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Kinetics of Hydrogenation of Heavy and Solid Hydrocarbon Raw Materials

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Abstract—Experimental results on the kinetics of hydrogenation of a wide fraction of coal tar (bp 230–300°C) in the presence of a Fe_3O_4 nanocatalyst are presented. The rate constants, overall rate constants, and activation energies were calculated. It was established that the conversion of preasphaltenes into asphaltenes is the rate-limiting stage of the conversion of a wide fraction (230–300°C) of coal tar into reaction products. The process of converting the wide fraction (230–300°C) into products takes place in the kinetic region of a heterogeneous process.

Keywords: kinetics, heavy hydrocarbons, coal tar, reactor design, hydrogenation
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Hydrogenation is one of the most important lines in the processing of solid and heavy hydrocarbon raw materials. It is necessary to study the kinetics of hydrogenation of the organic matter of coal in the modeling and optimization of technological processes parameters depending on the processes conditions. However, in this case, there are difficulties one of which is the identification of a large number of individual compounds; therefore, in actual practice, they have to be grouped according to certain conditional physicochemical properties [1].

To reduce the total pressure of hydrogen in the course of a hydrogenation process, it is necessary to develop a reliable method for reactor design. For this purpose, it is necessary to know the rate constants of main reactions, the activation energies, and other parameters that are determined by the formal kinetics of hydrogenation of a wide fraction (230–300°C) of coal tar.

Various methods for calculating the kinetic parameters of the hydrogenation of coal, coal tar, and highly viscous oil are well known [1–3].

The aim of this study was to establish the kinetic parameters of hydrogenation of a wide fraction of coal tar (230–300°C) and to develop a kinetic model of the process performed under autoclave conditions. This problem was solved by the processing of experimental data with the use of a heavy ball method.

EXPERIMENTAL

A wide fraction with a boiling point of 230–300°C, which was taken from coal tar by distillation, was used as a test material. The coal tar was obtained in the process of coal coking at an enterprise of AO Shubarkol'komir.

The elemental composition of the wide fraction of coal tar was the following (%): C, 81.11; H, 9.63; O, 8.32; N, 0.70; and S, 0.24. The H/C atomic ratio was 1.43. The yield of the wide fraction with a boiling point of 230–300°C from coal tar was 42.7%.

The experiments on the hydrogenation of the wide fraction (230–300°C) of coal tar were carried out in a 0.05-L high-pressure reactor with an internal stirrer at an initial hydrogen pressure of 3.0 MPa.

The preliminarily mixed starting materials (the wide fraction of coal tar and a nanocatalyst) were placed in an autoclave (the weight concentration of the

nanocatalyst in the initial fraction was 1.0%), which was closed and purged with hydrogen, and an excess pressure of hydrogen was given. Then, the autoclave was heated (the heating rate was 10 K/min) to a required temperature and kept for a specified time, after which it was cooled to room temperature. The autoclave was opened after 24 h, and the hydrogenation products were thoroughly washed with benzene.

The mixture of polyaromatic hydrocarbons in the hydrogenation products was determined using gas chromatography–mass spectrometry (GC–MS) analysis. The concentrations of tars, asphaltenes, and oils in the hydrogenation products obtained upon the hydrogenation of the wide fraction (230–300°C) of coal tar were quantitatively determined using a standard procedure [4]. Oils, tars, and asphaltenes were separated from the hydrogenation products according to a published method [2].

The GC–MS analysis of polyaromatic hydrocarbons (PAHs) was performed on an Agilent Technologies 7890A gas chromatograph with a 5975C mass-spectrometric detector. An SE mobile phase of grade A and an HP = 5HS chromatographic column (length, 30 m; thickness, 0.25 mm; and adsorbent thickness inside the capillary, 0.25 μm) were used for the analysis. The column temperature was gradually varied from 60 to 300°C with time; helium was supplied at a flow rate of 8 mL/s.

The test sample with a volume of 1 μL was introduced into the column using a 7683B autosampler. After separation in the column, the test sample entered the ionization chamber of the mass spectrometer. In the chamber, the arrived molecules underwent fragmentation by electron impact with an energy of 70 eV at a temperature of 250°C. The fragments extracted from the ionization chamber by an electrostatic field arrived at a quadrupole capacitor, with the use of which the mass spectra of test sample components were obtained.

The chromatograms and mass spectra were processed using the MSD ChemStation E02.00.493 software. To identify substances by mass spectra, the NIST-8 database of mass spectra was used.

The method used for producing Fe_2O_3 iron nanoparticles was first published by Jongham et al. [5]; then, it was unified for the processing of solid and heavy hydrocarbon raw materials [6].

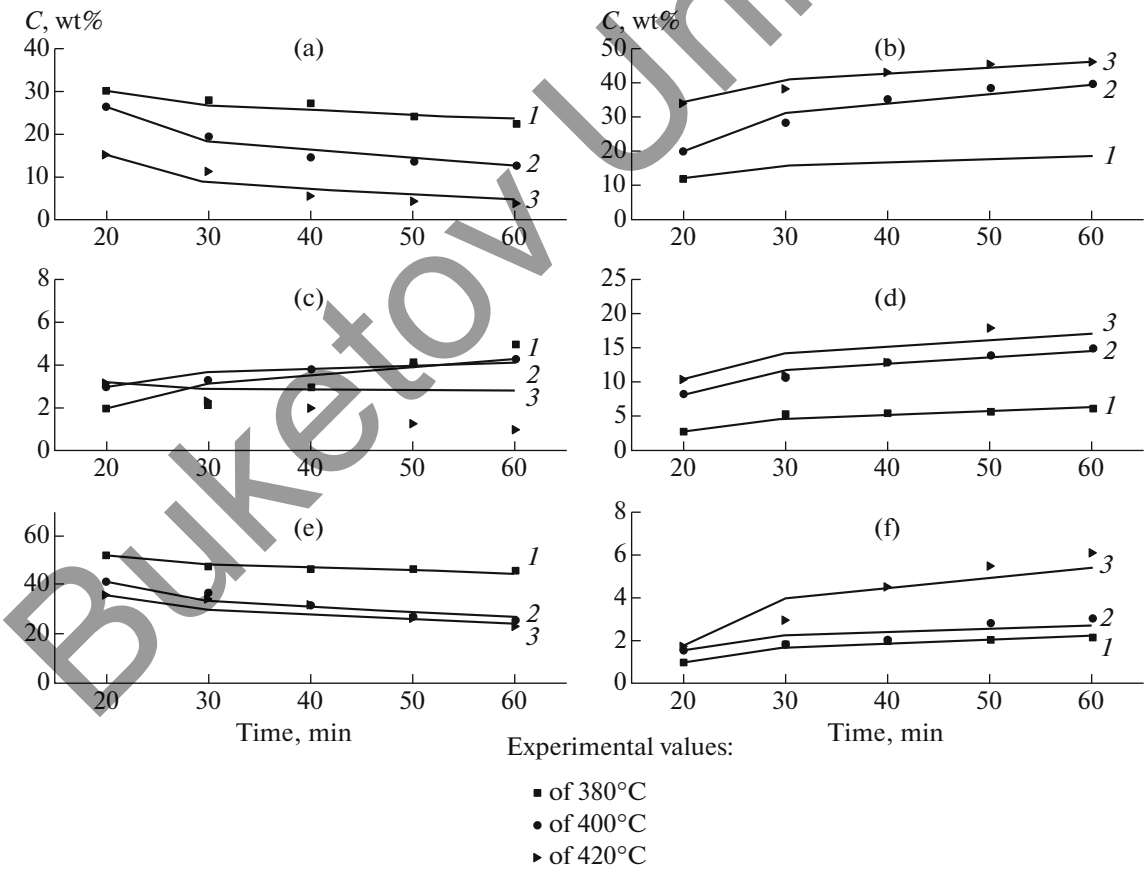

Fig. 1. The time dependence of the yields of products on the hydrogenation of the wide fraction (230–300°C) of coal tar at different temperatures. Reaction products: (a) fractions of 230–300°C, (b) tars, (c) asphaltenes, (d) oils, (e) a mixture of PAHs, and (f) solid products. Calculated yields at (*1*) 380, (*2*) 400, and (*3*) 420°C.

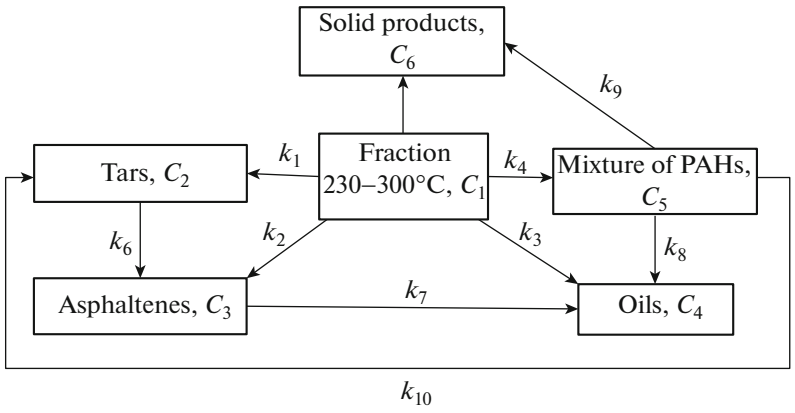

Fig. 2. Schematic diagram of the hydrogenation of the wide fraction (230–300°C) of coal tar in the presence of a Fe_3O_4 nanocatalyst.

A mixture of chemically pure iron chloride $FeCl_3 \cdot 6H_2O$ (2.7 g, 10 mmol) with sodium oleate $C_{17}H_{33}COONa$ (9.1 g, 30 mmol) was added to a prepared mixture consisting of hexane (35 mL), ethanol (20 mL), and water (15 mL); then, the solution was heated for 4 h at a temperature of 70°C and stirred. The upper organic layer was separated from the aqueous portion and washed three times with water to obtain a reddish brown aqueous solution consisting of iron oleate. A mixture of iron oleate (9 g, 10 mmol), oleic acid $C_{17}H_{33}COOH$ (1.4 g), and 1-octadecene (50 g) was heated to a temperature of 100°C with stirring and kept in a vacuum for 30 min. The resulting solution was stirred and gradually heated to 320°C; then, it was kept in an inert gas atmosphere of nitrogen for 3 h. A solid solution containing Fe_3O_4 nanoparticles was cooled to room temperature, and an excess of ethanol was added; the mixture was washed three times with ethanol and centrifuged. The Fe_3O_4 iron nanoparticles obtained were dried at a temperature of 60°C for further use in catalytic reactions.

The kinetic rate constants of hydrogenation of the wide fraction with a boiling point of 230–300°C from coal tar were calculated using the heavy ball method [7–11].

RESULTS AND DISCUSSION

Figure 1 shows the yields of components in the hydrogenation products as functions of time (from 20 to 60 min) at different temperatures (from 380 to 420°C) during the hydrogenation of the wide fraction (230–300°C) of coal tar in the presence of a Fe_3O_4 nanocatalyst.

In a study of the effects of time and temperature on the results of the hydrogenation of a coal tar fraction of 230–300°C under an initial hydrogen pressure of 3.0 MPa, we found that the stage of conversion of the fraction (230–300°C) into various components increased with temperature and experiment time. The mixtures of PAHs in the wide fraction of 230–300°C are reactive (Fig. 1). This is evidenced by the relatively deep transformations of organic substances in the fraction (230–300°C) in the initial period of time and at a temperature of 420°C. The yields of oils and tars increased from 10.4 to 20.1 and from 33.9 to 46%, respectively, and the yields of a PAH mixture and asphaltenes decreased from 35.8 to 23.2 and from 3.2 to 1%, respectively, with time at a temperature of 420°C. As the temperature was increased from 380 to 420°C, the yields of oils and preasphaltenes increased from 6.1 to 20.1 and from 18.7 to 46%, respectively, and the yields of a PAH mixture and asphaltenes decreased from 46 to 23.2 and from 5 to 1%, respectively.

The experimental results obtained indicate the activity of the Fe_3O_4 nanocatalyst in given time and temperature intervals in the hydrogenation and hydrogenolysis of a mixture of PAHs in the wide fraction (230–300°C) of coal tar. It should be noted that the Fe_3O_4 nanocatalyst exhibited the highest activity in hydrogenation and hydrogenolysis reactions in the course of the hydrogenation of the wide fraction (230–300°C).

Based on the above experimental data, we proposed a hydrogenation reaction scheme for the wide fraction (230–300°C) of coal tar in the presence of the Fe_3O_4 nanocatalyst (Fig. 2).

Based on the kinetic scheme (Fig. 2), we compiled a kinetic model for the hydrogenation of the wide fraction (230–300°C) of coal tar, which was represented as the following system of differential equations:

$$\frac{dC_1}{d\tau} = -(k_1 + k_2 + k_3 + k_4 + k_5)C_1,$$

$$\frac{dC_2}{d\tau} = k_1C_1 + k_{10}C_5 - k_6C_2,$$

$$\frac{dC_3}{d\tau} = k_2C_1 + k_6C_2 - k_7C_3,$$

Table 1. Calculated rate constants of hydrogenation of the wide fraction (230–300°C) of coal tar

Rate constant, min^{-1}	T, °C		
	380	400	420
k_1	0.001274	0.005316	0.005867
k_2	0.00079	0.001349	0.00008
k_3	0.000681	0.002357	0.004576
k_4	0.001076	0.002396	0.004615
k_5	0.00025	0.000741	0.004236
k_6	0.001441	0.000012	0.000339
k_7	0.001615	0.001857	0.007357
k_8	0.000786	0.001636	0.001619
k_9	0.000275	0.00018	0.000792
k_{10}	0.002024	0.006678	0.005192

$$\frac{dC_4}{d\tau} = k_3C_1 + k_7C_3 + k_8C_5,$$

$$\frac{dC_5}{d\tau} = -(k_8 + k_9 + k_{10})C_5 + k_4C_1,$$

$$\frac{dC_6}{d\tau} = k_5C_1 + k_9C_5.$$

The initial conditions for solving the system of differential equations were as follows: $C_1 = 100$, and $C_2 = C_3 = C_4 = C_5 = 0$. The system of differential equations was calculated using the heavy ball method. Table 1 summarizes the calculated rate constants.

Analyzing the results on the rate constants presented in Table 1, we obtained the following series of rate constants for the conversion of the wide fraction into hydrogenation products for temperatures of (1) 380, (2) 400, and (3) 420°C:

$$k_{10} > k_7 > k_6 > k_1 > k_4 > k_2 \approx k_8 > k_3 > k_9 > k_5, \quad (1)$$

$$k_{10} > k_1 > k_4 > k_3 > k_7 > k_9 > k_8 > k_2 > k_5 > k_6, \quad (2)$$

$$k_7 > k_1 > k_{10} > k_3 > k_4 > k_5 > k_8 > k_9 > k_6 > k_2. \quad (3)$$

The above data indicate that the conversion of the 230–300°C fraction into solid products is a rate-limiting stage of the hydrogenation of the fraction (230–300°C) of coal tar at 380°C, whereas the conversion of tars into asphaltenes and the conversion of the initial fraction into asphaltenes are rate-limiting stages at temperatures of 400 and 420°C, respectively.

Figure 1 shows the experimental and calculated yields of the hydrogenation products of the wide fraction at 380, 400, and 420°C. It can be seen that the yield of a mixture of PAHs decreases significantly and the yield of oil increases with time and temperature. These parameters indicate that the hydrogenation process of the coal tar fraction is optimal.

The yield of asphaltenes also increases with temperature and time.

The rate constant of the conversion of tars into asphaltenes (Table 1) k_6 decreases with an increase in the temperature from 380 to 400°C; at 400°C, the condensation of tars into asphaltenes is unlikely. However, at 420°C, the rate constant of the conversion of tars into asphaltenes increases to explain the fact that an increase in temperature to 420°C leads to the formation of asphaltenes from tars.

The rate coefficients for the process of hydrogenation of the wide fraction of coal tar at temperatures of 380, 400, and 420°C were calculated using the first-order equation

$$K_\Sigma = \ln\frac{C_0}{C}/t,$$

where K_Σ is the rate coefficient, which depends on the degree of conversion of the coal tar fraction into reaction products, min^{-1}; C_0 is the initial concentration of the wide fraction of coal tar, fraction of unity; C is the concentration of the unconverted fraction of coal tar in a time interval of 20–60 min, fraction of unity; and t is the duration of the hydrogenation process, min.

Figure 3 shows the dependence of the rate coefficient of the conversion of the 230–300°C fraction into products on the reciprocal temperature and the influence of temperature on the rate coefficient of a heterogeneous process (the mechanism of the heterogeneous process can be judged from the slope). The found activation energy of 60.6 kJ/mol indicates that the conversion of the 230–300°C fraction into reaction products takes place in the kinetic region of the heterogeneous process.

CONCLUSIONS

In the course of the kinetic studies on the hydrogenation of the wide fraction (230–300°C) of coal tar in the presence of a nanosized Fe_3O_4 catalyst (in a temperature range from 380 to 420°C at process times from 10 to 60 min), we found that the reaction scheme of the conversion of the wide fraction (230–300°C) of coal tar has five stages: tars, asphaltenes, oils, a mixture of PAHs, and solid products. The rate constants of each stage, the overall rate constant of the conversion of the wide fraction into reaction products, and the activation energy of the hydrogenation of the wide fraction of coal tar were calculated. It was established that the conversion of tars into asphaltenes is a rate-limiting stage of the process. It was found that a system of differential equations that describe the kinetics of hydrogenation of a wide fraction of coal tar can be calculated with a difference between the calculated and experimental values of no greater than 2% using the heavy ball method. Based on the kinetics of products

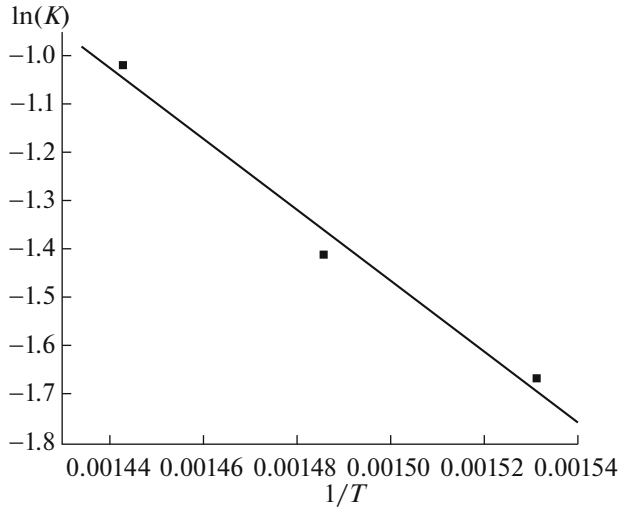

Fig. 3. Dependence of the logarithm of the rate coefficient of conversion of the fraction 230–300°C into products on the reciprocal temperature.

formation from the wide fraction, it was found that the synthesized Fe_3O_4 nanocatalyst exhibits the highest activity in oil formation reactions in the process of hydrogenation of the wide fraction of coal tar.

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