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Isomerization of Phenols from a Coal Tar Fraction

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Abstract—A new method for the hydrogenation of a primary coal tar fraction in the presence of a nanocatalyst at an elevated pressure in an atmosphere of hydrogen was proposed. The effect of the relative H-donor ability of the primary coal tar fraction on the yields of hydrocarbon fractions to 300°C and the solid residue was studied.

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The oil and gas processing industry and the coal processing industry form the basis of the fuel–energy complex of any state. The study of fuel and chemical raw materials obtained as processing by-products is currently a promising and priority line in petroleum chemistry and power engineering [1].

Current studies in this area showed that coal tar is subjected to dehydration and fractional distillation; phenols, benzene, pyridine bases, naphthalene, and other chemical products are obtained from individual fractions by alkali and acid extraction, crystallization, and hydrofining [2, 3]. Primary coal tar is obtained under the conditions that prevent high-temperature pyrolysis; this makes it possible to use the tar as raw material for industrial organic synthesis, which is of great interest for the production of commercial phenols and hydrogen donors. The primary coal tar obtained in the process of low-temperature carbonization is very similar to the organic matter of the initial coal in terms of structure and the types of functional groups and structural fragments. Coking tar, which mainly consists of polyaromatic hydrocarbons and high-molecular-weight compounds, finds industrial use.

Note that, in the Republic of Kazakhstan and the CIS countries, primary coal tar does not find industrial use for the production of motor fuel and organic substances, including commercial phenols, which pose an environmental problem in the course of thermal processing [4–6].

Highly effective catalysts based on molybdenum salts or disposable unproductive catalysts and a long petroleum distillate, which plays the role of a hydrogen donor, are used in the process of the hydrogenation of primary coal tar and coal [7]. It was found [8, 9] that nanocatalysts are more effective in the process of coal hydrogenation than well-known catalysts: the degree of conversion of the organic matter of coal varied from 15 to 20% in favor of nanocatalysts. It should also be noted that, with the use of disposable iron-containing catalysts, their consumption varied within a range of 5–7%; the hydrogenation of primary coal tar and coal in the case of nanocatalysts can be performed using from 0.5 to 1%. The synthesized nanocatalyst with different particle sizes of iron was tested for activity and selectivity in the processes of the hydrogenation of model organic substances or their mixtures [4, 10].

The effect of the formation of nanocatalytic iron particles with different sizes in the reaction zone makes it possible to improve the extractability of total phenols from the primary coal tar and also to obtain low-molecular-weight organic substances, which can be the sources of the production of motor fuel and the active donors of hydrogen in the hydrogenation of coal or heavy petroleum residues.

Chistyakov [4] studied the hydrogenation of coal tar for the production of crude benzene. However, the hydrogenation processing of primary coal tars for the production of motor fuel and valuable organic substances was not performed. Consequently, it was necessary to study the hydrogen-donor properties of a long coal tar distillate under the action of a β-FeOOH nanocatalyst in hydrogenation processing.

Table 1. Chemical composition of the initial fraction of primary coal tar (water content, 2.5 %; kinematic viscosity, 10.7 P)

Time	Substance	Concentration	Probability
		%	
3.189	Methyl-2-octylcyclopropene-1-octanoate	7.38	87
6.054	*N*-Methylacetamide	1.776	63
6.947	Heptane	7.9	91
7.375	Methylcyclohexane	12.62	91
7.853	*N*,*N*-Dimethylformamide	6.04	86
8.063	Toluene	29.36	95
8.455	2-Methylpropyl acetate	0.693	64
11.230	Phenol	3.83	94
12.587	2-Methylphenol	2.976	97
12.950	4-Methylphenol	8.2	97
14.140	2-Ethylphenol	0.848	94
14.335	3,4-Dimethylphenol	4.004	97
14.690	2-Ethylphenol	6.288	90
15.157	Naphthalene	0.9	94
15.783	2-Ethyl-6-methylphenol	0.94	81
15.975	4-Ethyl-3-methylphenol	1.026	93
16.337	2-Ethyl-4-methylphenol	1.213	64
17.301	2-Methylnaphthalene	1.43	96
17.404	Tridecane	1.042	96
19.098	Tetradecane	0.815	94
20.728	Pentadecane	0.836	96

Table 2. Experimental conditions (reactor volume, 0.02 L)

Experiment number	T, min	T_{set}, °C	P, MPa	Tar, g	Catalyst		Yield, %
					g	%	
1	180	420	3.0	20.00	0.1	0.5	88
2	180	420	3.0	20.00	0.2	1.0	92
3	180	420	3.0	20.00	0.6	3.0	82
4	180	420	3.0	20.00	1.0	5.0	78

EXPERIMENTAL

A coal tar fraction with T_b to 175°C from TOO Sary-Arka Spetskoks (Karaganda, the Republic of Kazakhstan), whose technical characteristics and group composition are given in Table 1, was used as a test material.

The hydrogenation experiments were carried out in an autoclave system; the volume of a chemical reactor was 0.02 L. β-FeOOH, which was synthesized in the Peoples' Republic of China in accordance with a published procedure [4], was used as a nanocatalyst.

The preliminarily dehydrated primary coal tar fraction was subjected to catalytic hydrogenation in an atmosphere of hydrogen with the addition of the nanocatalyst in an amount of 0.5–5%. Table 2 summarizes the process conditions in detail.

The group composition of the hydrocarbon part of the coal tar fraction was studied by gas chromatography–mass spectrometry on an HP 5890/5972 MSD instrument from Agilent (the United States). Chromatographing conditions: column, DB-XLB5, 30 mm × 0.5 μm; carrier gas, helium, 0.8 mL/min; temperature programming, 50°C for 4 min, 50–

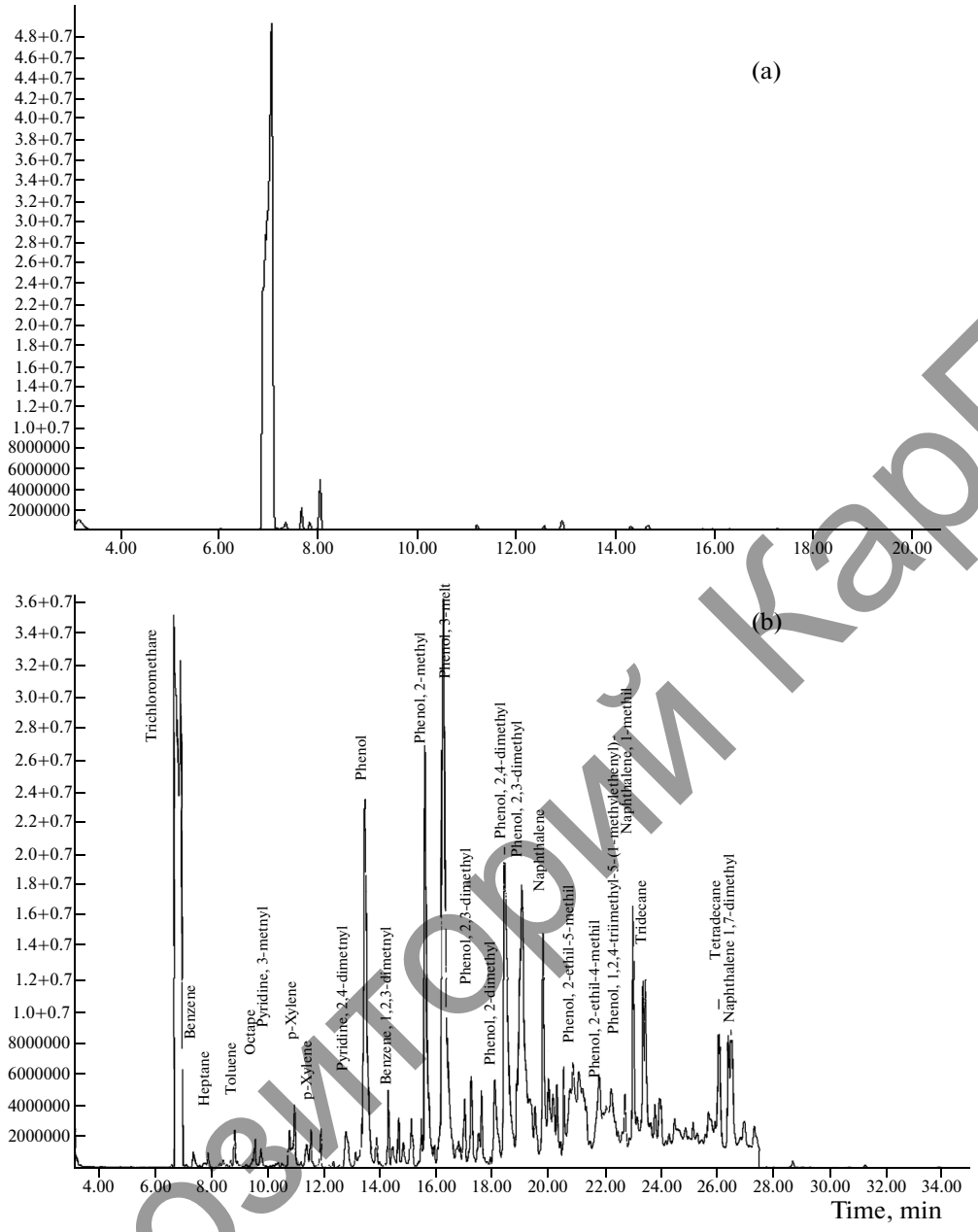

Fig. 1. Chromatograms of (a) the initial tar fraction and (b) the fraction upon its interaction with the nanocatalyst (5%).

150°C at 10 K/min, 150–300°C at 20 K/min, and 300°C for 4 min; injector temperature, 200–300°C. The substances were identified with the use of the NIST 98 mass-spectrometric database.

Figure 1 shows the chromatograms of tar fractions before and after the catalytic hydrogenation.

The surface topography of the β-FeOOH nanocatalyst and the solid residues of hydrogenation was studied 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 scanned in the AC-AFM mode using the Topography method of measurement. The scanned surface area was 20 × 20 μm, and the rate of scanning was 6 μm/s. In the course of scanning, CSC37/AIBS probes from Mikro Masch were used. The images obtained were analyzed with the aid of the Winspll Data Processing software.

RESULTS AND DISCUSSION

The experimental results showed that, at a nanocatalyst particle size of 200 nm, the catalyst activity per unit weight of the primary coal tar fraction noticeably increased. Comparing the behavior of the nanosized

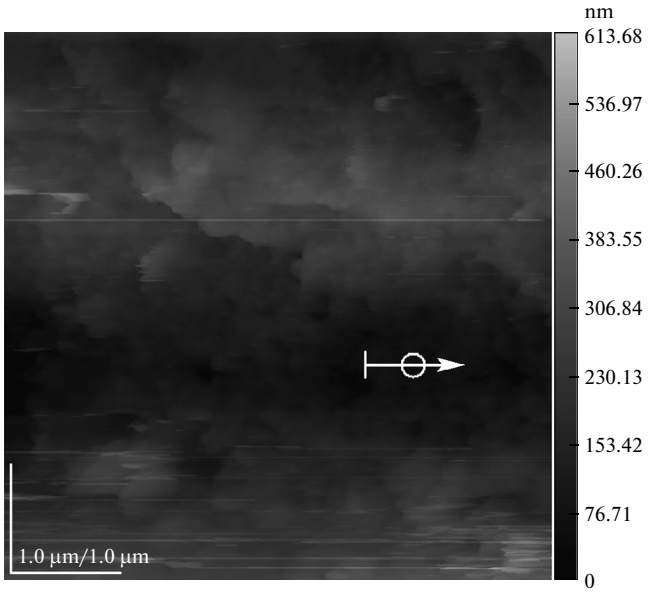

Fig. 2. Electron-microscopic image of the nanosized β-FeOOH catalyst.

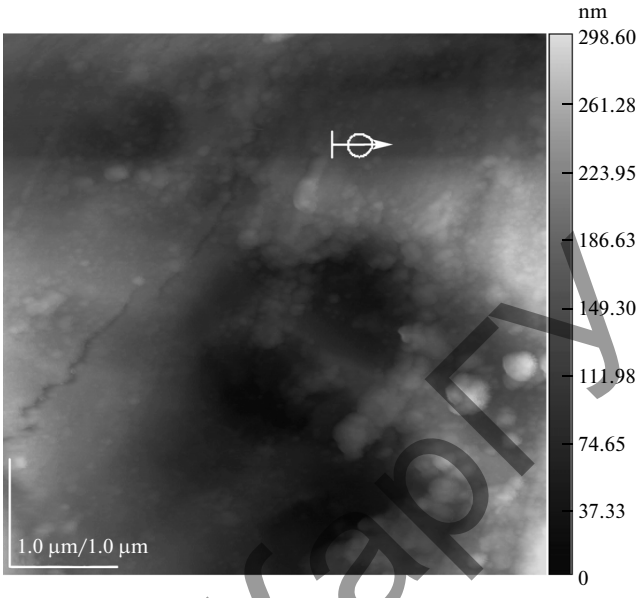

Fig. 3. Electron-microscopic image of the solid residue obtained with the use of 0.5% nanocatalyst.

β-FeOOH catalyst with that of well-known catalysts [8, 9], we can note that the nanosized test catalyst was characterized by higher selectivity for the formation of liquid products at the same level of C–O conversion. Figures 2 and 3 show the structures of the nanocatalyst and the solid residue of the primary coal tar fraction after the action of the nanocatalyst in an amount of 0.5%.

Organic substances interact with reaction centers to cause their deactivation; that is, the yield of hydrogenation products decreases and the yield of degradation products increases as the amount of the catalyst is decreased. Comparing the results obtained upon the hydrogenation of tar in the presence of the β-FeOOH nanocatalyst in different ratios in an atmosphere of hydrogen, we can conclude that the degree of tar conversion in the former case was lower than that in the latter because, in the process of hydrogenation in the presence of 0.5% nanocatalyst, the yield of the fraction was lower (78.71%) than that with the use of 5% catalyst (92.42%). The experiments performed demonstrated the effectiveness of the use of a nanocatalytic additive of β-FeOOH in the process of the hydrogenation of the coal tar fraction.

At the same time, it is well known that the stability of a suspension essentially depends on the size of solid particles: a strong decrease in their size noticeably decreases the tendency of the system toward settling [11]. The use of nanosized catalysts makes it possible to substantially stabilize the system and to almost completely avoid internal-diffusion limitations. The results of the experiments (Table 3) on the hydrogenation conversion of coal tar showed that, at a catalyst consumption of 3 or 5% in the process of hydrogenation, the yield of active atomic hydrogen, which prevents the development of condensation reactions and decreases the stability of associates, increases.

Based on the experimental studies on the hydrogenation of the primary coal tar fraction, we found that the structures of tars and asphaltenes contain the groups R–O–R; it is likely that the hydrolysis of these groups occurs with the formation of phenols [12, 13]. The concentrations of hydrocarbons and oxygen-containing compounds in the reaction products and a redistribution of the group components of the primary coal tar fraction upon hydrogenation transformations allow us to assume that the degradation of asphaltenes occurs at alkyl substituents, which contain carbon–heteroatom bonds [13]. In the process of the catalytic degradation of primary coal tar fractions, the concentration of phenols increased from 7.07 to 7.72%, as compared with that in the initial fraction (3.83%), in accordance with the added amount of the nanocatalyst. In terms of the mechanism of the occurring reaction, the heterolytic cleavage of the molecule of a parent substance occurs directly in the presence of the nanocatalyst by the carbonium ion mechanism with the predominant formation of hydrocarbons with a tertiary carbon atom (branched structures).

Comparing the results obtained for liquid products prepared upon the hydrogenation of tar in the presence of the β-FeOOH nanocatalyst at different ratios in an atmosphere of hydrogen, we already noted that the degree of tar conversion in the former case was

Table 3. Composition of coal tar fractions with the use of the β-FeOOH catalyst

Substance	Catalyst concentration, %			
	0.5	1	3	5
Phenol	7.07	4.091	7.336	7.723
2-Methylphenol	–	–	6.433	6.119
4-Methylphenol	6.179	2.777	13.622	14.65
2-Ethylphenol	1.026	0.950	1.824	1.758
3-Ethylphenol	–	–	4.429	6.989
2,4-Dimethylphenol	4.034	–	7.386	–
3,4-Dimethylphenol;	5.891	3.443	–	–
2,6-Dimethylphenol	–	–	1.203	1.194
Naphthalene	0.784	1.236	2.343	2.589
2-Ethyl-5-methylphenol	–	1.5	2.065	2.482
2,4,6-Trimethylphenol	–	–	0.396	1.002
1-Methylnaphthalene	4.173	–	2.897	–
2-Methylnaphthalene	0.730	1.249	3.343	2.637
1-Ethylnaphthalene	–	–	0.624	0.414
Tridecane	0.830	–	–	1.691
Tetradecane	9.498	–	2.248	1.729
Pentadecane	8.414	–	1.744	–
Hexadecane	6.864	–	0.959	–
2,3-Dehydro-1,6-dimethyl-1*H*-indene	–	–	1.054	0.581
2,3-Dehydro-4,7-dimethyl-1*H*-indene	–	–	1.414	3.114
2,3-Dehydro-1,1,3-trimethyl-1*H*-indene	–	–	0.379	0.360
2,6-Dimethylnaphthalene	4.814	–	0.469	–
1,4-Dimethylnaphthalene	13.93	–	1.780	1.357
2,3-Dimethylnaphthalene	2.645	–	0.662	2.122
1,4,6-Trimethylnaphthalene	1.993	–	0.484	–
1,6,7-Trimethylnaphthalene	6.855	–	0.198	–
Heptadecane	3.685	–	0.976	–
Ethylbenzene	–	–	0.642	0.454
1,3-Dimethylbenzene	–	–	0.858	0.826
o-Xylene	–	–	0.325	0.302
Nonane	–	–	0.386	0.332
1,2,3-Trimethylbenzene	–	–	0.578	0.51
Decane	–	–	0.314	0.323
Indan	–	–	0.389	0.520
Undecane	–	–	0.875	0.816
Dodecane	–	–	0.596	0.914
α,β,β-Trimethylstyrene	–	–	1.632	0.659

lower than that in the latter case because the yield of phenol and its derivatives in the process of hydrogenation in the presence of 0.5% nanocatalyst was lower (26.63%) than that with the use of 5% catalyst (47.56%).

The selectivity of the catalyst for the formation of liquid hydrocarbons noticeably increased upon its addition in a 5% amount to reach a 45.60% yield of phenol and its derivatives. In this case, the yield of naphthalene and its derivatives was 37.99%, and the yield of paraffins was 32.75%. These results likely indicate the agglomeration of the nanoparticles of the β-FeOOH catalyst.

Thus, we evaluated the effect of a catalytic additive of β-FeOOH on the process of coal tar hydrogenation. Based on the experimental results, we can conclude that the nanosized catalyst is a newly developed catalytic additive, which facilitates the deeper chemical modification and degradation of the organic matter of hydrocarbon raw materials to result in a much higher yield of light-oil products. Therefore, a search for and the use of nanocatalytic additives in the processing of primary coal tar makes it possible to increase the efficiency of well-known technologies in this area.

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