

Effect of New Catalytic Systems on the Process of Anthracene Hydrogenation

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Abstract—The hydrogenation of anthracene in the presence of the nanosized catalysts based on iron β -FeOOH and Fe(OA)₃ (OA refers to oleic acid) and the spherical catalysts NiO/SiO₂ and Fe₂O₃/SiO₂ obtained from ash and slag from thermal power plants was studied. It was found that the above catalytic systems can arranged in the following order according to the yields of hydrogenation and destruction products upon the hydrogenation of polycyclic hydrocarbons: β -FeOOH, Fe(OA)₃, and Fe₃O₄ nanoparticles > NiO/SiO₂ and Fe₂O₃/SiO₂ spherical catalysts > commercial cobalt–molybdenum catalyst. It was established that the test catalysts are promising for the hydrogenation of polycyclic hydrocarbons, and they can be used for the direct liquefaction of coal.

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A search for effective catalysts and the development of new technologies for the processing of solid hydrocarbon raw materials and petroleum residues is an important line in the development of petrochemical industry. The main task in the hydrogenation of heavy hydrocarbons is to increase the efficiency of heterogeneous catalytic reactions. The selection of effective catalysts and their application to the process of the destructive hydrogenation of heavy hydrocarbon raw materials make it possible to implement the process under milder conditions and to increase the conversion of organic matter and the yield and quality of distillate products. Consequently, considerable attention is paid to the development of scientific approaches to the creation of catalytic systems of a new generation, which possess increased activity and selectivity. Many versions of the preparation of hydrogenation catalysts, in particular, nanocatalysts and natural materials, which can be used as accessible catalysts for the conversion of hydrocarbon raw materials, have been considered [1].

An analysis of published data showed that the current use of aluminosilicate microspheres as a promising raw material for the production of catalysts that can operate under the conditions of corrosive media and high temperatures is in increasing demand. Model compounds, such as anthracene, phenanthrene, pyrene, and naphthalene, are frequently used for determining the mechanisms of activity and selectivity of the selected catalysts in the process of hydrogenation. This makes it possible to study in more detail the

mechanisms of processing heavy coal and to develop scientifically advanced methods for the prediction of the processing [2]. Therefore, in this work, we studied the effects of the spherical catalysts NiO/SiO₂ and Fe₂O₃/SiO₂ and the nanocatalytic systems based on iron β -FeOOH, Fe(OA)₃ (OA refers to oleic acid), and Fe₃O₄ on the process of the catalytic hydrogenation of anthracene as a model substance.

EXPERIMENTAL

For studying the effects of the spherical catalysts NiO/SiO₂ and Fe₂O₃/SiO₂ and the nanocatalysts β -FeOOH, Fe(OA)₃, and Fe₃O₄ on the yield of products from the model substance anthracene in the process of hydrogenation, we performed the experiments in a high-pressure reactor (autoclave) with a volume of 0.2 L at temperatures of 300 and 400°C. The preliminarily mixed initial components (1 g of anthracene and 0.1 g of a catalyst) were placed in the reactor and hydrogenated for 60 min in the presence of hydrogen at a pressure of 3 MPa. The autoclave heating rate was 10 K/min.

The products of the process of anthracene hydrogenation were analyzed by gas chromatography–mass spectrometry on an HP 5890/5972 MSD instrument from Agilent (the United States). The chromatographing conditions were the following: DB-XLB-5 column, 30 mm × 0.5 μ m; carrier gas, helium (0.8 mL/min); temperature programming from 50°C (4 min) at a rate of 10 K/min in a range of 50–150°C, at a rate of

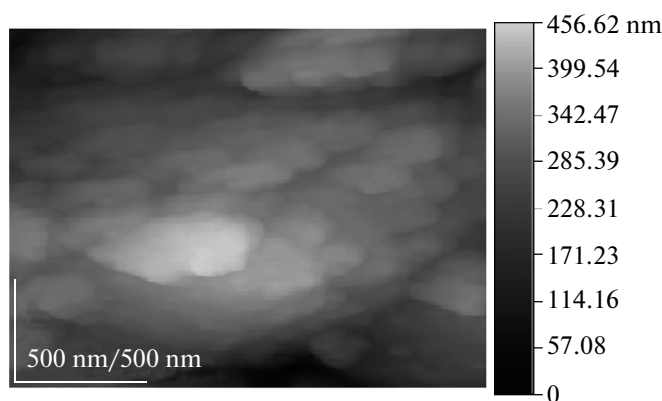


Fig. 1. Surface morphology of the spherical catalyst NiO/SiO₂.

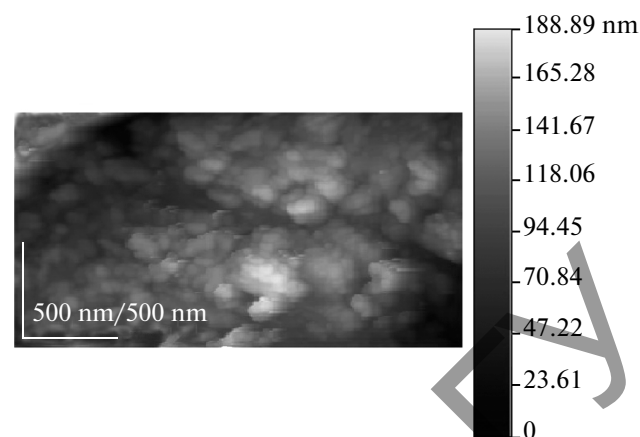


Fig. 2. Surface morphology of the spherical catalyst Fe₂O₃/SiO₂.

20 K/min in a range of 150–300°, and an exposure of 4 min at 300°C; injector temperature, 200–300°C. The substances were identified using the NIST 98 mass-spectrometric database.

The nanocatalytic systems based on iron β -FeOOH, Fe(OA)₃, and Fe₃O₄ were synthesized in the People's Republic of China in accordance with a published procedure [3]. Gudun et al. [4] tested the physicochemical characteristics of the nanocatalysts β -FeOOH, Fe(OA)₃, and Fe₃O₄ and their morphological types, activity, and selectivity.

The spherical catalysts NiO/SiO₂ and Fe₂O₃/SiO₂ are nickel and iron oxides evenly distributed over the external surface of a microspherical silicon-containing support. The microspherical silicon-containing support is an ash component of slag from coal-burning power plants, which is formed upon the combustion of coal in the boilers of the power plants because of the granulation of the fusion of the mineral matter of coals and the blowing of crushed small drops by internal gases. As a result of this process, hollow silicate microspheres with an almost ideal spherical shape are obtained.

The concentration of the microspherical silicon-containing support was determined by the X-ray spectrometry analysis (%): SiO₂ 55.391, Al₂O₃ 2.014, Fe₂O₃ 7.715, TiO₂ 1.745; CaO, 2.606; K₂O 2.354; MgO, 1.531; Na₂O 2.734; and other unidentified substances, 1.

The microspherical silicon-containing support was separated from the ash and slag waste under laboratory conditions by the immersion of the above waste in distilled water. The natural flotation separation of the ash and slag waste occurred due to a difference of densities; in this case, a heavy sol fraction settled at the bottom, and light hollow aluminosilicate microspheres came to the top of the liquid. These microspheres were

collected from the liquid surface and dried. Then, the 10% solutions of nickel and iron salts (NiCO₃ and FeSO₄ · 9H₂O) were prepared, applied to the microspherical silicon-containing support with the subsequent stages of drying and heat treatment at 600°C for 60 min, and introduced in an amount of 1%.

The porous structure parameters of the spherical catalysts NiO/SiO₂ and Fe₂O₃/SiO₂ were studied on an ASAP Micromeritics instrument (the United States).

The surface topography of the spherical catalysts was measured on a JSPM-5400 atomic force microscope from JEOL. The sample was pressed into a tablet with the aid of a press. The surface was measured in the AC-AFM mode (reversible coupling type) using the Topography measurement method. The scanned surface area was 20 × 20 μm, and the rate of scanning was 6 μm/s. CSC37/AIBS probes from MikroMasch were used in the process of scanning. The resulting images were analyzed with the aid of the WinspIIDataProcessing software.

RESULTS AND DISCUSSION

Figures 1 and 2 show the surface morphologies of the spherical catalysts NiO/SiO₂ and Fe₂O₃/SiO₂. It is believed that the nature of the support played a key role in the production of the highly dispersed particles of NiO/SiO₂ and Fe₂O₃/SiO₂. The supported salts of iron and nickel are evenly distributed over the external surface of the microspherical silicon-containing carrier. It was found [5–8] that the catalysts that are introduced into a process in the form of highly dispersed particles evenly distributed in the entire volume of a raw material are more effective in hydrocarbon conversion processes. The applicability of these particles to catalysis is determined by their chemical activity, which is proportional to the specific surface area of a

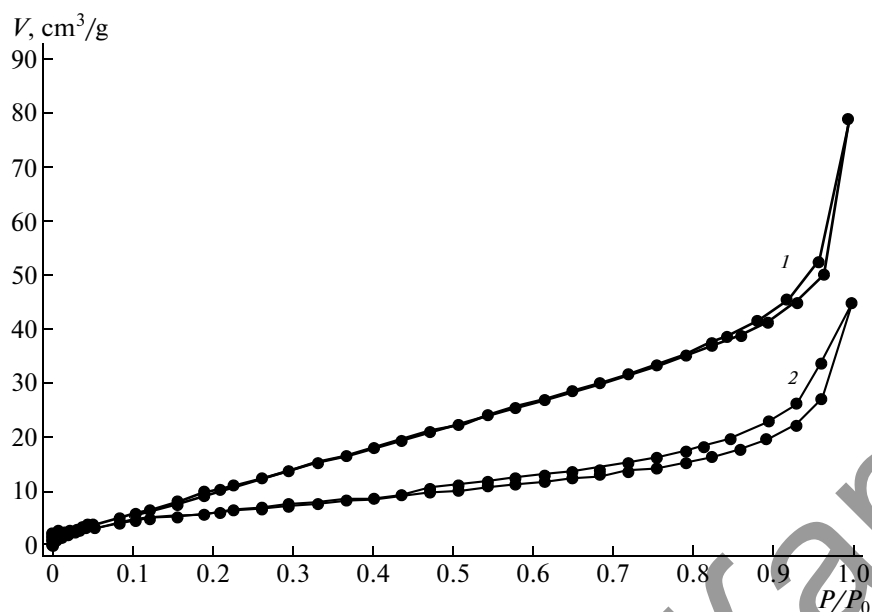


Fig. 3. Isotherms of nitrogen adsorption on the spherical catalysts (1) $\text{Fe}_2\text{O}_3/\text{SiO}_2$ and (2) NiO/SiO_2 .

catalyst. Note that, for increasing the activity of catalysts, it is required not only to simply increase the internal surface but also to develop a specific porous structure of catalyst grains, which is responsible for a sufficient rate of the supply of reactants to the most distant parts of the internal surface from the periphery of a grain and the removal of reaction products from them. For each catalytic process, the optimum porous structure that ensures a maximum reaction rate can be determined depending on process conditions, reaction kinetics, and the specific catalytic activity of the catalyst [9]. Many properties of catalysts depend on their sizes and porous structures; therefore, the activity and selectivity of a nanocatalyst can be controlled by changing them.

The analysis of the isotherms of nitrogen adsorption on the spherical catalysts showed that they contained pores of different sizes (Fig. 3). The shapes of hysteresis loops obtained in the isotherms (curves 1, 2) can be attributed to intermediates between H3 and H4 types, which indicate the presence of microporosity. Adsorption for this type of isotherms is composed of

adsorption in micropores and capillary condensation in mesopores [10].

Table 1 summarizes the porous structure parameters of the spherical catalysts $\text{Fe}_2\text{O}_3/\text{SiO}_2$ and NiO/SiO_2 determined based on the data of the adsorption isotherms of nitrogen.

According to the data of Table 1, the spherical catalysts $\text{Fe}_2\text{O}_3/\text{SiO}_2$ and NiO/SiO_2 can be attributed to mesoporous substances with small micropore contents (1.09 and 7.4%, respectively). In this case, pores with a diameter of 18–27 nm for $\text{Fe}_2\text{O}_3/\text{SiO}_2$ or 18–19 nm for NiO/SiO_2 were responsible for the main mesopore volume (Fig. 4).

Hydrogenation of anthracene in the presence of the nanocatalysts $\beta\text{-FeOOH}$, $\text{Fe}(\text{OA})_3$, and Fe_3O_4 . On the hydrogenation of anthracene in the presence of the nanocatalyst Fe_3O_4 , the yield of hydrogenation products reached a maximum of 84.65%. In the case of hydrogenation with the use of the nanocatalysts $\beta\text{-FeOOH}$ and $\text{Fe}(\text{OA})_3$, the yields of hydrogenation products were 75.38 and 79.09%, respectively. The yields of degradation products in the presence of the

Table 1. Main characteristics of the porous structure of the spherical catalysts $\text{Fe}_2\text{O}_3/\text{SiO}_2$ and NiO/SiO_2

Catalyst	S_{sp} , m^2/g	Total pore volume, cm^3/g	R , nm	Relative pore content, %	
				micropores <2 nm	mesopores 2–50 nm
NiO/SiO_2	42.8043	0.11878	0.85–27.9	7.4	92.6
$\text{Fe}_2\text{O}_3/\text{SiO}_2$	22.5666	0.06111	0.88–29.7	1.09	98.91

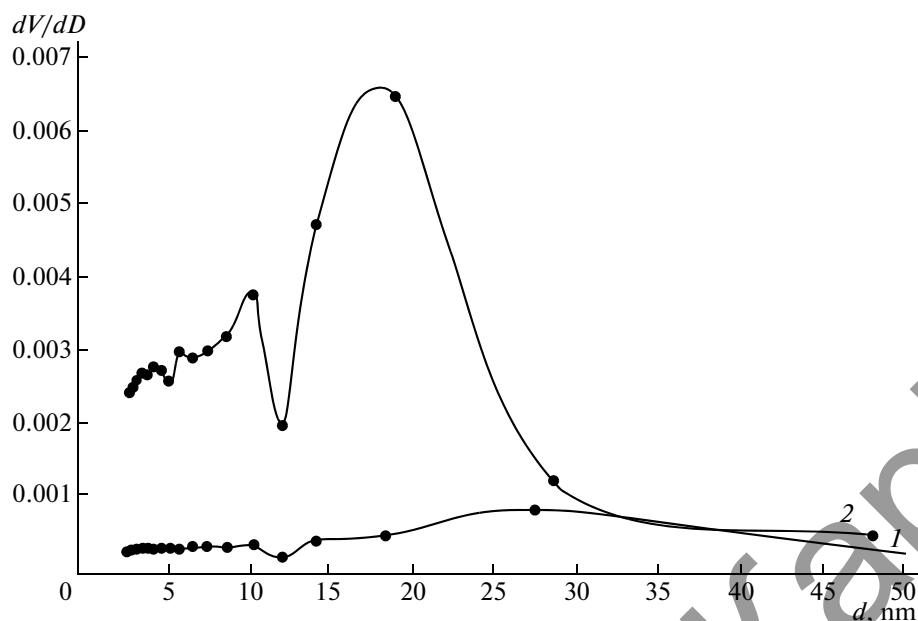


Fig. 4. Mesopore diameter distribution curves of the spherical catalysts (1) $\text{Fe}_2\text{O}_3/\text{SiO}_2$ and (2) NiO/SiO_2 .

nanocatalysts $\beta\text{-FeOOH}$, $\text{Fe}(\text{OA})_3$, and Fe_3O_4 were 24.11, 14.32, and 9.87%, respectively (Table 2).

A comparison between the results showed a significant change in the ratio between the products of hydrogenation and hydrogenolysis and, in general, the degree of conversion. Among all of the test nanocatalysts, the nanocatalyst $\beta\text{-FeOOH}$ was most effective in terms of the yield of hydrogenolysis products and the amount of unreacted substances; the nanocatalyst Fe_3O_4 was considered most effective in terms of the yield of hydrogenation products (Fig. 5).

Hydrogenation of anthracene in the presence of the spherical catalysts NiO/SiO_2 and $\text{Fe}_2\text{O}_3/\text{SiO}_2$. Table 3 summarizes the yields of the products of anthracene hydrogenation in the presence of the spherical cata-

lysts NiO/SiO_2 and $\text{Fe}_2\text{O}_3/\text{SiO}_2$ at temperatures of 300 and 400°C.

On the hydrogenation of anthracene at a temperature of 300°C in the presence of the spherical catalysts NiO/SiO_2 and $\text{Fe}_2\text{O}_3/\text{SiO}_2$, the yields of hydrogenation products were approximately 98% in both cases. It is necessary to note that the synthesized spherical catalysts NiO/SiO_2 and $\text{Fe}_2\text{O}_3/\text{SiO}_2$ at 300°C facilitated the selective hydrogenation of anthracene to 9,10-dihydroanthracene and 1,2,3,4-tetrahydroanthracene.

Upon the hydrogenation of anthracene (400°C) in the presence of the spherical catalysts NiO/SiO_2 and $\text{Fe}_2\text{O}_3/\text{SiO}_2$, the yields of degradation products were 25.49 and 11.56%, respectively. According to these data, it is possible to conclude that the spherical catalysts NiO/SiO_2 and $\text{Fe}_2\text{O}_3/\text{SiO}_2$ make it possible to

Table 2. Yields of the products of anthracene hydrogenation in the presence of the nanocatalysts $\beta\text{-FeOOH}$, $\text{Fe}(\text{OA})_3$, and Fe_3O_4 (wt %)

Compound	Catalyst		
	$\beta\text{-FeOOH}$	$\text{Fe}(\text{OA})_3$	Fe_3O_4
Naphthalene	2.15	2.43	2.7
1-Butylnaphthalene	20.93	11.04	5.5
2-Ethylbiphenyl	1.03	0.85	2
1,2,3,4-Tetrahydroanthracene	59.4	55.55	7.3
9,10-Dihydroanthracene	15.98	23.54	77.12
Anthracene	0.51	6.21	5.4
Degree of conversion	99.49	93.41	94.62

Yield of products, %

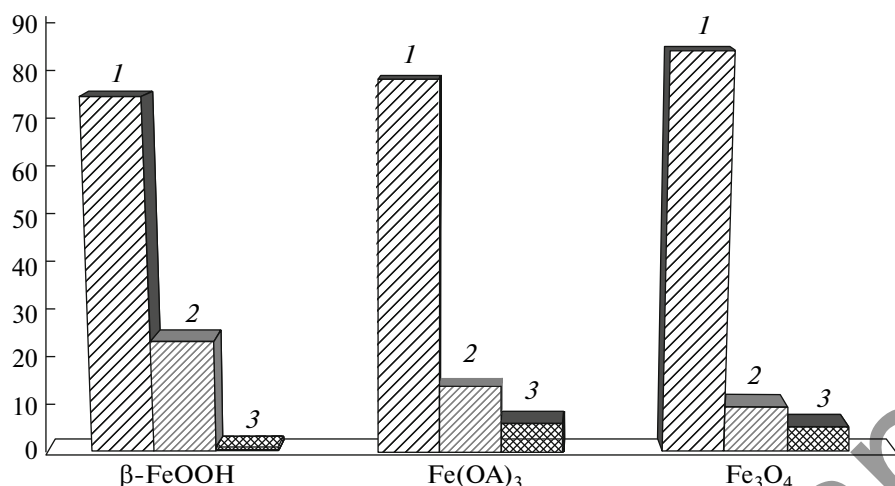


Fig. 5. Ratios between the products of hydrogenation and hydrogenolysis in the presence of the nanocatalysts β -FeOOH, Fe(OA)₃, and Fe₃O₄: (1) hydrogenation products, (2) degradation products, and (3) unreacted substances.

control the yields of the products of hydrogenation or destruction depending on temperature.

For comparison, note that Sharypov et al. [11], who performed the hydrogenation of anthracene in the presence of a commercial cobalt–molybdenum catalyst from the Ryazan Refinery at 430°C, did almost not observe the degradation of hydrocarbons because of the lower activity of the catalyst used. The hydrogenation products had the following composition: dihydroanthracene, 27.2%; tetrahydroanthracene, 65.7%; and octahydroanthracene, 7.1%. The high yield of hydrogenation products in the process of anthracene hydrogenation the presence of the spherical systems can be assumed due to the catalytic action related to the occurrence of the stepwise hydrogenation of anthracene to di- and tetrahydroanthracene; then, the cyclohexane rings of tetrahydroanthracenes are hydroisomerized and cracked to naphthalenes [12].

CONCLUSIONS

We evaluated the effects of the nanocatalysts β -FeOOH, Fe(OA)₃, and Fe₃O₄ and the spherical catalysts NiO/SiO₂ and Fe₂O₃/SiO₂ on the process of anthracene hydrogenation.

Based on the data on the adsorption isotherms of nitrogen and the surface morphology of spherical catalysts, we found that the spherical catalysts Fe₂O₃/SiO₂ and NiO/SiO₂ have almost an ideal spherical shape, and they can be attributed to mesoporous materials. In this case, pores with a diameter of 18–27 nm (Fe₂O₃/SiO₂) or 18–19 nm (NiO/SiO₂) are responsible for the main mesopore volume. The applicability of the spherical catalysts NiO/SiO₂ and Fe₂O₃/SiO₂ to the hydrogenation of model polycyclic hydrocarbons is related to chemical activity, which depends on the specific surface area, high dispersity, and porous structure of these catalytic systems.

Table 3. Yields of products upon the hydrogenation of anthracene in the presence of the spherical catalysts NiO/SiO₂ and Fe₂O₃/SiO₂ (wt %)

Compound	Catalyst			
	NiO/SiO ₂		Fe ₂ O ₃ /SiO ₂	
	300°C	400°C	300°C	400°C
1-Methylnaphthalene	1.68	0.71	—	8.22
1,6-Dimethylnaphthalene	0.11	24.78	—	4.34
1,2,3,4-Tetrahydroanthracene	65.48	0.18	88.72	86.47
9,10-Dihydroanthracene	32.73	69.48	10.26	—
Anthracene	—	0.74	1.02	0.1
Degree of conversion	100	95.15	98.98	99.03

We found that the spherical catalysts NiO/SiO₂ and Fe₂O₃/SiO₂ contribute to an increase in the rate of formation of hydrogenated anthracene derivatives, predominantly, 9,10-dihydroanthracene and 1,2-tetrahydroanthracene, in the process of anthracene hydrogenation at 300°C; at 400°C, they contribute to the formation of degradation products.

In the case of the use of the nanocatalytic systems, β-FeOOH is the most effective nanocatalyst of all of the test nanocatalysts in terms of the yield of hydrogenolysis products; the nanocatalyst Fe₃O₄ is most effective in terms of the yield of hydrogenation products.

Based on the results of the experiments, we can conclude that the nanosized and spherical catalysts are the new developed catalytic systems that facilitate the deeper chemical modification of model polyaromatic hydrocarbons.

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