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ZH. K. KAIRBEKOV, I. M. JELDYBAYEVA, E. T. YERMOLDINA

SSE Research Institute of New Chemical Technologies and Materials,
RSE Al-Farabi Kazakh National University, Almaty, Republic of Kazakhstan

DEVELOPMENT OF NANOSIZED IRON AND IRON-MOLYBDENUM CATALYST BASED ON MAGNETIC COMPOSITES FOR THE HYDROGENATION OF COAL

Abstract. In this paper present the results of catalytic hydrogenation coal from the Kenderlyk deposit contenting various amount of active phase for the process. The methods have been developed giving the ratio Fe (III): Fe (II) to two, which corresponds to magnetite. The dependence of the porous structure of catalysts on the composition and concentration active phase were studied. As a result, it became clear that the activity of the catalysts increases with increase the concentration of Fe_2O_3 on the carrier from 4.0 to 10.0 wt. %, while the yield liquid product increases from 36.0 to 53.1%, at the adding a molybdenum compound (0.5-5%) into the catalyst composition leads to increase the liquid yield to 69.5%, and the yield of the gasoline fraction increases to 20.8% by chromatographic method. Hydrocarbon composition of the gasoline fractions of synthetic oil was determined . The gasoline fraction obtained at the presence of magnetized catalysts, the amount of paraffin hydrocarbons decrease from 32.5 to 13.4% and olefins from 4.2 to 3.2% and in isoparaffin hydrocarbons increase from 22.2 to 28.7% and aromatic hydrocarbons from 25.0 to 36.2% accordingly. Therefore, the optimal catalyst for coal hydrogenation process from Kenderlyk deposit was 10% Fe_2O_3+5% MoO.

Key words: hydrogenation, coal, Kenderlyk, catalyst, magnetic fluids, magnetism, active phase, liquid yield, hydrocarbon composition.

Introduction. From the literature review, coal macromolecules consist of groups of condensed aromatic rings; on average, each group contains about three rings for coal of the middle stage of metamorphism [1-3]. These groups are connected by hydroaromatic and heteroaromatic structures, which determine the spatial three-dimensional arrangement of the macromolecule. The volume of open pores in the studied coal is distributed as follows: the volume (cm^3/g) with a diameter of < 1.2 nm (micropores) is 0.02-0.07; with a diameter of 1.2-3 nm (mesopores) is 0.04-0.1, over 30 nm (macropores) is 0.009-0.09. The total pore volume is 0.07-0.2 cm^3/g. By impregnating coal crushed to 5-10 μm by magnetic fluids prepared in advance according to the method of magnetite synthesis by chemical precipitation, using dispersion medium and hydrocarbon stabilizer with a boiling point of 350-380°C, a magnetic composite was obtained, which is characterized by a uniform distribution of the magnetic material over the surface of the sorbent with particle size from 20 to 100 nm [4, 5].

Herewith, the works on the preparation of the nanosized iron-molybdenum catalyst for coal hydrogenation on the basis of magnetic composites are relevant.

EXPERIMENTAL PROCEDURE

A vibration magnetometer with a working temperature range from 298 to 710 K was used for magnetic measurements, allowing phase analysis of Ni-Cu systems with copper contents from 0 to 56%. The measurement is based on the determination of current magnitude in the measuring coils of a magnetometer, being proportional to the magnetic moment of the sample under study. The nature of the dependence on the magnetization of the sample from the field is expressed by the equation:

$$\mathrm{I(H)} = \mathrm{I}_{\mathrm{Ni}}^{\mathrm{S}} \frac{\mathrm{I}}{\mathrm{I}_{\mathrm{max}}} \frac{\mathrm{V}_{\mathrm{Ni}}}{\mathrm{V}_{\mathrm{sample}}}, \tag{1}$$

where $\mathrm{I}_{\mathrm{Ni}}^{\mathrm{S}}$ is Ni calibration sample magnetization; V_{Ni} is Ni calibration sample bulk volume; $\mathrm{I}_{\mathrm{max}}$ is the magnitude of the current arising in the coils of a magnetometer in the field of N 6 kErst when placing the calibration sample.

Saturation magnetization of the samples under study was determined in a field of 6 kErst at room temperature. The relationship between the current in mA and the magnetization in G is expressed by the equation:

$$\mathrm{I^S[G]} = 0{,}2515\ \frac{\mathrm{G}}{\mathrm{mA}}\mathrm{I[mA]} \tag{2}$$

Since magnetization of the powders depends on their bulk density, a further recalculation was carried out through the specific saturation magnetization σ:

$$\sigma = \frac{\mathrm{I^S}}{\rho} \tag{3}$$

The dependences on the saturation magnetization of the samples on temperature were taken in order to carry out a magnetic phase analysis. The analysis is based on data indicating that Ni and Cu form a continuous series of solid solutions, the Curie temperatures of which fit well into a straight line when the ratio of Ni and Cu varies.

Available data allow calculating the percentage of copper in Ni-Cu systems from experimentally determined values of Curie temperatures.

The sensitivity of a magnetometer for nickel is not less than 0.1 mg, and the measurement error is 5%.

For testing, samples in the following ratio of components: 0.09 mol of Fe^{3+} to 0.06 mol of Fe^{2+} with 50 ml of 28% NH_4OH, 50 ml of fuel oil and 5 ml of oleic acid were prepared.

A nanosized magnetic composite was obtained by co-precipitation of ferrous iron or molybdenum and ferric salts according to the scheme ($Fe^{2+} + 2Fe^{3+} + 8OH^{-} = Fe_3O_4 + 4H_2O$), the fuel oil with a small amount of sodium oleate (3-5 wt.%) was used as the dispersed phase. The prepared high dispersion sample of coal was impregnated with the obtained magnetic fluid.

We have shown that the nanosized iron or iron-molybdenum catalyst is formed on the basis of magnetic composites. The optimal size of the active particles of the catalyst are 40-50 nm The specific surface of the catalyst, calculated from the total isotherms of low-temperature nitrogen adsorption by the Brunauer–Emmett–Teller (BET) method, is 24.0-51.7 m^2/g.

RESULTS AND DISCUSSIONS

In this research work, we synthesized 9 samples of the catalysts differing in the content of active components and the method of their deposition. Characteristics of the catalysts are shown in table 1.

Table 1 – Characteristics of magnetite catalysts

Catalyst No.	Composition of the active phase,% in terms of		Pore volume, cm^3/g		
	MoO	Fe_2O_3	V_Σ	V_{mi}^{MF}	V_{ma}
1	–	10.0	0.257	0.091	0.166
2	–	8.0	0.276	0.105	0.171
3	–	6.0	0.297	0.120	0.177
4	–	4.0	0.325	0.138	0.187
5	0.5	–	0.440	0.192	0.248
6	1.0	–	0.433	0.197	0.236
7	3.0	–	0.418	0.188	0.230
8	5.0	–	0.385	0.160	0.225
9	5.0	10,0	0.227	0.115	0.112

Note. V_{mi}^{MF} is micropore volume during magnetic fluid (MF) adsorption; V_{ma} is macropore volume.

The catalysts No. 1-4 were used to study the effect of Fe_3O_4 concentration on their catalytic activity. In the presence of samples No. 5-8, the effects of Mo concentration on the catalytic properties of catalysts on carbon carriers were studied. The catalyst No. 9 was synthesized to study the effect of the sequence of deposition of the active phase.

The dependence of the porous structure of the catalysts on the composition and concentration of the active phase was studied. As shown by the experimental data, the active phase of the catalyst is evenly distributed in all the pores of the carrier; the volume of micropores and macropores decreased in proportion to the increase in the concentration of the active phase of the catalyst. Micropores with a radius of less than 0.5-0.7 nm had a significant proportion of the total pore volume in the structure in both the initial catalyst carrier and the catalysts. Almost the same contribution to the porous structure for all catalysts was made by macropores, the volume of which changed slightly with varying content of the active phase. The catalysts were characterized by a change in the distribution of pores in a wide range: V_{mi}^{MF} from 0.091 to 0.197 cm^3/g; V_{ma} – from 0.112 to 0.248 cm^3/g.

The developed catalysts are tested in the process of coal hydrogenation. The results of the experiments on coal hydrogenation using magnetic catalysts on a carbon carrier are shown in table 2.

Table 2 – Results of coal hydrogenation in the presence of catalysts with different content of the active phase in the atmosphere of synthesis gas. The ratio of coal : paste-forming agent is 1 : 1,5; Pressure is 5.0 MPa; Temperature is 410 °C

Catalyst No.	Composition of the active phase, %		Magnetization μ_S, experim.	V_{gas}, %	The yield of liquid products, wt. %				Residue, %	Losses, %
	Fe_2O_3	MoO			80-180 °C	180-250 °C	250-320 °C	$\Sigma_{L.P.}$		
–	–	–	–							
4	4.0	–	42.3	12.2	7.2	7.8	21.0	36.0	46.8	5.0
3	6.0	–	43.4	12.1	10.2	9.5	25.0	44.7	38.4	4.8
1	10.0	–	44.8	12.8	12.5	11.5	29.1	53.1	29.2	4.9
8	–	5.0	43.7	12.3	10.4	9.6	29.5	49.5	33.0	5.2
9	10.0	5.0	69.3	10.1	20.8	22.6	26.1	69.5	15.8	4.6

Table 2 shows that the activity of the catalysts increases with increasing concentration of Fe_2O_3 on the carrier from 4.0 to 10.0 wt. %, while the liquid yield is increased from 36.0 to 53.1%. Introduction of Mo compound to the catalyst composition leads to an increase in the liquid yield to 69.5%. This increases the yield of the gasoline fraction to 20.8%.

The effect of increasing the total porosity of the carrier on the activity of the catalyst during hydrogenation can probably be primarily explained by the simultaneous growth of not only the volume, but also the size of all pores in the structure, which makes the active phase of the catalyst more accessible to reagent molecules (table 1). However, such a change in the structure of the carrier (respectively, the catalyst) causes an increase in desorption time of the reaction products adsorbed on the catalyst, which contributes to an increase in the depth of destruction of the coal substance and, consequently, an increase in the liquid yield.

In addition to the porous structure, the content of active components, such as Fe and Mo oxides, has a great effect on the activity of heterogeneous catalysts in coal hydrogenation. It was found that for deep conversion of organic coal mass, the content of Fe oxide in the wide-porous catalyst may not exceed 4-10%, and the total content of active components – 5-10.0%. A higher content of active components leads to a decrease in the activity of wide-porous Mo-Fe catalysts during coal hydrogenation.

The results obtained by us during hydrogenation of coal from the Kenderlyk deposit in the presence of molybdenum-iron catalysts allow us concluding that, like in the case of industrial Al-Mo-Co catalysts, samples with large pores in the amount of 0.227 cm^3/g contain 10% Fe_2O_3 and 5.0% Mo oxide in their composition.

It should be noted according to table 2 that, apart from porosity, the magnitude of the magnetic composites used is of great importance to the activity of the studied catalysts, and the higher the magnetic properties of the catalyst, the more active they are in the process of coal hydrogenation.

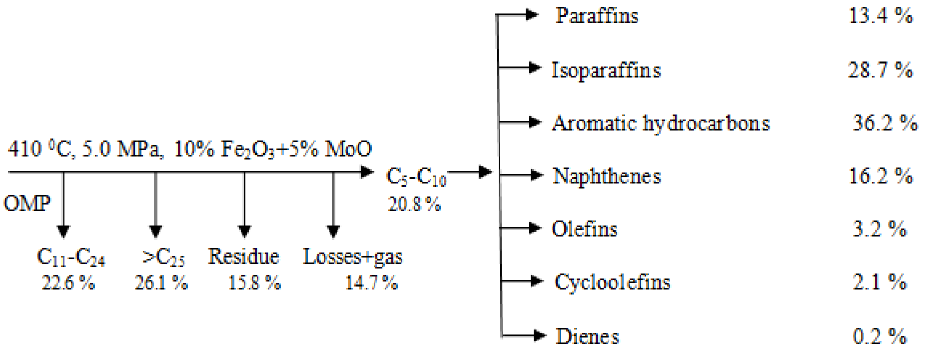
Further a chromatographic study of the products obtained was carried out (table 3).

Table 3 – Hydrocarbon composition of the gasoline fractions,
obtained by hydrogenation of coal from Kenderlyk deposit

Hydrocarbons	Hydrocarbon composition, %			
	Initial	Fe_2O_3	MoO	10 % Fe_2O_3 + 5 % MoO
Paraffins	32.5	23.2	14.7	13.4
Isoparaffins	22.2	27.6	26.0	28.7
Aromatic hydrocarbons	25.0	22.7	34.1	36.2
Naphthenes	14.2	17.2	17.8	16.2
Olefins	4.2	3.8	3.8	3.2
Cycloolefins	1.9	5.2	3.5	2.1
Dienes	–	0.3	0.1	0.2

According to the obtained data of chromatographic analysis, it can be seen that in the composition of the initial gasoline fractions obtained by hydrogenation of coal from the Kenderlyk deposit compared with the gasoline fractions obtained in the presence of magnetized catalysts, the amount of paraffin hydrocarbons decreases from 32.5 to 13.4% and olefins from 4.2 to 3,2%, and an increase in isoparaffin hydrocarbons from 22.2 to 28.7% and aromatic hydrocarbons from 25.0 to 36.2% is observed, which has a positive effect on the performance of motor fuels.

A scheme was drawn for the transformation of the organic mass of coal paste in the hydrogenation process (figure) based on the results obtained (tables 2, 3).



Scheme of transformation of the organic mass of paste during hydrogenation
of distillates of coal liquefaction

Thus, in the process of performing the work, it was established that the advantage of magnetic adsorbents and catalysts compared to ordinary (non-magnetic one) is that possessing high sorption and catalytic capacity, they can be controlled using a magnetic field, which greatly simplifies the processes and increases the completeness of adsorbent development, eliminates time-consuming stages of separation of the spent adsorbent from the solution and catalyst regeneration, replacing them with magnetic separation.

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Резюме

Ж. К. Каирбеков, И. М. Джелдыбаева, Э. Т. Ермолдина

КӨМІРДІ ГИДРОГЕНДЕУ ҮШІН МАГНИТТІ КОМПОЗИТТЕР НЕГІЗІНДЕ НАНОӨЛШЕМДІ ТЕМІР ЖӘНЕ ТЕМІРМОЛИБДЕНДІ КАТАЛИЗАТОРЛАРДЫ АЛУ

Бұл мақалада үрдістің катализаторы ретінде әртүрлі құрамды белсенді фазаның қатсында Кендірлік кен орнынан алынған көмірді гидрогенизациялау нәтижелері келтірілген. Магнетитке сәйкес келетін Fe (III) мен Fe (II) арасындағы сәйкестікті екіге дейін келтіру әдістері әзірленді. Катализаторлардың кеуекті құрылымының белсенді фазасының құрамы мен концентрациясына тәуелділігі зерттелінді. Нәтижесінде, Fe_2O_3 концентрациясының 4-ден 10,0% - әзгеруі катализаторлардың белсенділігі артүрадырады , сұйық өнімдердің шығымы 36,0-ден 53,1% -ға дейін артады. Ал катализаторлық композицияға молибден қосылысын (0,5-5%) енгізу, сұйық өнімдердің шығымын 69,5%-дейін арттырады. Бұл бензиннің үлесін 20,8%-ға дейін арттырады. Хроматографиялық әдіс арқылы синтетикалық мұнайдан алынған бензин фракцияларының көмірсутектік құрамы анықталынды. Магниттелген катализаторлардың қатысуымен алынған бензин фракциясында парафинді көмірсутектердің мөлшері 32,5-тен 13,4%-ға және олефиндер 4,2-ден 3,2%-ға дейін төмендеуі байқалады, сондай-ақ изопарафин көмірсутектерінің 22,2-ден 28,7-ге дейін және ароматты көмірсутектер 25,0% -дан 36,2% -ға дейін артуы байқалады. Демең Кендерлік кен орны көмірін гидрогендеу үрдісінің оңтайлы катализаторы ретінде 10% Fe_2O_3 + 5% MoO ұсынылады

Түйін сөздер: гидрогендеу, көмір, Кендірлік, катализатор, магнитті сұйықтықтар, магнетизм, белсенді фаза, сұйық өнімдер шығымы, көмірсутектік құрамы.

Резюме

Ж. К. Каирбеков, И. М. Джелдыбаева, Э. Т. Ермолдина

ПОЛУЧЕНИЕ НАНОРАЗМЕРНЫХ ЖЕЛЕЗНЫХ И ЖЕЛЕЗО-МОЛИБДЕНОВЫХ КАТАЛИЗАТОРОВ ДЛЯ ГИДРОГЕНИЗАЦИЙ УГЛЯ НА ОСНОВЕ МАГНИТНЫХ КОМПОЗИТОВ

В данной статье приведены результаты гидрогенизации угля месторождения Кендерлык с различным содержанием активной фазы в качестве катализаторов процесса. Разработаны способы доведения соотношения Fe(III) к Fe(II) до двух, что соответствует магнетиту. Была изучена зависимость пористой структуры катализаторов от состава и концентрации активной фазы. В результате выяснилось, что активность катализаторов возрастает с увеличением концентрации Fe_2O_3 на носителе с 4,0 до 10,0 масс. %, при этом выход жидких продуктов увеличивается с 36,0 до 53,1 %, а введение в состав катализатора соединении молибдена (0,5-5 %) приводит к увеличению выхода жидких продуктов до 69,5 %. При этом увеличивается выход бензиновой фракции до 20,8 %. Хроматографическим методом определен углеводородный состав бензиновых фракций синтетической нефти. В бензиновых фракциях, полученных в присутствии намагниченных катализаторов, наблюдается уменьшение количества парафиновых углеводородов с 32,5 до 13,4 % и олефинов с 4,2 до 3,2 %, а также наблюдается увеличение изопарафиновых углеводородов с 22,2 до 28,7 % и ароматических углеводоров с 25,0 до 36,2 %. Поэтому оптимальным катализатором для процесса гидрогенизаций угля месторождения Кендерлык был выбран 10% Fe_2O_3+5% MoO.

Ключевые слова: гидрогенизация, уголь, Кендерлык, катализатор, магнитные жидкости, магнетизм, активная фаза, выход жидких продуктов, углеводородный состав.