

Hydrogenation of a Model Mixture of Anthracene with Benzothiophene

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Abstract—The reactivity of an anthracene–benzothiophene mixture in the presence of various catalytic additives was studied. The efficiency of the catalytic additives was evaluated from various standpoints.

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The main trend in the development of world petroleum refining and coal-chemical industries is the introduction of new technologies to make the most of the use of hydrocarbon materials (coals, peat, shale, heavy oils, etc.) for the manufacture of high-quality target products. The catalytic conversion of solid and heavy hydrocarbon materials into gaseous and liquid products is currently one of the most important problems [1].

A technological aspect in the production of synthetic liquid fuel from solid hydrocarbon materials is a search for efficient catalytic systems or hydrogen donors. Because hydrocarbon materials (coals, peat, shale, heavy oils, etc.) are complex mixtures of organic and mineral substances, they are difficult to characterize. Model compounds (anthracene, phenanthrene, pyrene, naphthalene, etc.) are frequently used to imagine the mechanisms of processes and the activity and selectivity of chosen catalysts because the dependence of reactivity on the chemical structure of substances can be studied based on model organic compounds that can fragmentarily represent the organic matter of coal. In addition, model compounds do not undergo degradation in the temperature range of destructive hydrogenation.

The aim of this work was to study the dependence of the reactivity of an anthracene–benzothiophene mixture in the presence of various catalysts in the course of destructive hydrogenation.

EXPERIMENTAL

Two model compounds—anthracene and benzothiophene—were taken to perform the experiments. Pyrite concentrate, iron oxide, elemental sul-

fur, Steel (nonferrous metallurgy waste), a catalyst from Shenhua, and nickel sulfate were used as catalytic additives.

The mixture of anthracene and benzothiophene was hydrogenated in a 0.2-l high-pressure reactor with an inner stirrer (autoclave) at a temperature of 375–400°C and an initial gas pressure of 6.0 MPa for 30 min. The point in time at which the autoclave reached a temperature of 400°C was taken as the onset of reaction. The autoclave heating rate was 10 K/min; the amounts of anthracene and benzothiophene were 1.0 and 0.5 g, respectively.

The mixture was stirred, and the resulting mass was placed in the autoclave. Then, the autoclave was closed and purged with hydrogen, and an excess pressure of hydrogen was generated. The autoclave was heated to a required temperature and kept for a specified time. After the experiment, it was cooled to room temperature; the volume of released gaseous products was measured with a GSB-400 gas meter, and the weight of gas was calculated based on gas-chromatographic analysis data.

The composition of hydrogenation effluent gases was determined on a stainless steel chromatographic column and a KhL-4 chromatograph. The hydrogenation products of the model compounds were determined on an HP 5890/5972 MSD instrument from Agilent (United States). The substances were identified using base data from the NIST 98 library.

RESULTS AND DISCUSSION

Experiments with various compositions of additives were performed to study the effect of catalyst

Table 1. Composition of catalysts (g) in the hydrogenation of a model mixture of anthracene and benzothiophene

Experiment no.	Catalyst					
	Fe ₂ O ₃	FeS ₂	S	Steel	Shenhua catalyst	NiSO ₄
1	—	—	—	—	—	—
2	0.0357	—	0.0143	—	—	—
3	—	—	0.3430	0.0881	—	—
4	—	0.0482	—	—	—	—
5	—	—	—	—	0.0450	—
6	0.0357	—	0.0143	—	—	0.01

Table 2. Yields of reaction products in the hydrogenation of a model mixture of anthracene and benzothiophene (experiment numbers are specified in Table 1)

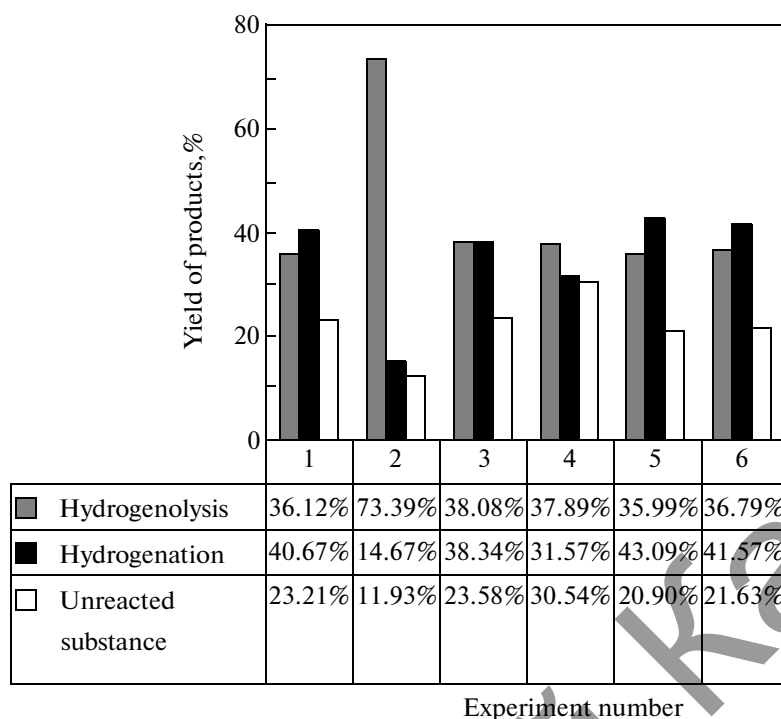
Reaction products	Yields of reaction products, %					
	1. With no catalyst	2. Fe ₂ O ₃ + S	3. Steel + S	4. FeS ₂	5. Shenhua	6. Fe ₂ O ₃ + S + NiSO ₄
Anthracene	12.69	8.66	12.97	17.54	10.02	11.02
Benzothiophene	10.52	3.27	10.61	13.00	10.88	10.61
1,2,3,4-Tetrahydroanthracene	23.23	6.91	20.17	25.21	23.56	21.40
2,2'-Dimethylbiphenyl + 3-ethylbiphenyl	11.58	7.98	13.68	12.86	12.00	11.72
9,10-Dihydroanthracene	12.49	6.96	14.07	—	13.86	16.31
Toluene	13.42	16.24	8.38	6.87	10.14	10.83
2,3-Dihydrobenzothiophene	4.11	0.80	4.10	5.44	4.61	3.86
1-Benzyl-2-methylbenzene	3.08	7.21	5.23	6.27	4.21	4.62
2-Ethyl-naphthalene	1.84	7.12	3.26	3.29	2.81	3.15
2-Methylbiphenyl	1.56	7.90	3.36	2.91	2.45	2.77
2-Methylnaphthalene	1.35	6.00	2.48	2.20	2.22	2.06
2-Butylnaphthalene	2.0	—	1.69	2.33	2.16	1.64
1,2,3,4,5,6,7,8-Octahydroanthracene	0.84	—	—	0.92	1.06	—
Heptane	1.25	1.26	—	—	—	—
Benzene	—	16.95	—	—	—	—
Naphthalene	—	1.89	—	—	—	—
Diphenylmethane	—	0.84	—	—	—	—
2,3-Dimethylbenzothiol + 3,4-dimethylbenzothiol	—	—	—	1.16	—	—

nature on the results of the hydrogenation of the model compounds (Table 1).

In the course of the uncatalyzed hydrogenation of the model compounds, cracking products and hydrogenation products can be formed in almost the same amounts. Hydrogenation products prevailed in an insignificant amount (Table 2). In this case, more than 23% substance remained unreacted (10.52% benzothiophene and 12.69% anthracene).

Upon the addition of a catalyst of iron oxide and elemental sulfur to the system of anthracene and benzothiophene, the main reaction products were cracking products. The concentrations of unreacted anthracene and benzothiophene in the reaction products were 8.66 and 3.27% (Table 2).

The results obtained in the hydrogenation of the model compounds in the presence of a mixture of elemental sulfur and nonferrous metallurgy waste indicate that the concentration ratio between hydrogenol-



Effect of catalytic additives on the yield of products.

ysis and hydrogenation products was 1 : 1 (Table 2). In this reaction, benzothiophene and anthracene residues were 10.61 and 12.97%, respectively.

Published data [2–5] indicate that iron sulfides like pyrite and pyrrhotine can be used as active catalytic additives, for example, in the destructive hydrogenation of solid and heavy hydrocarbon materials (coals, shale, peat, heavy oil residues, and heavy oils). The high catalytic effect of iron sulfides is likely due to the dissociation of hydrogen sulfide on the pyrrhotine surface according to the following reaction scheme:



where the resulting radicals like HS' and H' are hydrogenating agents.

However, the experimental results demonstrated that, in the hydrogenation products, cracking and hydrogenation products accounted for 38 and 32%, respectively (Table 2). Unreacted products also accounted for a noticeable fraction of almost 31% (including 13% benzothiophene and 17.54% anthracene).

The catalyst developed by Shenhua is a nanocatalyst. Currently, it is industrially tested at a plant with the output of 6 million tons of liquid products from coal per annum in Inner Mongolia (PRC) [6]. The

results of experiments on the hydrogenation of a mixture of anthracene and benzothiophene with the use of the nanocatalyst demonstrated that the concentrations of hydrogenation and cracking products were 43 and 36%, respectively (Table 2). Note that the nanocatalyst exhibited high selectivity for anthracene hydrogenation products. The ratios of unreacted benzothiophene to anthracene were almost the same (10.88 and 10.02%, respectively).

To increase the yield of target products in the hydrogenated feed, we performed an experiment with the use of a mixture of iron oxide, elemental sulfur, and nickel sulfate as a catalytic additive. It is well known that nickel and cobalt salts are used as additives in the manufacture of commercial hydrocracking and hydrofining catalysts. The experimental results showed that the amount of hydrogenation products in hydrogenated feed was greater than the amount of hydrogenolysis products. The ratio between unreacted substances was also approximately the same (Table 2).

CONCLUSIONS

The efficiency of catalytic additives can be evaluated in different ways (see the figure).

If we consider the results in terms of the yield of hydrogenolysis products, the mixture of iron sulfide and elemental sulfur is the most efficient among all of the catalytic additives used (experiment 2). In the

same experiment, the lowest amount of unreacted starting material was detected.

The hydrogenation reaction occurs most efficiently on the Shenhua catalyst.

The results of the hydrogenation of the mixture in the presence of iron sulfide did not confirm a predicted increase in the ratio of hydrogenation products to hydrogenolysis products.

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