

Catalytic Hydrogenation of Anthracene in Ethanol

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Abstract—The results of the hydrogenation of anthracene in ethanol in the presence of different catalysts (the nanosized powders of Fe, Cu, and β -FeOOH and Ni and Fe supported on carbon microspheres) are reported. The greatest catalytic effect was observed upon the introduction of 1.5% Fe nanopowder.

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The main trend in the development of the world oil refining and coal chemistry industry is the introduction of new technologies that make it possible to maximally use crude hydrocarbons (coal, peat, shale, heavy oil, heavy petroleum residue, etc.) for the production of high-quality target products. Current studies are directed toward a search for polyfunctional catalysts characterized by an optimum combination of properties, which ensure a maximum yield of aromatic compounds with lower molecular weights.

In order to study the mechanism of hydrogenation of crude heavy hydrocarbons in the presence of a hydrogen donor and the activity and selectivity of catalysts, we used anthracene as a model substance, which makes it possible to represent the organic matter of coal in terms of fragments. Because a study of the hydrogenation of polycyclic aromatic compounds forms the scientific basis of the process of coal liquefaction and the hydrofining of the resulting liquid products, in this work, we examined the selectivity of catalysts in the hydrogenation of anthracene in ethanol.

EXPERIMENTAL

The following catalytic systems were studied in the process of anthracene hydrogenation: nanosized Cu and Fe powders, spherical Ni and Fe catalysts, and a reference nanocatalyst of β -FeOOH. The nanosized powders were prepared in accordance with a published procedure [1] and introduced in an amount of 1–2% on a raw material basis. The active component was supported onto carbon microspheres, which were separated from fly ash. The microspheres were treated

with a 10% salt solution, dried, and calcined at a temperature of 600°C (60 min). The hydrogenation of anthracene in ethanol was also performed without a catalyst and hydrogen. The highly dispersed iron hydroxide oxide—goethite (β -FeOOH)—was taken as a reference catalyst. The degree of conversion of the raw material was evaluated based on residual anthracene. Ethanol was used as a solvent.

The experiments on the hydrogenation of the model substance were carried out in a high-pressure reactor with a volume of 0.05 L. The initial components (2 g of anthracene and 5 g of ethanol) were preliminarily mixed and then placed in the reactor. The autoclave was closed and purged with hydrogen; an excess pressure of hydrogen to 2.0 MPa was produced. The mixture was heated to a necessary temperature (320°C). The rate of heating was 10 K/min. The duration of an isothermal exposure was 240 min; thereafter, the autoclave was cooled to room temperature, and the liquid products of hydrogenation were analyzed.

The composition of anthracene hydrogenation products was determined by gas chromatography–mass spectrometry (GC–MS) on an HP 5890/3972 MSD instrument from Agilent with a DB-5MS capillary column (30 m \times 0.25 mm \times 0.5 μ m) and by gas–liquid chromatography (GLC) on a Kristallyuks 4000M with a flame ionization detector and a ZB-5 capillary column (30 m \times 0.32 mm \times 0.5 μ m) under temperature programming conditions in a range of 60–300°C with a rate of 15 K/min. The catalysts were studied by electron microscopy on a Mira 3LM instru-

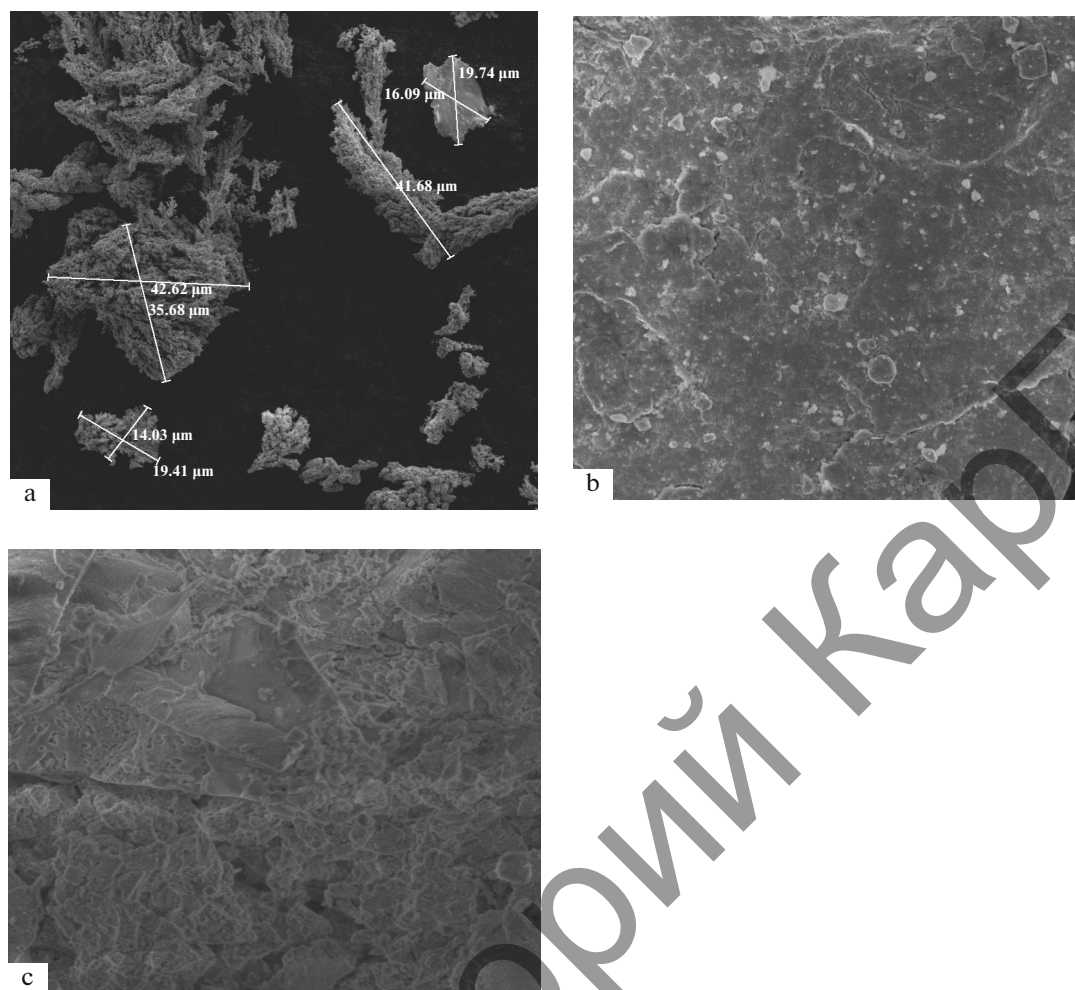


Fig. 1. Micrographs of catalyst surfaces: (a) Cu, (b) Fe, and (c) β -FeOOH.

ment. Figure 1 shows the micrographs of catalyst surfaces.

RESULTS AND DISCUSSION

It is well known that the hydrogenation of anthracene occurs gradually with the formation of hydrogenation (hydroanthracenes) and hydrogenolysis (naphthalenes) products [2]. Initially, the hydrogenation of anthracene to di-, tetra-, and octahydroanthracenes occurs. Then, the cyclohexane rings of hydroanthracenes undergo isomerization to five-membered rings and further cracking to naphthalenes. In turn, the naphthalenes undergo hydrogenation and isomerization; then, one of the rings is cracked to alkylbenzenes. The hydrogenate obtained in the experiment mainly contained alkylaromatic compounds, it also contained hydrogenation and hydrogenolysis products (Table 1).

The ease of hydrogenation increases in the order benzene < toluene < anthracene. The higher rate of hydrogenation of polyarenes, as compared with that of benzene, at a high pressure of hydrogen is explained by

the fact that the fraction of catalyst surface occupied by hydrogen increases with pressure and hydrogen becomes accessible to all shortened bonds. The component compositions of the hydrogenates obtained on different catalysts were qualitatively similar. However, tetrahydronaphthalene appeared in small amounts on a copper catalyst (0.325%) and iron catalysts (2.0% on β -FeOOH and Fe) (Table 1).

It is well known from the literature [3, 4] that low-molecular-weight alcohols exhibit H-donor ability in the process of hydrogenation. The stabilizing role of aliphatic alcohols consists in their ability to interact with active radical centers to prevent their recombination. Stabilization is possible due to both hydrogen atom transfer and hydrogenation. In this case, alcohols are oxidized to corresponding aldehydes or ketones, as confirmed previously [3, 4]. The use of alcohols makes it possible to obtain liquid products in the absence of catalysts and molecular hydrogen; in this context, we carried out the hydrogenation of anthracene under similar conditions.

Table 1. Composition of the products of anthracene hydrogenation in the presence of different catalysts, %

Component	Without catalyst*	Without H ₂	Cu	Ni _{sph}	Fe _{sph}	FeOOH	Fe, 1.0%	Fe, 1.5%	Fe, 2.0%
Naphthalene	1.08	0.77	0.83	0.58	1.15	1.07	0.99	1.52	1.03
Tetrahydronaphthalene	—	—	0.33	—	—	0.09	—	—	0.04
1-Methylnaphthalene	4.10	1.34	1.51	1.93	4.30	4.09	4.15	5.63	3.74
1-Ethylnaphthalene	4.58	1.04	1.80	2.10	4.33	4.68	4.71	6.82	4.38
2,3-Dimethylnaphthalene	0.44	0.17	0.08	0.26	0.49	0.45	0.49	0.36	0.44
2-Ethylnaphthalene	0.42	—	0.19	0.19	0.42	0.48	0.41	0.40	0.40
1-Methyl-2-phenylmethylbenzene	5.07	1.33	2.08	2.85	4.55	4.87	4.94	9.61	5.30
2-Butylnaphthalene	1.39	0.24	1.70	0.99	1.13	1.83	1.31	2.69	1.59
2-Methyl-1,1-biphenyl	5.39	1.47	3.05	2.61	5.26	4.80	5.43	5.54	5.01
2-Ethylbiphenyl	14.10	2.07	6.96	8.71	12.6	13.67	11.85	13.14	14.34
Dihydroanthracene	14.16	10.20	8.29	13.22	13.9	14.45	11.69	19.07	15.76
Octahydroanthracene	0.12	—	0.13	0.11	0.62	0.02	0.10	—	0.03
Tetrahydroanthracene	15.11	2.76	12.8	13.1	12.82	17.16	14.40	24.71	17.34
Phenanthrene	1.22	0.34	0.68	0.64	1.21	0.22	1.06	0.29	1.29
Anthracene	22.67	71.78	49.65	39.91	25.6	18.42	24.88	7.96	18.00
Unidentified products	10.142	6.53	9.92	12.87	11.5	13.7	13.60	2.27	11.32

* Initial hydrogen pressure, 2 MPa.

In the absence of hydrogen (Table 1), the hydrogenation of anthracene occurred weakly: the minimum yields of hydroanthracenes and naphthalenes (products of the deeper hydrocracking of anthracene) were noted, and the formation of anthracene hydrogenation products—hydroanthracenes (probably, due to the internal resources of hydrogen) was observed. Under the conditions of low pressures, the hydrogenation of polyaromatic compounds was hindered, as confirmed by a high yield of anthracene (71.78%) and a low yield of hydroanthracenes. Under these conditions, the degree of conversion of the raw material was the smallest (Fig. 2).

The composition of a gas phase was determined by GC–MS analysis; CH₄, CO₂, C₂H₄, C₂H₆, and C₃H₈ were predominant among the gases of hydrogenation. Light hydrocarbon components were formed as a result of cracking. The presence of CO₂ in the gas phase was, probably, a consequence of the interaction of CO and H₂O, which, in turn, resulted from the destruction of alcohols.

An insignificant contribution of catalysts based on iron (1.0%) to the hydrogenation of anthracene should be noted: the catalytic effect was only a few percents (Fig. 2). This fact indicates that, in principle, hydrogenation can be performed in low-molecular-weight alcohol solvents and in the absence of a catalyst; that is, ethanol hydrogenates multiple bonds in the absence of catalysts. All of the test catalysts were characterized by the formation of phenanthrene in commensurable

amounts (Table 1); this was likely due to isomerization, and the experimental results are indicative of almost the same isomerizing abilities of the test catalysts.

The highest degree of conversion of the raw material was observed for the 1.0% β-FeOOH catalyst, when higher yields of hydrogenation (31.91%) and

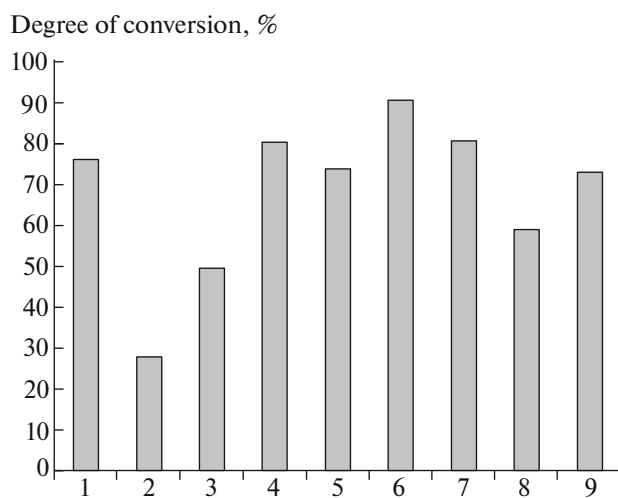


Fig. 2. Effects of catalysts on the degree of anthracene conversion: (1) no catalyst, (2) no hydrogen, (3) 1.0% Cu, (4) 1.0% β-FeOOH, (5) 1.0% Fe, (6) 1.5% Fe, (7) 2.0% Fe, (8) 1.0% Ni_{sph}, and (9) 1.0% Fe_{sph}.

Table 2. Effect of catalysts on the group composition of the hydrogenation products

Catalyst	Components, %				Hydrogenation products, %	Hydrogenolysis products, %	Unidentified products, %
	naphthalenes	hydroanthracenes	anthracene	biphenyls			
Without catalyst	12.02	29.69	22.67	19.49	29.69	36.62	10.42
Without H ₂	3.55	12.94	71.78	3.54	12.94	8.42	6.25
Fe, 1.0%	12.05	26.19	24.88	17.28	26.19	33.29	13.60
Cu, 1.0%	6.15	21.22	49.65	10.0	21.55	17.37	9.92
β-FeOOH	12.59	31.63	18.42	18.47	31.91	34.87	13.70
Fe, 1.5%	17.4	43.78	7.96	18.68	43.77	44.18	2.27
Fe, 2.0%	11.61	33.13	18.0	19.35	33.17	35.20	11.32
Ni _{sph} , 1.0%	6.05	26.38	39.91	11.32	26.38	19.63	12.87
Fe _{sph} , 1.0%	11.82	27.34	25.67	17.9	26.79	33.13	11.50

hydrogenolysis (34.87%) products were observed, as compared with other catalysts taken in an amount of 1.0% or in the absence of catalysts (Table 2). The 1.0% Cu catalyst, which manifested activity in the dehydrogenation of alcohols, exhibited the worst results: a low degree of conversion and low yields of hydrogenation (21.55%) and hydrogenolysis (17.37%) products.

The commensurable amounts of hydrogenation (26.19 and 31.91%, respectively) and hydrogenolysis (33.29 and 34.87%, respectively) products were obtained on the 1.0% Fe and 1.0% β-FeOOH catalysts. The 1.0% β-FeOOH and 2.0% Fe catalysts were characterized by almost identical degrees of conversion of the raw material (Fig. 2), and they manifested similar catalytic activities. Iron nanopowder (1.0% Fe) and 1.0% Fe_{sph} supported on carbon microspheres gave almost identical results of catalysis.

The 1.0% Ni_{sph} catalyst was close to copper nanopowder (1.0%) in terms of catalytic activity (Fig. 2). A high degree of conversion of the raw material was observed upon the introduction of the 1.5% Fe catalyst (92%), when the yields of hydrogenation (43.77%) and hydrogenolysis (44.18%) products increased. On the contrary, the presence of the copper catalyst (1.0%) led to a decrease in the degree of anthracene conversion.

The activity of the catalysts in the hydrogenation of anthracene increased in the order 1.0% Cu < 1.0% Ni_{sph} < 1.0% Fe_{sph} < 1.0% Fe < β-FeOOH < 2.0% Fe < 1.5% Fe.

CONCLUSIONS

Catalytic effect depends on the introduced catalyst amount. The introduction of a catalyst based on iron (1.0%) exhibited an insignificant efficiency. The greatest degree of conversion of the raw material was noted on the nanosized iron catalyst introduced in an amount of 1.5%. The β-FeOOH and 1.0% Fe catalysts were characterized by commensurate catalytic activities in this process. We found that the qualitative composition of liquid products changed insignificantly.

As a result of this study, we demonstrated the H-donor function of ethanol. The gaseous hydrogenation products contained carbon dioxide, which was formed by the interaction of CO and H₂O resulting from the destruction of the alcohol.

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