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КАТАЛИЗАТОРЫ ДЕСТРУКЦИИ УГЛЕВОДОРОДНОГО СЫРЬЯ НА ОСНОВЕ ХЛОРИДА БАРИЯ

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Эффективным катализатором пиролиза углеводородного сырья в олефинсодержащий газ при сравнительно невысоких температурах является барийсодержащий катализатор. В работе исследовали применение новых катализаторов пиролиза прямогонного бензина, рафината платформинга, бензинов термического крекинга на основе хлорида бария. Исследованы прочностные свойства таблетированных катализаторов с добавками графита, диэтаноламида СЖК (синтетические жирные кислоты), фенолфурановой смолы и глины. При формовании катализаторов сравнительно легко осуществляется введение добавок, модифицирующих активность. Получены результаты экспериментальных данных на катализаторе хлориде бария с данными модифицирующими добавками. Эти данные свидетельствуют о том, что производство катализаторов на основе хлорида бария экономически целесообразно, так как основано на использовании недорогих и доступных химических реагентов, а это в свою очередь способствует повышению эффективности использования природного невозобновляемого сырья и энергосбережению в процессах его переработки. Для катализаторов, формованных с добавлением тетрахлоралюмината натрия, характерно появление каталитической активности в процессах крекинга и изомеризации. Проведены испытания на определение длительности срока службы катализаторов с различными модификациями. Получены результаты: в течение 700 ч работы при температуре 500 °С катализатор, сформованный с 3,0% мас. графита, сохраняет активность по газообразованию и выходу низших олефинов при данных режимах работы. При этом выход кокса на пропущенное сырье для всех модификаций катализаторов не превышает 2,5% мас. за 30 ч работы при температуре 700 °С. Примечательно, что катализатор, содержащий $NaAlCl_4$ характеризуется относительно невысоким коксообразованием.

Ключевые слова: катализаторы пиролиза, электрофильные добавки, каталитическая активность, бензиновая фракция, тетрахлоралюминат натрия

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CATALYSTS FOR DESTRUCTION OF HYDROCARBON RAW MATERIALS BASED ON BARIUM CHLORIDE

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A barium-containing catalyst is the new effective catalyst for the pyrolysis of hydrocarbons into olefin-containing gas at relatively low temperatures. This article discusses options for the development of new straight-run gasoline pyrolysis catalysts, platformer raffinates and barium chloride-based thermal cracking gasolines. The strength properties of tableted catalysts with the addition of graphite, FAS (fatty acid synthesis) diethanolamide, phenol-furan resin and clay were studied. When forming the catalysts, the introduction of activity modifying additives is relatively easy. The results of experimental data on a barium chloride catalyst with these modifying additives were obtained. These data indicate that the production of barium chloride-based catalysts is economically feasible, since it is based on the use of inexpensive and affordable chemical reagents, and this in turn helps to increase the efficiency of using natural non-renewable raw materials and energy saving in the processes of its processing. The catalysts formed with the addition of sodium tetrachloroaluminate are characterized by catalytic activity in cracking and isomerization processes. Tests were carried out to determine the duration of the catalyst lifetime with various modifications, and the following results were obtained: during 700 h of operation at a temperature of 500 °C, the catalyst formed with 3.0% wt. graphite, retains activity on gas formation and the yield of lower olefins. In this case, the coke yield on the skipped feedstock for all catalyst modifications does not exceed 2.5% wt. for 30 h of operation at a temperature of 700 °C. It is noteworthy that the catalyst containing $NaAlCl_4$ is characterized by a relatively low coke formation.

Key words: pyrolysis catalysts, electrophilic additives, catalytic activity, gasoline fraction, sodium tetrachloroaluminate

INTRODUCTION

Catalytic pyrolysis seems to be an important direction in the group of secondary oil refining processes for solving of the task of yield increasing of useful hydrocarbon products. Such processes make it possible to expand the range of hydrocarbon feedstock involved to obtain gaseous hydrocarbons, represented mainly by ethane-ethylene, propane-propylene fractions, which are valuable raw materials for petrochemical industries and the production of consumer goods, especially plastics. Liquid products formed in the main thermal cracking processes, in particular, such as thermally cracked gasoline, straight-run gasoline, platforming raffinate also replenish the market of secondary hydrocarbon raw materials, the use of which can and should more effectively serve as a powerful additional source of raw materials. Until now, attempts to use some types of such low-quality secondary raw materials [1-5], in particular, and cracked gasolines, have not opened up the possibility of their inclusion in the traditional processing scheme. In this regard, it seems promising to involve them in the stage of catalytic processing to obtain gaseous products. With creation of effective catalytic forms for pyrolysis processes, it would be possible to solve the problem of processing

secondary fractions into useful hydrocarbon products. This determines the need to find active forms of new catalytic systems and establish experimental conditions for their high efficiency. In accordance with the task set, the ongoing research should be aimed at identifying the patterns of changes in the activity of the catalyst under conditions of variation of both the experimental parameters and the composition of the processed secondary raw materials.

Development of a technologically acceptable catalyst modification is a condition for industrial implementation of gasoline catalytic pyrolisis in ethylene/propylene in the presence of $BaCl_2$ [1-3]. The use of a finely divided powder catalyst leads to a number of undesirable processes, such as an increase in hydrodynamic resistance in a catalyst fixed-bed reactor, which subsequent coking makes a fixed bed impassable or powder particles with gasoline processed are entrained in a catalyst fluid-bed reactor. Therefore, barium chloride as a crystal powder cannot be used in an industrial process.

Availability of $BaCl_2$, an active component, enables to consider simpler and effective ways for obtaining industrial modifications of catalysts. Granules (tablets) obtained by moulding are an optimal form to fixed-bed reactors. Thus, the purpose of this paper is to develop ways for obtaining industrial modifications of barium-containing catalysts using the introduction of additives, i.e. from textural components, which relieve forming, up to components, which are able to perform co-catalytic functions.

EXPERIMENTAL

Barium chloride salt (GOST 4108-72-Barium chloride 2-aqueous) was used as a basic form of pyrolysis catalyst. By drying the salt for 20 h at a temperature of 171-175 °C, the bound water was evaporated from the crystalline hydrate, then the salt was subjected to heating at a temperature of 350 °C in a muffle furnace. To prepare catalyst samples, anhydrous barium chloride was mixed with various additives: diethanolamides of the FFA fraction (TU 38-107-250-83), phenolfuran resin (FF-65C), clay of the montmorillonite group (Kuganak deposit), graphite powder (OSCH 8- 4, GOST 23463-79). NaCl (GOST 4233-77) and $AlCl_3$ (GOST 4452-66) were sintered at 154 ± 1 °C in a stoichiometric ratio to obtain the double salt $NaCl{\cdot}AlCl_3$. The double salt in the form of a melt was applied onto a powdered barium chloride ($BaCl_2$) preliminarily heated at 350 °C.

The catalytic charge was used to form tablets 5×3 mm in size on a RTM-41 M2V tablet machine. Tableting was carried out by pressing at a temperature of 25 °C, then the carriers were impregnated.

Experimental technique. The oil feedstock was fed from the measured raw material tank with preheating, using a peristaltic pump of the RR-2-1B type to the preheating furnace, from where it entered the upper part of the reactor with a stationary catalyst bed. The reaction zone was heated using a PTF 12/50/250 laboratory tube furnace. Temperature control was carried out using thermocouples in the temperature range from 500 to 750 °C. The degradation products condensed in the condensing system, and the liquid product entered the receiver for liquids. Gaseous products, having passed through the trap, enter the drum counter with a liquid seal. The composition of the products was determined on a Shimadzu GCMS-QP2020 chromato-mass spectrometer with Rxi-5 ms capillary column.

The low-temperature nitrogen adsorption-desorption method (77 K) was used to determine the characteristics of the porous structure of the catalyst on an ASAP-2020 Micromeritics sorbtometer. Prior to analysis, the samples were subjected to evacuation for 6 h at a temperature of 350 °C. The specific surface area was calculated using the BET method at a relative partial pressure P/P0 = 0.2. The total (total) pore volume was determined by the BJH (Barrett-Joyner-Halend) method at a relative partial pressure P/P0 = 0.95.

A granular catalyst was obtained in the shape of cylindrical tablets 5×6 mm in size by forming on a high capacity-tableting machine.

The conditions for base catalysts, which conform to the technological requirements, were defined based on experimental data researches on granule forming of various sizes.

The study of $BaCl_2$ finely-divided powder showed that the best tablet strength properties are observed for 0.25-0.50 mm fraction (Table 1). Granule mechanical stability is also increased more when performing prior thermal processing of a mixture with post-calcination of granules. Powder fraction preliminary thermal processing at 175-300 °C, i.e. it is above the temperature of crystal water evaporation from $BaCl_2$ crystalline hydrates, increases the strength of ready granules by 5 times.

Variability in characteristics of a particle contact for $BaCl_2$ in a powder form when forming catalysts, for instance, adhesive strength between particles, has a great impact on structural and mechanical properties of granules.

Adhesion reliability can be regulated by surface energy attenuation in friction zones as a result of formation of SAA (surface active agent) adsorbed beds introduced into a catalyst system [4-7]. The use of lubricated agents, which lower concentration of subsurface stresses in areas of pressed mixture particles contact, ensures strengthening of ready granules. A reinforcing effect of specific additives, for example, when

using polymer resins, is explained by formation of a space skeleton in the shape of a chemically cross-linked network [8-10].

It is of importance to note that finely divided mixture moisturization (up to 5% water) helps to increase the efficiency of mechanical performance for a ready catalyst, but at the same time strength spread is observed in various modifications. The introduction of a SAA (surface active agent), such as FAS (fatty acid synthesis) diethanolamide of C_{10}-C_{13} fraction in the amount of 0.25-3.0% wt. has no effect on strength. Highly dispersed graphite may serve as an effective shaping additive in the amount of no more than 5.0% wt. (to a mixture). A narrow spread in strength values of 8-16 kg/tablet is observed by the content of graphite 3.0% wt. (to a mixture). When optimizing characteristics, such as composition, a dispersion component value, conditions for raw material preparation, the best performance by granule fracture strength is achieved axially and radially by 55 and 35 kg/tablet, respectively and it is considered to be in compliance with the use of such catalysts in production.

Considering reduced strength of granules radially, leading to catalyst damage when in loading-unloading thermally reactive components should be applied as auxiliary additives, ensuring catalyst modifications isotropic in strength.

The effect of phenol-furan resin as an auxiliary additive was studied. Tablets of a catalyst were obtained containing phenol-furan resin 0.5-5.0% wt. and calcined at 300-400 °C within 30-60 min, which strength reaches 50-60 kg/tablet both axially and radially (Table 1).

Table 1

Strength properties of $BaCl_2$-Based tablet catalysts

Таблица 1. **Прочностные свойства таблетированных катализаторов на основе $BaCl_2$**

Catalyst weight		Conditions of thermal processing		Crushing strength, kg/tablet	
$BaCl_2$ powder fraction, mm	Additive, % wt.	T, °C	t, h	Axially	Radially
0.16-1.00 unfractioned	–	–	–	0.7-1.6	0.6-0.9
0.5-1.00	–	–	–	0.4-0.8	0.2-0.5
0.16-0.25	–	–	–	8.0-1.6	0.2-0.6
0.25-0.50	–	–	–	1.4-2.0	0.8-1.3
0.25-0.50	–	175	10	8.0-12.0	2.0-9.0
0.25-0.50	–	175	20	10.0-15.0	4.0-9.0
0.25-0.50	–	175	25	10.0-16.0	4.0-9.0
0.25-0.50	–	300	10	10.0-16.0	9.0-14.0
0.25-0.50	–	400	10	10.0-16.0	9.0-12.0
0.25-0.50	–	500	10	10.0-16.0	9.0-12.0
Graphite					
0.16-1.00	3.00	–	–	19.0-23.0	16.0-21.0
0.16-0.25	0.25	–	–	21.0-24.0	7.0-13.0
0.16-0.25	1.00	–	–	34.0-48.0	20.0-27.0
0.16-0.25	3.00	–	–	45.0-65.0	32.0-37.0
0.16-0.25	5.00	–	–	39.0-50.0	31.0-38.0
0.25-0.50	3.00	–	–	38.0-43.0	30.0-37.0
FAS (fatty acid synthesis) diethanolamide					
0.25-0.50	0.25	–	–	10.0-16.0	0.5-3.0
0.25-0.50	0.50	–	–	4.0-6.0	1.0-3.0
0.25-0.50	3.00	–	–	2.0-3.0	1.0-4.0
Phenol-furan resin					
0.25-0.50	0.5	–	–	1.0-1.3	0.5-1.3
0.25-0.50	0.25	–	–	0.6-0.9	0.6-0.8
0.25-0.50	5.0	–	–	1.0-1.2	0.5-1.2
0.25-0.50	0.5	300	0.5	6.0-9.0	5.0-9.0
0.25-0.50	2.5	300	0.5	10.0-15.0	4.0-12.0
0.25-0.50	5.0	300	0.5	20.0-24.0	18.0-24.0
0.25-0.50	5.0	400	0.5	50.0-64.0	47.0-60.0
0.25-0.50	5.0	500	0.5	55.0-61.0	55.0-60.0
0.25-0.50	5.0	600	0.5	56.0-66.0	51.0-65.0
Clay					
0.25-0.50	5.0	–	–	59.0	38.0

RESULTS AND DISCUSSION

In addition to affecting the strength properties, calcination and introduction of thermally reactive components into a catalytic mixture allows changing granule structural characteristics, such as a specific surface area and pores volume. Calcination of original $BaCl_2$ with subsequent calcination of ready granules leads to the growth in the specific surface area (Fig. 1). Adding water, graphite and FAS (fatty acid synthesis) diethanolamide significantly reduces the specific surface area as compared with the original catalyst.

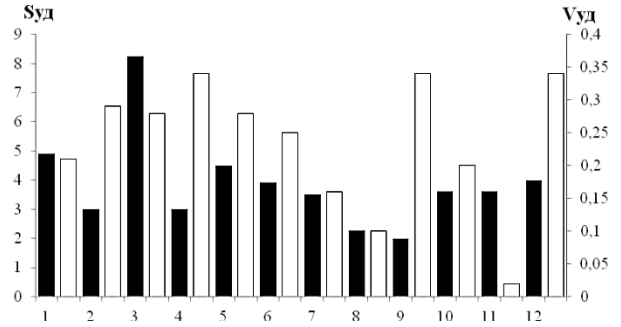

Fig. 1. Specific surface area (■) $S_{уд}$ ($m^2 \cdot g^{-1}$), pores specific volume (□) $V_{уд}$ ($cm^3 \cdot g^{-1}$) of barium-containing catalyst 1-12. 1 – original catalyst; 2 – tablets calcined at 175 °C; 3 – with preliminary calcination of the mixture at 175 °C; 4 – tablets calcined at 300 °C; 5 – with preliminary calcination of the mixture at 300 °C; additive component (wt. %): 6 – 1 of graphite, 7 – 3 of graphite, 8 – 5 of graphite, 9 – 1 of diethanolamide, 10 – 5 of water, 11 – 0.25 of graphite + 1 of water, 12 – 5 of phenol-furan resin

Рис. 1. Удельная поверхность (■) $S_{уд}$ ($м^2 \cdot г^{-1}$), удельный объем пор (□) $V_{уд}$ ($см^3 \cdot г^{-1}$) барийсодержащих катализаторов 1-12. 1 – исходный катализатор; 2 – таблетки, прокаленные при 175 °C; 3 – с предварительным прокаливанием шихты при 175 °C; 4 – таблетки, прокаленные при 300 °C; 5 – с предварительным прокаливанием шихты при 300 °C; добавка (% мас.): 6 – 1 графита, 7 – 3 графита, 8 – 5 графита, 9 – 1 диэтаноламида, 10 – 5 воды, 11 – 0,25 графита + 1 воды, 12 – 5 фенолфурановой смолы

During the application of various additives to the surface of barium chloride, layers are formed that prevent the penetration of raw material particles to the active center of the catalyst. As a result, the specific surface area and pore volume of the catalyst support are reduced.

The ambiguous effect of these factors on the surface-pore structure of granules is monitored. As a rule, thermal processing of an original material and formed catalyst increases the pores volume, but when used with various additives, the effect is of more complex nature, and the reaction of the agents introduced already significantly depends on the nature and concentration of additives. Thus, diethanolamide introduction (1.0% wt.) significantly increases the pores volume, water introduction up to 5.0% wt., does not effect this value, on the contrary. A slight increase in the pores volume is observed when adding graphite in the amount of 1.0% wt., as compared with the granules formed without calcination and in no additives. A subsequent increase in the content of graphite leads to a decrease in the porosity of granules.

The study on catalysts containing clay of a montmorillonite group, Kuganak deposit (Republic of Bashkortostan) as a binder, based on aluminosilicates of $xAl_2O_3 \times ySiO_2 \times nH_2O$ structure, was conducted. Satisfactory strength and ease through the tableting process can be achieved by introducing up to 5.0% wt. to a clay mixture (Table 1). With a high clay content in the catalyst (30.0 or 50.0% wt.), extrusion forming of a pre-wetted catalyst up to 25% wt. should be carried out. Catalysts with crushing strength of 178-240 kg/granules axially and 140-205 radially are produced by thermal processing at 350-400 °C. Catalysts forming with clay addition (up to clay 30.0% wt.) improves structural characteristics (Fig. 2a, b).

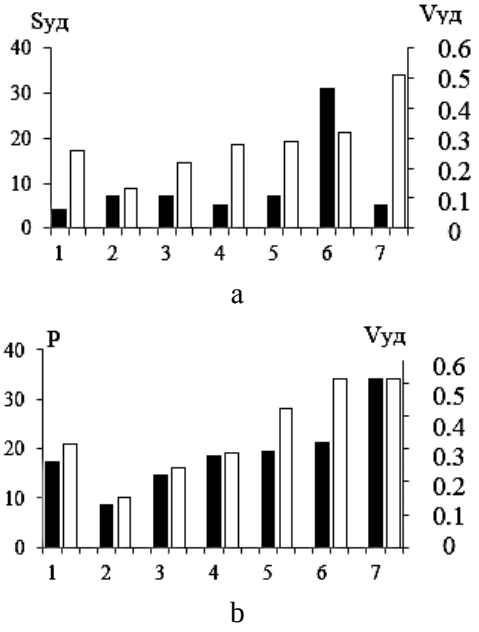

Fig. 2a. Dependence of specific surface area (■) $S_{уд}$ ($m^2 \cdot g^{-1}$) on pores specific volume (□) $V_{уд}$ ($cm^3 \cdot g^{-1}$) of barium-containing catalysts: 1 - catalyst without additives; clay addition as a binder (wt.%): 2 – 1.0; 3 – 5.0; 4 – 10.0; 5 – 20.0; 6 – 30.0; 7 – 45.0

Fig. 2b. Dependence of mechanical performance (■) P on specific pore volume (□) $V_{уд}$ ($cm^3 \cdot g^{-1}$) of barium-containing catalysts: 1 - catalyst without additives; clay addition as a binder (wt.%): 2 – 1.0; 3 – 5.0; 4 – 10.0; 5 – 20.0; 6 – 30.0; 7 – 45.0

Рис. 2a. Зависимость удельной площади поверхности (■) $S_{уд}$ ($м^2 \cdot г^{-1}$) от удельного объема пор (□) $V_{уд}$ ($см^3 \cdot г^{-1}$) барийсодержащих катализаторов: 1 – катализатор без добавки; добавка глины в качестве связующего (% мас.): 2 – 1,0; 3 – 5,0; 4 – 10,0; 5 – 20,0; 6 – 30,0; 7 – 45,0

Рис. 2b. Зависимость механической прочности (■) P от удельного объема пор (□) $V_{уд}$ ($см^3 \cdot г^{-1}$) барийсодержащих катализаторов: 1 – катализатор без добавки; добавка глины в качестве связующего (% мас.): 2 – 1,0; 3 – 5,0; 4 – 10,0; 5 – 20,0; 6 – 30,0; 7 – 45,0

The extrusion method allows granules to be formed into uninterrupted regular macroscopic lattice or honey-combed structures from a catalyst plastic mass. Such structural modification, as a rule, optimizes the reactor gas-dynamic operating mode. Pressurization in a reactor for more than 0.1 MPa leads to a decrease in the yield of desired products and growth of methane yield [11, 12]. The form and size of a catalyst are influencing parameters of the pressure and its differences in a reaction area during the movement of a reaction gas mixture through a catalyst bed. In the catalyst bed, a large pressure drop is accompanied by the process using tableted granules in the form of cylindrical solid particles, where the drop is 1.5-1.7 times greater than in the bed layer in the form of Raschig rings in average. The ethylene yield in average of 0.5-0.1% higher is observed at 790-795 °C in the catalyst bed based on potassium vanadate modified with boron compounds produced in the form of Raschig rings than when using a cylindrical catalyst. A regular honeycombed or lattice structure creates the most optimal gas-dynamic mode undoubtedly [13-15].

By introducing $BaCl_2$ into the original plastic clay mass, catalyst blocks with low strength and mechanical instability to high temperatures were obtained. An impregnation with an aqueous solution of barium chloride of a formed aluminum ceramic block may increase $BaCl_2$ content up to 45%. But it is worth noting that such blocks are destroyed when calcined at 800 °C. It is possible to prevent this process without changing the surface pore parameters of the aluminum ceramic matrix by reducing the content of barium chloride up to 18.0% wt.

For a catalyst containing $NaAlCl_4$ 10% wt., the temperature range from 650 to 750 °C was determined experimentally, at which a change in the nature of the process is observed.

Table 2

The yield of gaseous* gasoline pyrolysis products on various forms of barium-containing catalysts

***Таблица 2.* Выход газообразных* продуктов пиролиза бензинов на различных формах барийсодержащих катализаторов**

T, °C	V,** h^{-1}	Yield of products, % wt. on passed feedstock							
		CH_4+ H_2	C_2H_4	C_3H_6	C_3H_8	$\sum C_4H_8$	$\sum C_4H_{10}$	C_5	Total
Straight-run gasoline/ tableted catalyst with clay 30% wt.									
650	0.5	9.1	28.2	10.0	14.9	2.0	6.5	0.8	71.5
700	0.5	12.6	29.1	7.3	15.1	1.1	9.1	0.7	75.0
725	0.5	17.6	32.9	7.2	13.8	0.9	7.0	0.1	79.5
750	0.5	25.2	34.9	7.1	12.0	0.8	5.5	0.1	85.6
Straight-run gasoline/ tableted catalyst with $NaAlCl_4$ 10% wt.									
650	0.5	6.8	12.5	6.4	17.5	0.9	13.7	–	57.8
650	1.0	6.9	10.9	6.9	18.2	0.2	14.4	–	57.5
700	0.5	12.4	28.4	28.0	7.0	18.3	1.0	14.8	81.5
700	1.0	11.5	21.4	8.1	23.4	0.9	14.9	–	80.2
725	0.5	19.8	32.9	7.0	18.9	0.8	3.0	–	82.4
725	1.0	17.0	30.0	9.1	18.3	1.2	3.5	–	81.1
750	0.5	25.7	38.9	6.2	12.2	0.6	0.4	–	84.0
750	1.0	20.0	33.1	8.0	17.2	0.7	4.8	–	83.8
Straight-run gasoline/ honey-combed catalyst with $BaCl_2$ 18% wt.									
650	0.5	3.59	3.9	2.7	26.1	0.1	8.3	4.61	49.3
700	0.5	17.5	22.0	3.9	25.9	0.8	12.5	4.2	84.8
725	0.5	22.4	28.9	4.4	19.0	0.4	12.7	0.1	87.9
725	1.0	19.9	27.1	1.0	22.9	0.3	16.4	0.2	87.8
725	2.0	13.7	23.4	4.0	24.8	0.2	19.3	0.3	85.7
725	2.5	13.6	23.2	4.0	24.9	0.1	19.1	0.3	85.2
750	0.5	26.3	31.0	0.4	12.6	0.1	10.1	0.1	80.6

Note: *C_5 hydrocarbons condense in the refrigerator along with liquid products; **V – bulk feed rate

Примечание: *углеводороды C_5 конденсируются в холодильнике вместе с жидкими продуктами; **V – массовая скорость подачи

Straight-run gasoline pyrolysis at 650-700 °C gives a lower yield of ethylene as compared with the yields of propylene and butylenes (Table 2), while the content of butylenes in a pyrolysis gas mixture is significantly higher than in a thermal process. The composition of the gaseous products of the process is con-

sistent with the literature data on the cracking of hydrocarbons with the predominant formation of C_4 olefins using $NaAlCl_4$. However, the composition of products changes at a temperature of 725 °C and above, an increase in ethylene content occurs, and the content of butylene is reduced. The yield of ethylene reaches 38% and higher, with a gas formation rate of 80% on the introduced raw materials. In general, the composition of the products becomes typical for a high-temperature radical process [15].

According to the data [6, 16], low-temperature catalytic decomposition of hydrocarbons requires the introduction of water or other hydrogen donors into the system to activate electrophilic catalysts based on complex metal chlorides. The role of water in the activation of $MAlCl_4$ is based on its ability to dissociative adsorption on the surface of the catalyst. Thus, catalytically active metal chlorides under these conditions exhibit the properties of Brensted acids.

Statistical treatment of the results of analysis of the catalytic cracking straight run gasoline performed using «STATISTICA» program. The diagrams show the desirability responses of ethylene and propylene versus temperature and feed rate.

It can be seen from the figures that increase in temperature, the formation of ethylene, propylene is observed at a low feed rate, and with an increase in the feed rate of straight-run gasoline, the temperature decreases.

As a rule, the yield of ethylene varies depending on the degree of dilution of the feedstock with superheated water vapor (Table 3). A significant increase in the gas formation and the yield of ethylene is observed when steam is supplied up to 75% wt. from the feedstock. In addition, carbon oxide is identified in the composition of gases [17-19].

Liquid pyrolysis products contain aromatic hydrocarbons (Table 4).

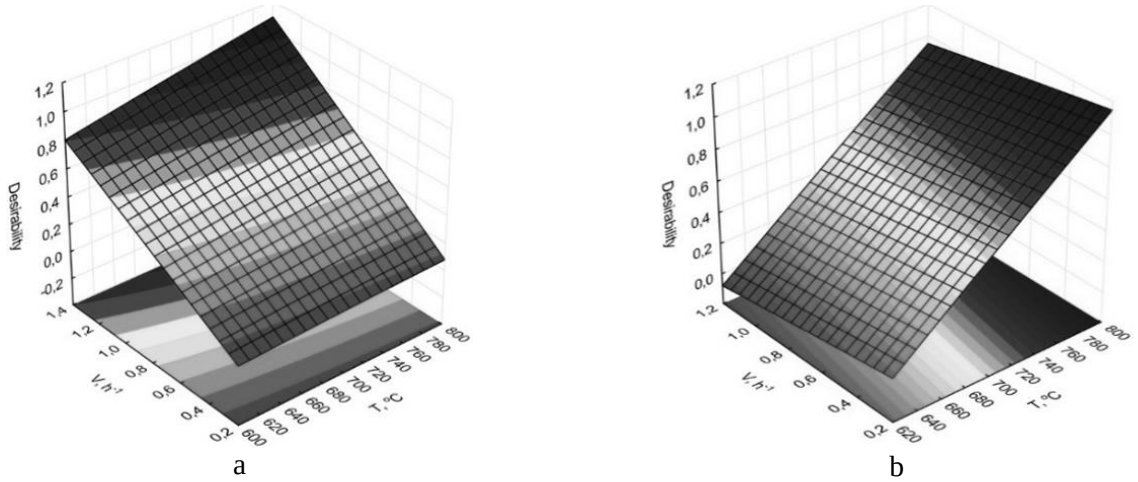

Fig. 3. The response of the "desirability" of the formation of a) C_2H_4, б) C_3H_6 from straight-run gasoline using a catalytic system of barium chloride tableted with 10% wt. $NaAlCl_4$

Рис. 3. Реакция "желательности" образования а) C_2H_4, б) C_3H_6 из прямогонного бензина с использованием каталитической системы хлорида бария, таблетированного с 10% масс. $NaAlCl_4$

Table 3

The yield and composition of gaseous products of straight-run gasoline pyrolysis on granular catalysts upon dilution of the feedstock with water vapor (temperature 725 °C, bulk feed rate 0.5 h^{-1})

Таблица 3. **Выход и состав газообразных продуктов пиролиза прямогонного бензина на гранулированных катализаторах при разбавлении сырья водяным паром (температура 725 °C, объемная скорость подачи сырья 0,5 $ч^{-1}$)**

Dilution, % wt. on the feedstock	Yield of gas % wt. on the passed feedstock								
	CH_4+H_2	C_2H_4	C_2H_6	C_3H_6	C_3H_8	C_4H_8	C_4H_{10}	Carbon oxides	Total
Catalyst with graphite 3% wt.									
–	19.1	31,6	7.9	10.9	0.7	5.5	0.2	–	75.9
50	20.8	32,5	4.6	12.9	1.0	6.5	0.1	1.2	79.6
100	25.0	31,9	4.0	12.0	0.6	4.0	0.8	1.9	80.2
Catalyst with clay 3% wt.									
–	17.6	32.9	7.2	13.8	0.9	7.0	0.1	–	79.5
50	18.1	34.8	9.1	16.8	1.0	7.0	0.3	1.4	88.5
100	20.0	34.0	8.0	16.1	0.4	5.1	0.1	2.0	85.7

Table 4

The composition of the light fraction of straight-run gasoline pyrolysis resin in the presence of barium-containing catalysts (bulk feed rate 0.5 h^{-1})

***Таблица 4*. Состав лёгкой фракции смолы пиролиза прямогонного бензина в присутствии барийсодержащих катализаторов (объемная скорость подачи сырья 0,5 $ч^{-1}$)**

Pyrolysis condensate component	Catalyst I				Catalyst II				Catalyst III			
	Composition, % wt. at pyrolysis temperature, °C											
	650	700	725	750	650	700	725	750	650	700	725	750
Paraffin-naphthene olefinic part	43.5	41.6	41.2	39.9	44.7	41.7	41.4	39.4	44.4	43.9	43.7	49.0
Benzene	15.9	16.1	16.9	12.0	12.7	13.6	16.9	15.6	12.1	10.9	9.3	9.9
Toluene	10.9	10.7	10.0	9.3	12.0	10.9	10.3	9.9	16.0	16.3	15.2	15.7
Ethylbenzene	2.1	2.0	1.1	0.9	4.3	3.7	3.4	3.1	3.4	7,.3	7.0	4.8
Xylenes	8.9	7.0	4.3	4.0	7.0	6.4	5.2	4.0	7.1	7.2	8.4	3.0
Cumene	3.8	3.5	3.3	2.9	7.5	3.5	1.9	0.8	1.2	0.9	0.4	0.6
Styrene	4.5	7.5	8.8	15.2	2.8	5.2	12.4	15.3	6.5	7.6	11.0	14.9
Indin	2.0	3.7	8.2	10.0	2.7	6.6	7.0	7.3	4.3	3.9	4.3	9.9
Unidentified components	8.4	7.9	6.2	5.8	6.5	8.4	1.5	4.6	5.0	2.0	0.7	2.2

Note: Catalyst 1 – formed, graphite 3.0% wt.; Catalyst 2 – formed, clay 30.0% wt.; Catalyst 3 – formed, $NaAlCl_4$ 10.0% wt
Примечание: Катализатор 1 – сформирован с 3,0% масс. графита; Катализатор 2 – сформирован с 30,0% масс. глины; Катализатор 3 – сформирован с 10,0% масс. $NaAlCl_4$

The study of the structure of both pure $BaCl_2$ and its modifications obtained by applying various additives showed that under the studied temperature conditions from 500 to 750 °C, the solid structure of the $BaCl_2$ catalyst undergoes some physical and chemical changes. In particular, the macro- and microstructures of the catalyst undergo certain physical changes. With prolonged exposure to temperature under operating conditions, recrystallization occurs, leading to a reduction in the specific surface of the catalyst or a decrease in the number of active catalytic centers per unit of its surface. However, when adding additives to the surface of the $BaCl_2$ catalyst base, such as graphite, FFA diethanolamide (synthetic fatty acids), phenolfuran resin, and clay, which do not have their own catalytic activity or have relatively little activity, it has been shown that the recrystallization rate of the active component of the catalyst decreases. The low proportion of compaction and coking processes on the surface of both pure and modified catalyst determines its activity during the long studied exposure period up to 700 h.

Interestingly, that the introduced raw materials for all structural modifications of the catalyst account for 2.5% wt. and less than the coke yield for 30 h of operation at a temperature of 700 °C. It is also noteworthy that processes using a $NaAlCl_4$-based catalyst are characterized by relatively low coking.

The study of the spent catalyst, in particular, the surface on the sections of tablets, showed that the distribution of coke deposits mainly occurs only in a thin surface layer. The pores structure and specific surface area of the granules were almost unchanged. As a result, in particular, the specific surface of the original and coked catalyst at 500 °C are 3.62 and 3.43 m^2/g, and the pores volume is 0.22 and 0.28 cm^3/g, respectively. In this regard, a certain decrease in the rate of coke deposition on the catalyst can be explained by partial desorption of intermediate compaction products – coke precursors into the gas phase [20]. This leads to a certain increase in the yield of heavy resins when reducing the yield of coke and it does not affect the yield of the desired gaseous pyrolysis products.

CONCLUSION

Catalysts based on barium chloride are promising in terms of obtaining light olefins during pyrolysis of gasoline fractions, and they also fully meet the level of requirements for thermal pyrolysis catalysts. The results obtained during the experiments indicate that the production of barium catalysts is economically feasible, since it is based on the use of inexpensive and affordable chemical reagents, and this in turn contributes to increasing the efficiency of using natural non-renewable raw materials and energy saving in its processing processes.

The authors declare the absence a conflict of interest warranting disclosure in this article.

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