ISSN 0361-5219, Solid Fuel Chemistry, 2013, Vol. 47, No. 2, pp. 107–113. © Allerton Press, Inc., 2013.
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Catalytic Hydrogenation of a Three-Component Mixture of Polyaromatic Hydrocarbons in the Presence of Iron-Containing Additives

M. I. Baikenov[a], Sh. K. Amerkhanova[a], and G. G. Baikenova[b]
[a] *Buketov State University, ul. Universitetskaya 28, Karaganda, 100028 Kazakhstan*
[b] *Modern Humanitarian Technical Institute, Karaganda, 100008 Kazakhstan*
e-mail: amerkhanova_sh@mail.ru

Received March 5, 2012

Abstract—The results of the catalytic hydrogenation of a three-component anthracene–benzothiophene–biphenyl mixture in the presence of different catalytic additives are given. It was found that the conversion of the mixture of model substances was 85.9 or 85.0% with the use of FeS_2 or Fe_2O_3 + S (1 : 1), respectively; in both cases, hydrocracking was the prevailing reaction path. A comparatively small difference was found in the products of hydrogenation and hydroisomerization, which was related to the hydrogenation of the structure of each particular component.

DOI: 10.3103/S036152191302002X

An important technological task in the processing of heavy hydrocarbon raw materials is the complex study of a hydrogenation process by determining optimum temperature and time conditions, pressure, catalytic systems, the mutual effects of raw material constituents, and the role of hydrogen donor components [1].

The determination of the mechanism of hydrogenation of anthracene, phenanthrene, benzothiophene, pyrene, etc. (separately and in a mixture) as the models of the composition and structure of heavy hydrocarbons is a line of inquiry into the process of hydrogenation. Special attention is paid to this problem because its solution will make it possible to understand the mechanism of the behavior of the organic matter of primary coal tar in the course of hydrogenation and to use hydrogenated polyaromatic hydrocarbons and polymers as the donors of hydrogen [2]. An analysis of data on the reactivity of compounds that simulate the structural elements of coal tar in the presence of different promoting additives allows one to forecast the selection of optimum catalysts and process conditions for the hydrogenation of coal tar.

The aim of this work was to evaluate the catalytic activity of different iron-containing additives in the hydrogenation of a three-component model mixture of polyaromatic hydrocarbons.

EXPERIMENTAL

Polycyclic hydrocarbons such as anthracene, benzothiophene, and biphenyl were used as the main test materials. Table 1 gives the experimental conditions of the hydrogenation of a three-component anthracene–benzothiophene–biphenyl mixture (in a ratio of 1 : 0.5 : 0.5) in the presence of catalytic additives (iron(III) oxide of analytical grade and iron sulfide FeS_2).

The experiments on the hydrogenation of the mixture of polycyclic hydrocarbons (anthracene, benzothiophene, and biphenyl) were carried out in an autoclave (V = 0.05 L). For this purpose, the mixture of the polycyclic hydrocarbons (in a ratio of 1 g : 0.5 g : 0.5 g) was loaded into the autoclave and purged with hydrogen, and an excess hydrogen pressure was produced. The mixture of the polycyclic hydrocarbons was pre-

Table 1. Experimental conditions of the hydrogenation of a three-component model mixture (0.05-L autoclave)

No.	Polyaromatic hydrocarbons in the mixture, wt %			Catalyst amount, wt %		Tetralin, wt %	T, °C	Elemental sulfur, wt %
	Anthracene	Benzo-thiophene	Biphenyl	Fe_2O_3	FeS_2			
1	50	25	25	1.5	–	–	400	1.5
2	50	25	25	–	3.0	25	400	–

liminarily stirred. The initial pressure of hydrogen was 6 MPa, and the operating pressure was 12 MPa. The contact time was 60 min. The point in time at which the autoclave reached the operating temperature was taken as the onset of reaction. The temperature was 400°C. The autoclave heating rate was 10 K/min.

Thereafter, the autoclave was cooled to room temperature, and the composition of the reaction products was determined by gas chromatography–mass spectrometry (GC–MS) on an Agilent instrument (the United States). The chromatographing conditions were the following: DB-5 column, 30 m × 0.25 mm × 0.5 μm; carrier gas, helium; gas flow rate, 0.8 mL/min; column oven temperature, 50°C for 4 min, 50–150°C at 10 K/min, 150–300°C at 10 K/min, and 300°C for 4 min; and injector temperature, 250°C. The identification of individual chemical substances was performed with the use of the NIST98 and NIST27LIB mass-spectrometric library data. Tables 2 and 3 summarize the individual chemical composition of the products of catalytic hydrogenation; compounds whose concentrations were lower than 1% are not shown.

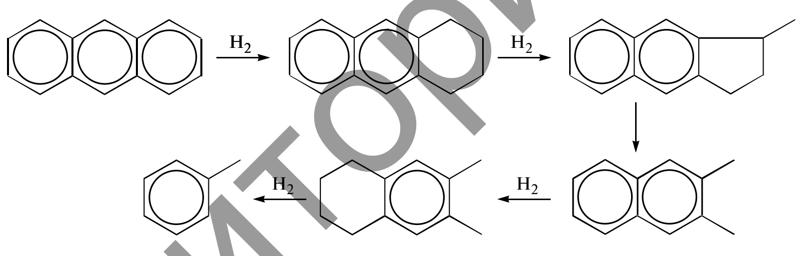
RESULTS AND DISCUSSION

The mechanisms of the main reactions of the processing of primary coal tar can be roughly understood because of the complexity of chemical composition and the difficulty of analysis. Therefore, the processing of a model mixture is performed to solve this problem; the high stability of polycyclic hydrocarbons makes it possible to use them as model substances in the process of destruction.

An analysis of published data [3–6] showed that the chemical structure primarily affects the rate of hydrogenation of polycyclic hydrocarbons under conditions uncomplicated by polymerization and degradation side reactions.

Earlier, we published the results of studying the hydrogenation of two-component anthracene–phenanthrene and anthracene–benzothiophene model mixtures in the presence of heterogeneous catalytic additives based on iron sulfide [7].

The hydrocracking of polycyclic hydrocarbons is described by a multistep mechanism, which includes hydrogenation, hydroisomerization, cracking, and repeated hydrogenation [8]. For example, the hydrocracking of anthracene occurs by the following mechanism:



At the first step of conversion, the stepwise hydrogenation of anthracene to di-, tetra-, and octahydroanthracenes occurs. The cyclohexane rings of tetra- and octahydroanthracenes then undergo isomerization and cracking to naphthalenes, and these latter are converted into alkylbenzenes through the steps of hydrogenation, isomerization, and cracking of one of the rings [9].

Based on the data of the GC–MS analysis of the hydrogenation products of the model mixture in the presence of a catalytic additive of Fe_2O_3 + S (1 : 1) (Table 2), we assumed that hydrocracking is the main direction of the process. We identified a number of the hydrogenation and hydrogenolysis products of the test mixture of the model substances; in particular, the following compounds were detected (%): 9,10-dihydroanthracene, 6.04; 1,2,3,4-tetrahydroanthracene, 4.74; octahydroanthracene, 2.38; and 2,3-dihydrobenzothiophene, 3.77.

Iron sulfides are used as active catalytic additives in the processes of the destructive hydrogenation of a heavy charge (coal, shale, peat, heavy petroleum residue, and heavy oils). Iron sulfide was used as a catalyst for the hydrogenation of the three-component mixture of compounds (anthracene, benzothiophene, and biphenyl) in the study of the hydrogenation of a heavy charge with the use of model substances.

The hydrogenation and hydrogenolysis products of the test mixture of model substances were determined by CG–MS analysis. Table 3 summarizes the main components of the mixture.

In the presence of iron sulfide, the conversion of the mixture of model substances was 85.9%, and hydrocracking was the prevailing reaction path (67.1%). The hydrogenate contained 18.8% of anthracene and benzothiophene hydrogenation products, whereas the products of biphenyl hydrogenation were not detected; the yields of the products were the following (%):9.10-dihy-

Table 2. Chemical composition of the products of the combined hydrogenation of anthracene, benzothiophene, and diphenyl (400°C; catalytic additive, $Fe_2O_3 + S$ (1 : 1); autoclave)

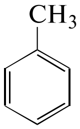
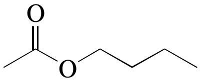
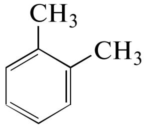
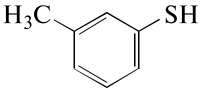
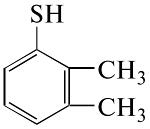
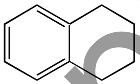
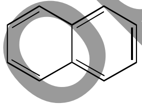
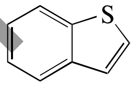
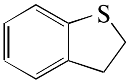
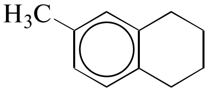
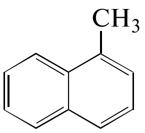
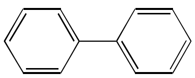
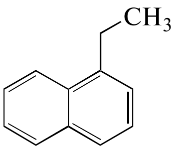
No.	Compound	Structural formula	τ_r, min	Relative concentration, wt %
1	Toluene		3.55	5.96
2	Butyl acetate		4.01	1.04
3	*o*-Xylene		5.13	2.63
4	*m*-Thiocresol		11.22	1.04
5	3,4-Dimethylthiophenol		14.44	4.15
6	1,2,3,4-Tetrahydronaphthalene		14.56	3.83
7	Naphthalene		15.32	2.17
8	Benzothiophene		15.99	4.49
9	2,3-Dihydrobenzothiophene		18.07	3.77
10	6-Methyltetrahydronaphthalene		18.17	1.08
11	1-Methylnaphthalene		19.45	4.03
12	Diphenyl		23.01	4.93
13	1-Ethylnaphthalene		23.24	4.64

Table 2. (Contd.)

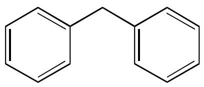
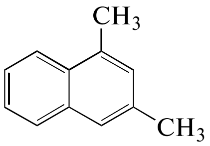
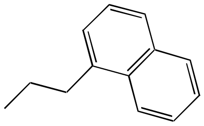
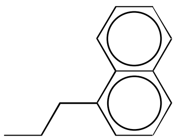
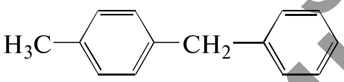
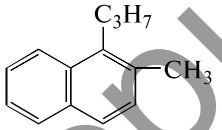
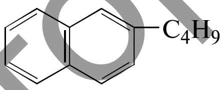
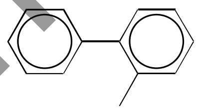
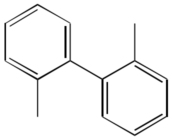
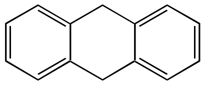
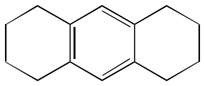
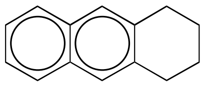
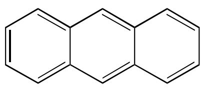
No.	Compound	Structural formula	τ_r, min	Relative concentration, wt %
14	Diphenylmethane		24.04	1.67
15	1,3-Dimethylnaphthalene		24.27	1.23
16	1-Isopropylnaphthalene		24.72	1.21
17	1-Propylnaphthalene		25.76	1.80
18	Benzyltoluene		27.38	4.62
19	1-Propyl-2-methylnaphthalene		27.57	1.34
20	2-Butylnaphthalene		29.23	2.31
21	2-Methylbiphenyl		29.89	4.30
22	2,2'-Dimethylbiphenyl		31.52	4.48
23	9,10-Dihydroanthracene		32.13	6.04
24	Octahydroanthracene		32.31	2.38
25	1,2,3,4-Tetrahydroanthracene		34.26	4.74
26	Anthracene		34.75	5.21

Table 3. Chemical composition of the products of the combined hydrogenation of anthracene, benzothiophene, and diphenyl (400°C; catalytic additive, iron sulfide FeS_2; autoclave)

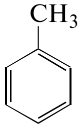
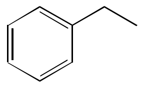
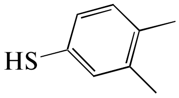
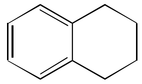
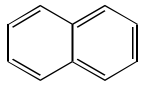
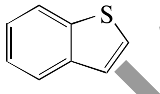
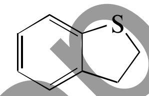
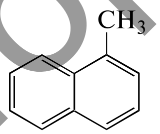
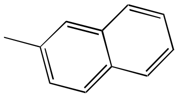
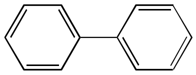
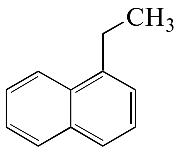
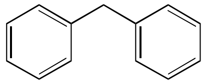
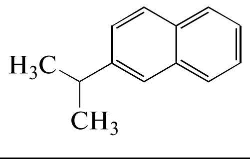
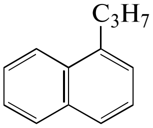
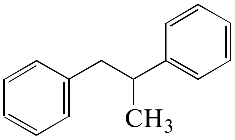
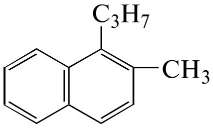
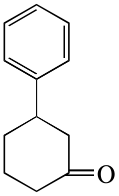
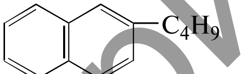
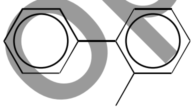
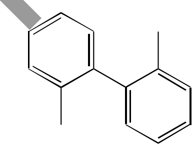
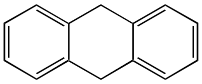
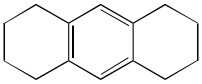
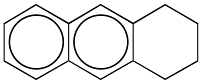
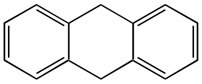
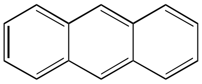
No.	Compound	Structural formula	τ_r, min	Relative concentration, wt %
1	Toluene		3.54	6.50
2	Ethylbenzene		4.98	3.73
3	3,4-Dimethylthiophenol		14.33	1.81
4	Tetrahydronaphthalene		14.50	4.08
5	Naphthalene		15.29	2.35
6	Benzothiophene		15.88	4.69
7	2,3-Dihydrobenzothiophene		18.02	3.88
8	1-Methylnaphthalene		18.13	1.21
9	2-Methylnaphthalene		19.40	4.14
10	Diphenyl		23.00	5.24
11	1-Ethylnaphthalene		23.22	5.33
12	Diphenylmethane		24.01	1.60
13	2-Isopropylnaphthalene		24.69	1.04

Table 3. (Contd.)

No.	Compound	Structural formula	τ_r, min	Relative concentration, wt %
14	1-Propylnaphthalene		25.73	1.67
15	1-Methyl-2-phenylmethylbenzene		27.35	4.75
16	1-Propyl-2-methylnaphthalene		27.55	1.41
17	Phenylcyclohexen-3-one		27.92	1.05
18	2-Butylnaphthalene		29.24	2.89
19	2-Methylbiphenyl		29.85	4.35
20	2,2'-Dimethylbiphenyl		31.53	4.76
21	Dihydroanthracene		32.16	4.49
22	Octahydroanthracene		32.32	3.13
23	Tetrahydroanthracene		34.28	5.17
24	Dihydroanthracene		34.37	2.13
25	Anthracene		35.32	4.17

droanthracene, 4.49; octahydroanthracene, 3.13; and 2,3-dihydrobenzothiophene, 3.88.

The mechanism of the catalytic action of an iron sulfide catalytic additive in the hydrogenation of the mixture of polyaromatic hydrocarbons consists in hydrogen transfer to the model substances (polyaromatic hydrocarbons) by means of hydrogen sulfide. Hydrogen sulfide, which is formed upon the reduction of pyrite, can cause catalysis and hydrogen transfer in reactions of the following type [9]:

$$\mathrm{Fe}_{1-x}\mathrm{S} + \mathrm{H_2S} \longleftrightarrow \mathrm{Fe}_{1-x}\mathrm{SH} + \mathrm{SH}^{\bullet}, \qquad (1)$$

$$\mathrm{FeS}_{1-x} + \mathrm{SH}^{\bullet} \longrightarrow \mathrm{FeS} + \mathrm{H}^{\bullet}. \qquad (2)$$

Hydrogen sulfide is thermally decomposed, and pyrite is converted into pyrrhotine. Furthermore, hydrogen sulfide and pyrrhotine accelerate the reactions of hydrocracking and isomerization.

It was found [10] that the composition of an artificial mixture containing two-, three-, and four-ring hydrocarbons (naphthalene, anthracene, and pyrene) changes in the course of hydrogenation in the presence of catalysts based on iron. It was also found that anthracene was hydrogenated more rapidly than pyrene. Mixed naphthenoaromatic hydrocarbons with one or two at the most naphthene rings predominated in the high-temperature hydrogenation products of polycyclic aromatic systems. Simultaneously with the hydrogenation reactions of a mixture of polyaromatic hydrocarbons, the reactions of C–S bond cleavage and hydrogenation in benzothiophene occur with the formation of 2,3-dihydrobenzothiophene and 2,6-dimethylthiophenol.

CONCLUSIONS

Thus, as a result of the hydrogenation conversion of a three-component model mixture in the presence of three different types of iron-containing catalytic additives, we obtained similar degrees of conversion and a comparatively small difference in the products of hydrogenation and hydroisomerization. This was likely due to the occurrence of the stepwise hydrogenation of anthracene, phenanthrene, and biphenyl to di-, tetra-, and octahydroanthracene; di- and octahydrophenanthrenes; and a biphenyl hydroisomerization product, respectively. The cyclohexane rings of tetra- and octahydroanthraceces and phenanthrene underwent further hydroisomerization and cracking to naphthalenes, and these latter were likely converted into alkylbenzenes through the steps of hydrogenation, hydroisomerization, and cracking of one of the rings.

REFERENCES

1. Zhubanov, K.A., *Prom–st. Kazakhstana*, 2001, no. 4, p. 60.
2. Nuzzi, M. and Marcandelli, B., *Fuel Proc. Technol.*, 2003, vol. 80, p. 35.
3. Krichko, A.A. Panova, E.G., et al., *Azerb. Khim. Zh.*, 1973, no. 1, p. 9.
4. Gagarin, S.G., Gyul'maliev, A.M., and Krichko, A.A., *Khim. Tverd. Topl.* (Moscow), 1990, no. 6, p. 28.
5. Sovetova, L.S., *Extended Abstract of Cand. Sci. (Chem.) Dissertation*, Moscow: IGI, 1964.
6. Krichko, A.A. and Zyuba, B.I., *Neftekhimiya,* 1970, vol. 10, no. 6, p. 813.
7. Ma Fen Yun', Baikenov, M.I., et al., *Vestn. KazNU im. Al'-Farabi*, 2009, no. 3, p. 92.
8. Kuznetsov, B.N., *Kataliz khimicheskikh prevrashchenii uglya i biomassy* (Catalysis of the Chemical Conversion of Coal and Biomass), Moscow: Nauka, 1990.
9. Baikenov, M.I., Khrupov, V.A., and Zhubanov, K.A., *Mater. mezhd. nauch.-prakt. konf. "Akademik E.A. Buketov, uchenyi, pedagog, myslitel"* (Proc. Int. Sci.-Pract. Conf. "Academician E.A. Buketov—A Scientist, Teacher, and Thinker"), Karaganda: Izd. KarGU, 2005, p. 291.
10. *Chemierohstoffe aus Kohle*, Falbe, J., Ed., Stuttgart: Georg Thieme Verlag, 1977.

Translated by V. Makhlyarchuk