохранении чётко регламентированного режима регенерации активность последнего восстанавливается.

Основной задачей проведённых исследований являлась разработка эффективных катализаторов превращения углеводородов C_3-C_4. Поэтому в первую очередь сопоставлялись показатели конверсии и селективности по АрУ. Предлагаемый катализатор характеризуется хорошими эксплуатационными свойствами (высокой активностью и продолжительным сроком службы), обеспечивая 59,2% масс выход целевой продукции при 98,8% конверсии углеводородов C_3-C_4.

Ключевые слова: нефтезаводские газы, углеводороды C_3-C_4, цеолитсодержащий катализатор, модификаторы, реакционно-регенерационные циклы.

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