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Catalytic Hydrogenation of a Model Mixture of Anthracene and Phenanthrene

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Abstract—The results of a study on the hydrogenation of a mixture of anthracene and phenanthrene in the presence of nanocatalysts (Fe_3O_4 and β-FeOOH) and catalytic additives (microspheres obtained from the ash of coals from the Republic of Kazakhstan and nickel and cobalt additives supported on the microspheres) are presented. The efficiency of a wet mixing method for the preparation of nickel and cobalt oxide catalytic additives on the microspheres in the process of the hydrogenation of a mixture of anthracene and phenanthrene was shown. The hydrogenation process of a mixture of polyaromatic hydrocarbons was represented as a combination of hydrogenation and destruction reactions. The individual chemical composition of the hydrogenation products of a mixture of anthracene and phenanthrene was investigated. The activity and selectivity of the catalysts and catalytic additives in the hydrogenation process of a mixture of polyaromatic hydrocarbons were established.

Keywords: polyaromatic hydrocarbons, anthracene, phenanthrene, catalytic hydrogenation
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In the context of increasing demand for petroleum products, a search for new approaches to the production of various types of liquid fuels is of considerable current interest. Therefore, special attention is paid to a study of the conversion of individual polyaromatic hydrocarbons and their mixtures, which simulate organic matter, in an atmosphere of hydrogen along with the development of the theory and technology of the hydrogenation of solid and heavy hydrocarbon raw materials and the establishment of principles for managing this process.

In order to make aromatic compounds the components of commercial products, they should be partially decomposed; as applied to polycyclic aromatic structures, this decomposition includes partial hydrogenation and the subsequent destruction of hydrogenated rings in the presence of catalysts, which are often responsible for not only reaction mechanisms but also the possibility of their occurrence. In this regard, it is difficult to separate the effects of the chemical structure of clusters on their reactivity in hydrogenation and destruction processes and the influence of the nature of catalysts [1].

The aim of this work was to study the dependence of the reactivity of a mixture of model compounds (anthracene and phenanthrene) in the process of destructive hydrogenation in the presence of nanocatalysts and catalytic additives and to evaluate their selectivity and activity in hydrogenation and destruction reactions.

EXPERIMENTAL

For the experiments, the polycyclic hydrocarbons anthracene (chemically pure) and phenanthrene (chemically pure) in a ratio of 1 : 1 were used as model compounds, Fe_3O_4 [2] and β-FeOOH [3] were used as nanocatalysts, and microspheres obtained from the ash of coals from the Republic of Kazakhstan and supported on the surface of the microspheres of nickel and cobalt salts by a wet mixing method were used as catalytic additives.

It was noted that microspheres, which are the main component of coal ash characterized by potential added value, can be used in many industrial processes due to unique properties, such as high thermal stabil-

Table 1. Chemical composition of microspheres and nickel and cobalt salts supported on the microspheres

Individual chemical composition	Substance concentration, wt %		
	microsphere	NiO/microsphere	CoO/microsphere
SiO_2	56.92	26.35	26.11
Al_2O_3	35.96	19.55	18.86
Fe_2O_3	2.97	2.28	4.05
CaO	0.78	1.06	1.03
MgO	1.25	1.93	0.48
K_2O	0.83	0.42	0.48
Na_2O	0.92	0.31	0.37
P_2O_5	0.09	0.08	0.06
MnO	0.04	0.06	0.06
TiO_2	1.72	0.93	0.92
NiO	–	47.03	–
CoO	–	–	47.58

Table 2. Experimental process conditions for the hydrogenation of a mixture of anthracene (0.5 g) and phenanthrene (0.5 g)

Experiment no.	Catalyst concentration, wt %					*T*, °C	*P*, MPa	τ, min
	Fe_3O_4	β-FeOOH	microsphere	NiO/microsphere	CoO/microsphere			
1	–	–	–	–	–	420	3.0	60
2	1	–	–	–	–	420	3.0	60
3	–	1	–	–	–	420	3.0	60
4	–	–	1	–	–	420	3.0	60
5	–	–	–	1	–	420	3.0	60
6	–	–	–	–	1	420	3.0	60

ity, processability, and strength. Ranjbar and Kuenzel [4] considered the formation of microspheres and their characterization and extraction from ash.

The individual chemical composition of the microspheres used as a catalytic additive and as a substrate for applying the solutions of nickel and cobalt salts was determined according to GOST [State Standard] 10538-87 (Table 1).

The use of catalysts on supports with a uniform distribution of the active phase throughout the sorbent decreased the consumption of active components and increased the activity of the catalysts [5]. One of the conditions for the preparation of a catalyst with a constant chemical composition of the active center is the transfer of activating additives from a solution to the surface of insoluble oxides and their uniform distribution on the surface. Nickel and cobalt salts were supported onto the microspheres by a wet mixing method; for this purpose, 20% aqueous solutions of nickel and cobalt sulfates were used (the weight ratio between the salts and microspheres before calcination was 2 : 1). The mixture was thoroughly stirred; after the formation of a thick mass, it was dried in a drying oven at 105°C. The samples obtained were subjected to heat treatment in a muffle furnace for 2 h at 500°C.

Figure 1 shows the micrographs of the surfaces of microspheres and nickel and cobalt catalytic additives on the microspheres obtained with an MIRA3 TESCAN electron microscope. It can be seen that there were micropores with a size of 200–400 nm and irregularities on the microsphere surface.

The particle sizes of the microspheres and nickel and cobalt salts on the microspheres (Fig. 2) were determined using a Zetasizer Nano S90 laser particle-size meter and the DTS Zetasizer Nano software.

According to the particle-size measurement data, the average diameters of NiO/microsphere and CoO/microsphere particles were 2.82 and 3.67 μm, respectively, and the average particle size of the microspheres was 17.8 μm.

The mixture of anthracene and phenanthrene was hydrogenated in a 0.05-L autoclave with an internal stirrer (manufactured in the People's Republic of China) at an initial hydrogen pressure of 3.0 MPa and

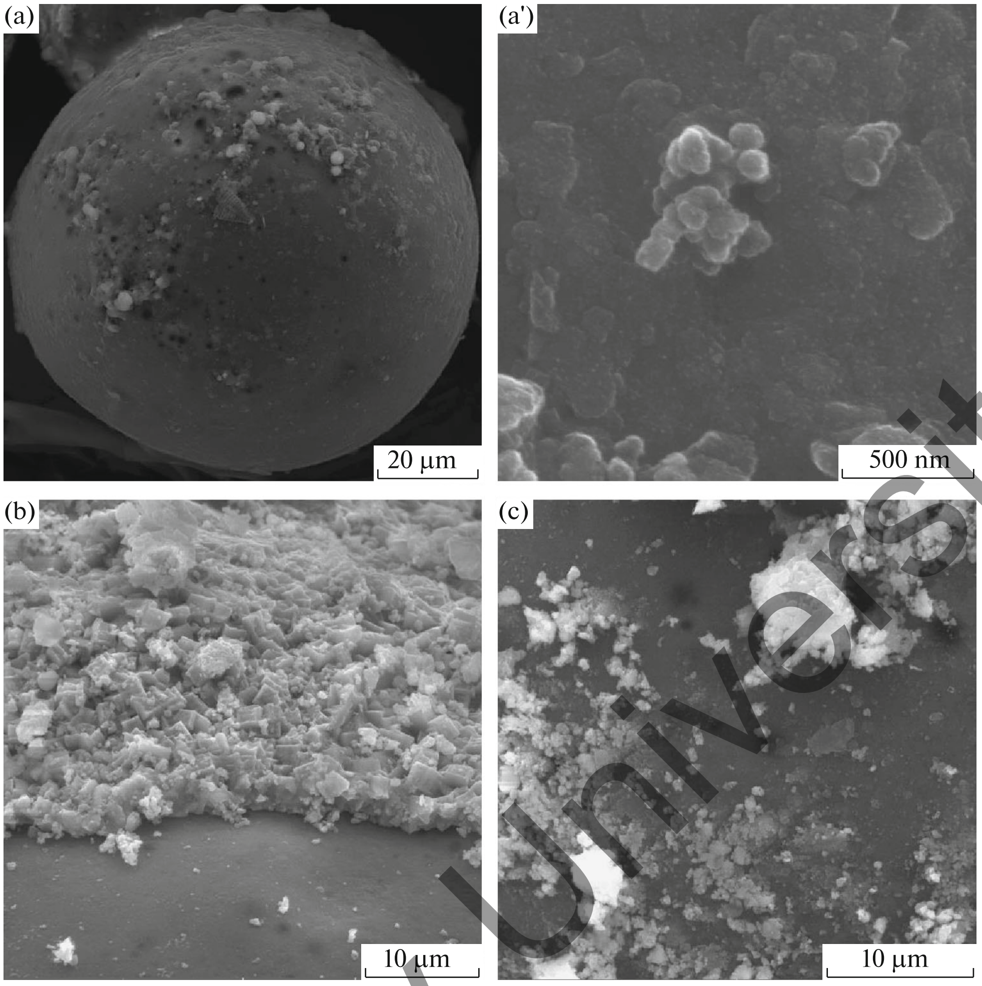


Fig. 1. Micrographs of the surfaces of catalytic additives: (a) microsphere (20 μm), (a') microsphere (500 nm), (b) NiO/microsphere, and (c) CoO/microsphere.

a temperature of 420°C for 60 min. The beginning of the reaction was considered at the point in time when the autoclave temperature reached 420°C and the pressure was 12.0 MPa. The weight concentration of nanocatalysts and catalytic additives in the mixture was 1.0% on an initial basis (Table 2).

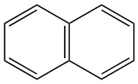
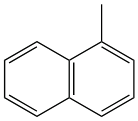
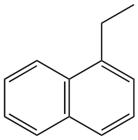
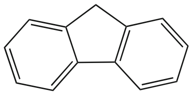
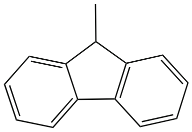
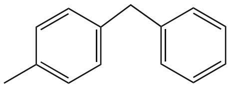
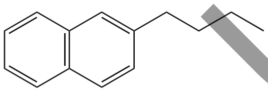
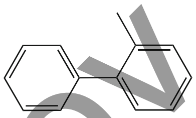
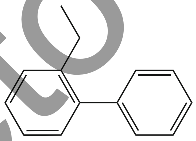
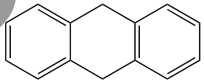
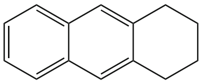
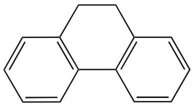
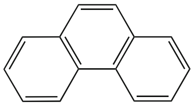
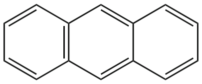
The mixture was preliminarily stirred, and the prepared mass was loaded in the autoclave. The reactor was purged with hydrogen, and the gas was pressurized. Then, the reactor was heated to a required temperature and maintained for a specified time. The heating rate of the autoclave was 10 K/min. After the experiment, the autoclave was cooled to room temperature, and the reaction mixture was dissolved in benzene. The composition of the reaction products was determined by gas chromatography–mass spectrometry (GC–MS) on an Agilent Technologies 7890A gas chromatograph with a 5975C mass-spectrometric detector and on a Kristallyuks 4000M chromatograph with FID/TID/ECD.

Figure 3 shows a chromatogram of the hydrogenation products of the model mixture in the presence of a Fe_3O_4 nanocatalyst.

RESULTS AND DISCUSSION

The results of studies on the hydrogenation of the model mixtures of anthracene–benzothiophene [6], anthracene–benzothiophene–biphenyl [7], and anthracene–benzothiophene–biphenyl–phenanthrene [8] in the presence of various catalytic additives were reported previously. An analysis of the literature data showed that, on the hydrogenation of the model mixtures of polyaromatic compounds, a ratio between the products of hydrogenation and hydrogenolysis and the degree of conversion are primarily influenced by their structures. For example, in the case of the hydrogenation of a two-component model mixture of anthracene–benzothiophene without a catalyst, the concentration of unreacted substances was 23% [6], and the hydrogenation of a four-component mixture without a catalyst

Table 3. Yields of the hydrogenation products of anthracene and phenanthrene

Compound	Structural formula	Yield of hydrogenation products, wt %	
		anthracene, Ni_{sph} catalyst*	phenanthrene, NiO/SiO_2 catalytic additive **
Naphthalene		0.58	0.14
1-Methylnaphthalene		1.93	0.11
1-Ethylnaphthalene		2.10	–
Fluorine		–	0.98
9-Methyl-9*H*-fluorene		–	0.42
1-Methyl-4-phenylmethylbenzene		2.85	–
2-Butylnaphthalene		0.99	–
2-Methyl-1,1'-biphenyl		2.61	–
2-Ethylbiphenyl		8.71	–
9,10-Dihydroanthracene		13.20	0.41
1,2,3,4-Tetrahydroanthracene		13.10	–
9,10-Dihydrophenanthrene		–	4.50
Phenanthrene		0.64	83.10
Anthracene		39.90	8.80

* Nanospheric catalyst obtained by an electrochemical method upon the reduction of $NiSO_4$.

** Catalytic additive prepared by a sol–gel method.

Table 4. Yield of reaction products under the conditions of hydrogenation of a model mixture of anthracene and phenanthrene (experiment numbers are specified in Table 2)

	Compound	Concentration, wt %					
		with no catalyst	Fe_3O_4	β-FeOOH	microsphere	NiO/microsphere	CoO/microsphere
1	Naphthalene	–	–	–	–	–	0.98
2	2-Methylnaphthalene	–	–	–	1.80	3.53	2.63
3	1,7-Dimethylnaphthalene	–	–	–	–	7.67	5.96
4	2-Ethylnaphthalene	–	–	–	3.02	–	–
5	2-Butylnaphthalene	1.06	–	–	–	2.50	4.18
6	1-Methyl-4-phenylmethylbenzene	3.27	1.40	2.79	5.25	11.42	15.49
7	Fluorine	–	–	–	1.62	3.78	4.73
8	9-Methyl-9H-fluorene	–	–	–	–	–	2.90
9	Diphenylmethane	–	–	–	–	–	1.29
10	2-Methyl-1,1'-biphenyl	–	–	–	1.65	4.01	3.07
11	2-Ethyl-1,1'-biphenyl	1.80	–	1.53	2.17	7.61	10.39
12	9,10-Dihydroanthracene	14.65	23.72	18.46	13.29	22.66	32.65
13	9,10-Dihydrophenanthrene	3.10	1.73	3.39	2.64	–	–
14	1,2,3,4-Tetrahydroanthracene	11.58	12.28	13.47	9.21	–	6.20
15	1,2,3,4-Tetrahydrophenanthrene	–	–	–	–	15.98	2.04
16	Anthracene	12.81	18.96	12.63	10.73	3.94	1.32
17	Phenanthrene	51.31	41.92	47.74	48.60	16.81	6.15

exhibited a high degree of conversion of polyaromatic hydrocarbons [8].

The results of the hydrogenation process of two-, three-, and four-component mixtures of polyaromatic hydrocarbons in the presence of heterogeneous and pseudohomogeneous catalysts reported previously [6–8] showed that the consumption of catalysts varied from 2 to 5%. This optimal amount makes it possible to increase the yield of active atomic hydrogen, which interferes with condensation reactions and lowers the stability of associates, in the course of the hydrogenation of polyaromatic hydrocarbons, and the synthesized β-FeOOH nanocatalyst [3] is superior to the nanocatalysts and catalytic additives described in the literature in terms of activity and selectivity at a consumption of no higher than 1%.

Previously, Gudun et al. [9] performed the hydrogenation of individual anthracene and phenanthrene under the following conditions: $T = 380°C$, $P = 3.0$ MPa, $\tau = 120$ min, and a catalyst amount of 1.0 wt %. Table 3 summarizes the yields of hydrogenation products.

In the study of the hydrogenation of the individual model compounds, it was found that the conversion of anthracene was greater than that of phenanthrene; the latter was isomerized into anthracene to a greater degree than in anthracene isomerization into phenanthrene, and another isomerization product, 9-methyl-9*H*-fluorene (0.42%), was formed upon the hydrogenation of phenanthrene.

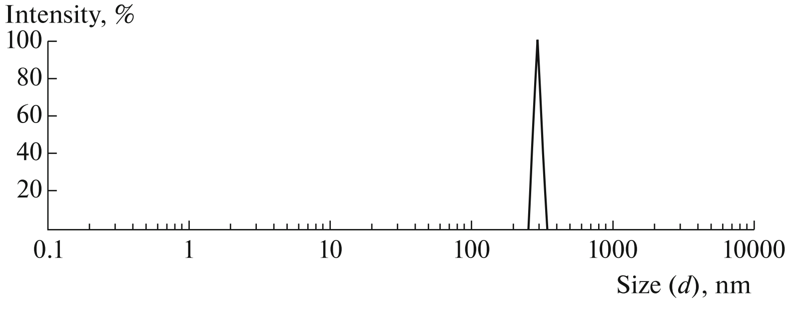


Fig. 2. Size and distribution of particles in a solution of the CoO/microsphere catalytic additive.

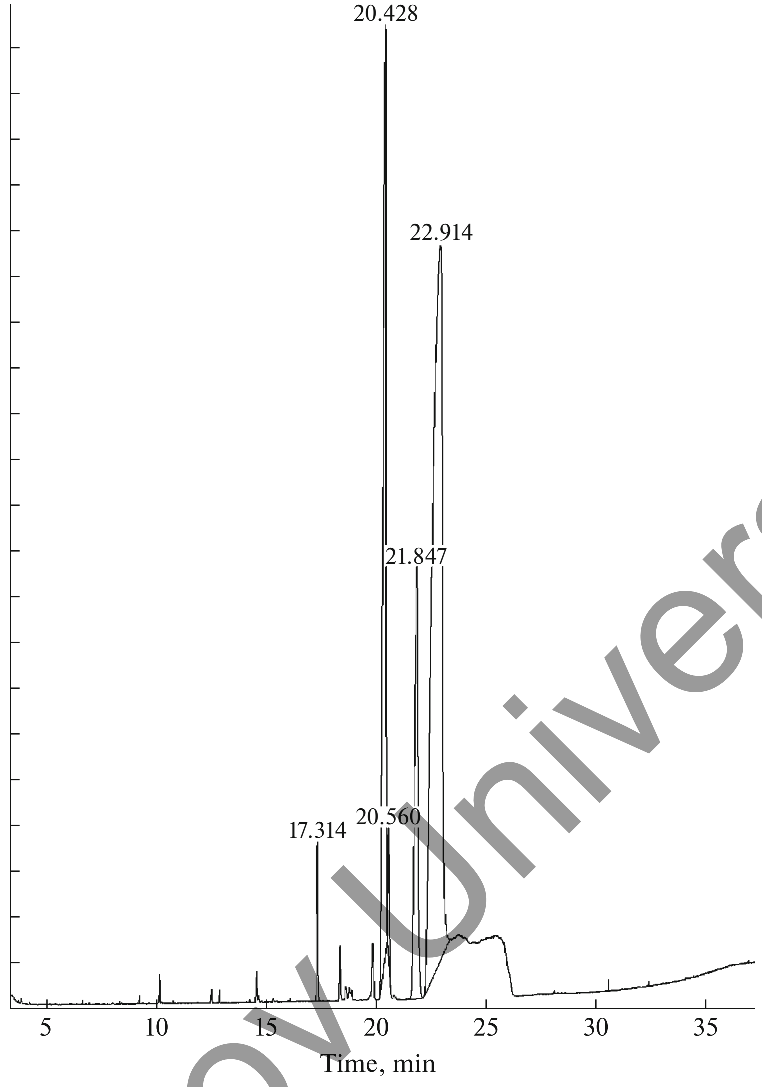


Fig. 3. Chromatogram of the hydrogenation products of a mixture of anthracene and phenanthrene in the presence of a Fe_3O_4 nanocatalyst.

Table 4 summarizes the chemical composition of the products of the catalytic hydrogenation of a mixture of anthracene and phenanthrene.

The fact that the electronic structure of a molecule plays an important role in the process of hydrogenation follows from the fact that isomers with different arrangements of substituents differ significantly in reactivity. The linear and angular structures of anthracene and phenanthrene, respectively, not only characterize the stability of the entire molecules as a whole but also indicate reactive positions in the ground state to explain the stability of phenanthrene and its noticeable reactivity in the 9- and 10-positions (Table 3).

The isomerization of six-membered rings into five-membered ones was observed along with cleavage and hydrogenation reactions during the conversion of a mixture of polyaromatic hydrocarbons in the presence of catalysts and catalytic additives. Figure 4 shows a schematic diagram of the hydrogenation of a mixture of anthracene and phenanthrene according to the data obtained by the GC–MS analysis of the reaction products.

It is well known that the hydrogenation of anthracene and phenanthrene proceeds stepwise with the formation of hydrogenation products (hydroanthracenes and hydrophenanthrenes) and destruction products (biphenyls and naphthalenes). According to the above schematic diagram, hydrogenation initially occurs; then, 9,10-dihydrophenanthrene is isomerized into 9-methyl-9*H*-fluorene and, possibly, 9,10-dihydroanthracene. Fluorene is further cleaved into biphenyl and its derivatives; the tetrahydro derivatives of anthracene and phenanthrene are cleaved to naphthalene and naphthalene derivatives.

A comparison between the results of the separate hydrogenation of polyaromatic hydrocarbons (anthra-

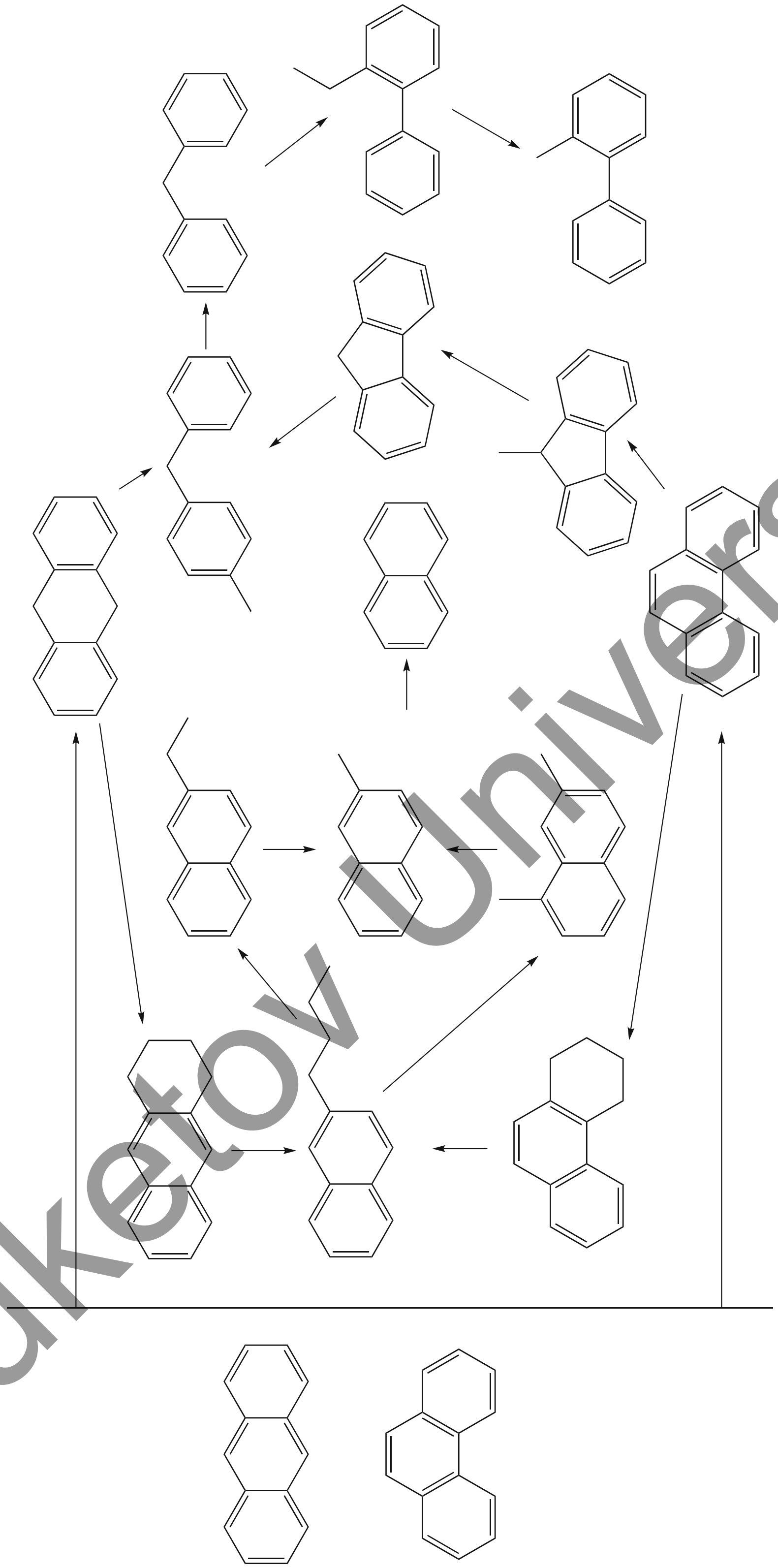


Fig. 4. Schematic diagram of the conversion of a mixture of anthracene and phenanthrene on hydrogenation.

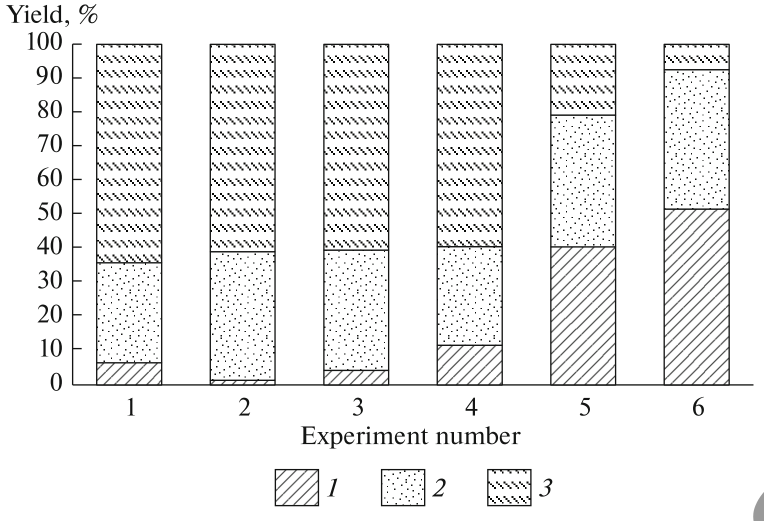


Fig. 5. Yield of reaction products obtained without a catalyst and in the presence of various catalysts and catalytic additives: (*1*) degradation products, (*2*) hydrogenation products, and (*3*) unreacted substances (see Tables 2 and 4 for experiment numbers).

cene and phenanthrene) suggests that the phenanthrene is a source of fluorene in the hydrogenation products of the mixture. An insignificant amount of 9-methyl-9*H*-fluorene formed upon the hydrogenation of the mixture in the presence of a CoO/microsphere catalytic additive is an isomerization product of the hydro derivatives of phenanthrene.

Meiramov [5] described the angular–linear isomerization of 9,10-dihydrophenanthrene and 1,2,3,4-tetrahydrophenanthrene into 9,10-dihydroanthracene and 1,2,3,4-tetrahydroanthracene, respectively. Further, dihydro- and tetrahydroanthracene are dehydrogenated to form anthracene.

In the course of the hydrogenation of the mixture, the cleavage of hydro derivatives and partial dehydrogenation occur. The hydro derivatives of polyaromatic hydrocarbons act as hydrogen donors [10]. Because anthracene is more easily hydrogenated than phenanthrene, we can conclude that phenanthrene is well hydrogenated in the presence of NiO/microsphere (38.6%) and CoO/microsphere (40.9%) catalytic additives, and the hydro derivatives of phenanthrene give the hydro derivatives of anthracene as isomerization products. Table 4 indicates that the NiO/microsphere and CoO/microsphere catalytic additives are more active and selective in the hydrogenation process of a mixture of polyaromatic hydrocarbons than the Fe_3O_4 and β-FeOOH nanocatalysts and a catalytic additive in the form of microspheres. Figure 5 illustrates the experimental results obtained in the hydrogenation and hydrogenolysis reactions of a mixture of polyaromatic hydrocarbons.

In the process of hydrogenation of a mixture of polyaromatic hydrocarbons without a catalyst and a catalytic additive, the yield of cleavage products was 6.5%, and the yield of hydrogenation products was 29.3%. At the same time, more than 64% of the substance remained unreacted, including 51.3% phenanthrene and 12.8% anthracene.

The experimental results of the hydrogenation of a mixture of anthracene and phenanthrene with the use of Fe_3O_4 as a nanocatalyst showed that hydrogenation products predominated in significant amounts; in this case, the concentration of hydrogenation products was 37.7%, whereas the concentration of cleavage products was only 1.4% (Fig. 5).

From the results of an analysis of experiments on the hydrogenation of the mixture in the presence of β-FeOOH, it follows that the amount of hydrogenation products (35.3%) in the reaction products was greater than the amount of cleavage products (4.3%). The addition of Fe_3O_4 and β-FeOOH nanocatalysts to the system led to an increase in the hydrogenation products and a decrease in the degradation products, as compared with those in the hydrogenation process of the mixture performed without catalysts and catalytic additives.

Upon the addition of microspheres as a catalytic additive to the mixture, the yield of degradation products was 11.7%, and the yield of hydrogenation products remained almost unchanged and amounted to 29% compared to the yield of hydrogenation products upon the hydrogenation of the mixture without a catalyst.

In the case of a nickel catalytic additive, the ratio between the concentrations of degradation and hydrogenation products in the reaction product was closer to 1 : 1 (40.5 and 38.6%, respectively), and the amount of degradation products was 10% higher in the case of a cobalt catalytic additive.

The study of the effects of nanocatalysts and catalytic additives on the hydrogenation of a mixture of anthracene and phenanthrene allowed us to construct the following order of efficiency of the nanocatalysts and nanocatalytic additives: CoO/microsphere > NiO/microsphere > microsphere > β-FeOOH ≈ Fe_3O_4.

The effect of nickel and cobalt catalytic additives on the high conversion of phenanthrene in the mixture into the products of hydrogenation and hydrogenolysis and an increase in the donor ability of the hydro derivatives of anthracene should be noted. It is likely that the sizes of nickel and cobalt nanoparticles influence the activity and selectivity of the nickel and cobalt catalytic additives.

CONCLUSIONS

Thus, iron oxide and iron oxyhydroxide are ineffective nanocatalysts for a model mixture of anthracene and phenanthrene with respect to the yield of cleavage products (Table 2, experiment nos. 2 and 3).

Note that NiO/microsphere and CoO/microsphere exhibited high activity as catalytic additives in the hydrogenation of a mixture of anthracene and phenanthrene. The concentration of unreacted products was several times lower than that obtained with the use of other catalysts and catalytic additives or in the hydrogenation carried out without a catalyst or a catalytic additive (Table 2, experiment nos. 5 and 6).

The cobalt catalytic additive was most effective in terms of both the yield of degradation products and the yield of hydrogenation products. Catalytic additives based on cobalt oxide were most selective in the hydrogenolysis reaction of a mixture of anthracene and phenanthrene.

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