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Hydrogenation of the model object in the presence of nanocatalysts

The catalytic hydrogenation of the model object anthracene was presented in the article. The selection of conditions for the proceeding of the process was conducted. Hydrogenation process was carried out using nanocatalysts β-FeOOH, $Fe(OA)_3$ and Fe_3O_4 in the ratio of 1 % in the presence of hydrogen. The effect of initial hydrogen pressure on the yield of the products during the reaction was detected. The most effective additive for the catalytic hydrogenation of the model object anthracene was determined.

Key words: catalytic hydrogenation, anthracene, nanocatalysts, polynuclear aromatic hydrocarbons, hydrocarbon feedstock, effective additive, model objects.

The hydrogenation of solid and heavy hydrocarbons is a versatile alternative method of producing synthetic liquid fuels in the fuel-processing industry [1]. The growing interest to the problem of coal liquefaction and processing of heavy oil residues, coal tar and its fractions is due to the necessity of involving additional resources in the fuel and energy balance and expansion of the source of raw materials for organic synthesis industry. A fundamental study of model compounds has a great importance in the study of physical and chemical properties and reactivity of organic mass of coal [2], which allows for a more detailed set of processing mechanisms and develop science-based methods for predicting their conducting. Polynuclear aromatic hydrocarbons can be regarded as analogues of high-boiling petroleum fractions and residues, fragments of the organic mass of coal and primary coal tar and its fractions, which include aromatic structures, the relative share and structural features of which depend on the degree of metamorphism of coal [3, 4]. Furthermore, model compounds can not be exposed to the destruction in the area of the destructive hydrogenation temperatures.

The hydrocarbon feedstock (coal, peat, oil shale, heavy oil, coal tar, etc.) is a complex mixture of organic and mineral substances, hardly amenable for studies. Model compounds such as anthracene, phenanthrene, pyrene, naphthalene, etc. are often used to determine the mechanism of the process of activity and selectivity of selected catalysts.They may be fragmented to provide the reactivity dependent behavior weight organic material [5].

The use of catalysts in the process of destructive hydrogenation of heavy hydrocarbon feedstock allows carrying out the process under more mild conditions and increasing the conversion of organic matter, yield and quality of the distillable products.

The application of catalysts based on ore materials and metallurgical sludge production is advantageous from an economic point of view. Literature data indicate that this class of catalysts has been used in coal liquefaction processes for a long time. The active component of many catalysts is iron ore. Many of the catalytically active components accelerating hydrogenation of coal are presented in the mineral substances of coal. In connection with it, the application of coal ash for hydrogenation processes is an urgent task [6].

It is reasonable to use highly dispersed catalysts, which are equally dispersed in the raw material in pseudo-homogeneous state in order to prevent their deactivation. The search of new catalysts and the development of efficient technologies for solid hydrocarbons and petroleum residues are one of the main directions in the development of energy and petrochemical industries. The increase of the efficiency of heterogeneous catalytic reactions is one of the main problems in the hydrogenation of heavy hydrocarbon feedstock [7]. Therefore, much attention is paid to the development of scientific approaches to create a new generation of catalytic systems, which have increased activity and selectivity.

A study of the influence of nanocatalysts in the hydrogenation process on the product yield of model objects was carried out. Nanocatalyst was obtained by the procedure described in papers [8, 9]. Samples of model objects were subjected to the hydrogenation process in the reactor of high pressure (autoclave). Premixed source components were placed in the reactor and flushed with hydrogen. The reaction mixture was heated to 400 ºC for 60 minutes in an excess of hydrogen at a pressure of 3 MPa. Start of the reaction was considered to the moment of reaching the operating temperature by autoclave. Autoclave heating rate was 10 ºC per min. The resulting product was washed with benzene. Conditions of proceeding the hydrogenation process of model objects were shown in the Table 1.

Table 1

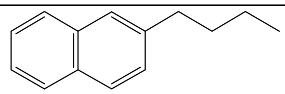
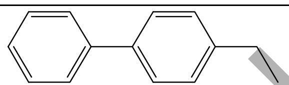
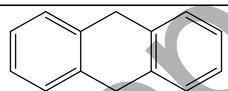
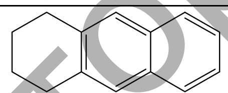
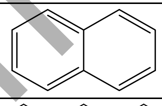
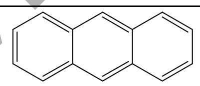
Conditions for the hydrogenation of coal tar in the presence of nanocatalysts

№	Anthracene, g	Nanocatalyst		*T*, ºC	P, MPa	τ, min
		β-FeOOH, g	$Fe(OA)_3$, g			
1	1	0,01	1	400	3	60

The study of fractional composition of the carbohydrate portion of the model objects was carried out with the method of adsorption using high-performance chromatograph Agilent Technologies 5975. The content of hydrocarbons in the mixture was detected, names of which were given below shown in the Table 2.

Table 2

Product yield of the hydrogenation process of model objects

Name	Structural formula	Nanocatalyst, β-FeOOH		Nanocatalyst, $Fe(OA)_3$	
		300 ºC	400 ºC	300 ºC	400 ºC
2-Butylnaphthalene		–	33,04	0,38	11,04
2-Ethyl-1,1'-biphenyl		2,42	1,03	2,61	0,85
9,10-Dihydroanthracene		–	59,55	–	55,55
1,2,3,4-Tetrahydroanthracene		–	15,98	–	23,54
Naphthalene		6,55	2,15	4,32	2,43
Anthracene		7,25	0,51	6,38	0,38

It should be pointed out that in the process of hydrogenation of anthracene using nanocatalyst β-FeOOH, the yield of products turned out to be the highest and was 65 % and the yield of degradation products was 6.4 % by adding 1 % of the catalyst, the percentage of an unreacted material was 23.30 %. Hydrogenation product yield was 48.29 % in the case of hydrogenation with using nanocatalyst $Fe(OA)_3$. Degradation products yield was 14.57 %, the percentage of unreacted material was 27.30 % adding 1 % of the catalyst. It demonstrates the advantage of using nanocatalyst β-FeOOH in hydrogenation of polyaromatic hydrocarbons.

A significant change in the ratio of hydrogenation and hydrogenolysis products, and the ratio of conversion depending on the ratio of the catalyst were shown comparing the results of this hydrogenation. Apparently, it is due to the increase in the amount of oxygen in the form of increased concentration of hydroxyl groups, which can be referred to the hydrogen bonding. Number of fragments containing a quaternary carbon atom sharply decreased after the hydrogenation, and the number of fragments (>C=) conversely increased, i.e. the transition from the more substituted compounds to less substituted can be seen.It reforms with literature data very good, which show that from hydrocarbons with three or more rings collinear compounds are hydrogenated faster than the angular [5]. From the viewpoint of the mechanism of a reaction, heterolytic decomposition of precursor molecule occurs directly in the presence nanocatalyst by carbonium ion mechanism with the predominant formation of hydrocarbons having tertiary carbons (branched structure). Organic substances, contacting with the reaction centers, deactivate them, i.e. while reducing the amount of hydrogenation catalyst, the product yield decreases and the yield of degradation products increases.

The most optimal amount of nano-catalysts in a ratio of 1 % allows to achieve the crease in the yield of active hydrogen atoms, which prevents the reactions of condensation and decreases the stability of the associates in the hydrogenation of polynuclear aromatic hydrocarbons Thus, the estimation of the influence of nanocatalysts β-FeOOH and $Fe(OA)_3$ on the hydrogenation process of model object was carried out. It was determined that β-FeOOH nanocatalyst shows improved activity and selectivity compared to nanocatalyst $Fe(OA)_3$. As results of the experiments, it can be concluded that nanoscale catalysts are newly developed catalytic additives that contribute to a deeper chemical modification and degradation of the organic mass of hydrocarbons, resulting in a significantly higher yield of light products. Such multiplet systems as coal, coal tar, or its fractions can be used for the hydrogenation. The search and application of nanocatalytic additives will make possible increasing the efficiency of known in this area techniques.

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Модельді объектінің нанокатализаторлар қатынасындағы гидрогенизациясы

Мақалада модельді объект — антраценнің каталитикалық гидрогенизация үрдісі қарастырылған. Гидрогенизация процесінің жүру жағдайлары анықталған. Сутегі ортасында β-FeOOH, $Fe(OA)_3$ және Fe_3O_4 нанокатализаторларының 1 % мөлшерінің қатынасындағы гидрогенизация процесі жүргізілген. Бастапқы сутегі қысымының өнім шығымына әсері зерттелген. Антраценнің гидрогенизациясын жүргізудегі каталитикалық қоспаның ең тиімді қатынасы алынған.

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Гидрогенизация модельного объекта в присутствии нанокатализаторов

В статье представлена каталитическая гидрогенизация модельного объекта — антрацена. Осуществлен подбор условий протекания процесса. Проведен процесс гидрогенизации с использованием нанокатализаторов β-FeOOH, $Fe(OA)_3$ и Fe_3O_4 в соотношении 1 % в среде водорода. Выявлено влияние начального водородного давления на выход продуктов в процессе реакции. Установлена наиболее эффективная каталитическая добавка для гидрогенизации антрацена.