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INFLUENCE OF THE COMPOSITION OF CATALYST SUPPORTED BY ZEOLITE IN THE HYDROGENATION OF FUEL OIL

Abstract. Hydrocarbon raw material consists of condensed aromatic hydrocarbons and other high-molecular compounds, is a complex mixture of organic and mineral substances. The results of the hydrogenation of heavy hydrocarbon feedstocks - fuel oil fraction. In the process of hydrogenation of the fuel oil fraction, in the presence of a zeolite carrier impregnated with highly disperse iron-containing additives, it can be stated that the synthesized catalyst exhibits high activity in hydrogenation processes, hydro destruction of the object of investigation. Determined amount of gas and coke fraction. The amount of gas + fraction is taken as the depth of decomposition. With an increase in the activity of the zeolite more energy intensive coke formation of condensed mechanism increases faster than the polymerization-redistribution mechanism.

Key words: hydrogenation, fraction of oil, temperature, hydrogen pressure, catalyst.

Introduction. The study of the theory and practice of the heavy hydrocarbon feedstock hydrogenation (HFH) in the Common wealth of Independent States (the CIS) and other countries shows that the main reactions of hydrogenation processes which comprise HFH are hydrogenation and dehydrogenation. Analysis showed that the nature of these processes is that they involve movable equilibrium position is determined by factors such as pressure and hydrogen temperature [1-4].

At present, despite the ever-increasing volumes of oil production and refining, not only in the Republic of Kazakhstan, but all over the world, large-scale, intensive research aimed at more efficient use of high molecular weight hydrocarbon feedstock [5].

It should be noted that today in many countries of the world continue to research and pilot projects to improve and improve the performance of the individual stages processes hydrogenation processing HFH and liquefaction products that can significantly improve the efficiency of the method as a whole.

Transformations occurring during the destructive hydrogenation of complex organic substances, which are representatives of oil, fuel oil, coal, etc., are best shown in the individual hydrocarbon compounds.

Previously, the authors synthesized composite catalysts based on Group VIII metal compounds (Fe, Ni, Co) deposited on zeolites (Fe_2O_3/CaA (Fe_2O_3/ZSM), NiO/CaA (NiO/ZSM), their activity in the hydrogenation of model compounds (anthracene), a number of active catalysts [6].

In order to continue research conducted to study the influence of a catalyst system based on zeolites and compounds of iron and cobalt hydrogenation process heavy hydrocarbon feedstock, particularly heavy fuel oil fraction.

Fuel oil is a liquid hydrocarbon product of dark brown color. A mixture of heavy distillation residues of gasoline, kerosene and gas oil (boiling at temperatures below 350-360^{0}C) of oil products or its recycling [7].

EXPERIMENTAL PART

Experiments of hydrogenation fuel oil fraction was carried out in a high pressure autoclave «CJF-0,05» of heat-resistant stainless steel with a capacity 0.05 L. Pre-mixed starting components were placed into the reactor was sealed, purged with hydrogen and the hydrogen was pumped to 4.0 MPa, heated to 400°C at a heating rate of 10°C per minute.Process duration was 60 minutes after reaching the operating temperature of the autoclave. After the end of the experiment, the reactor was cooled to room temperature the composition of the reaction mixture was determined by chromatography-mass spectrometric (CMS) and gas-liquid (GLC) analysis.

By varying the conditions can be controlled with progress of the hydrogenation process of obtaining target products. Composition of fuel oil fraction identified during the experiment (table 1).

GLC analysis of the initial fraction fuel oil and products of hydrogenation was conducted on a chromatograph "4000 Krystallux M" with PID detector column ZB-5 30 m x 0.53 mm x 1.50 μm. with the programming of the temperature of the thermostat 60-250^{0}C at a temperature rise rate of 6 ^{0}C/min. GLC analysis of gaseous products was carried out on a chromatograph "Krystallux 4000 M" (Russia) with the detector module 2DTP/PFID, on a column of CaA 1 -3 m, d-3 mm for constant gases and column Porapak R 1- 3 m, d-3 mm for hydrocarbon gases. GLC analysis of the liquid components was carried out on a chromatograph "Krystallux 4000 M" with a PID detector on a column DB-5 ms 30 mm x 0.250 mm x 0.50 μm. Data processing was provided by the program "NetChrom v. 2.1" (table 1 and figure 1).

The premixed starting components were placed in a reactor, sealed, flushed with hydrogen, and hydrogen overpressure. The onset of the reaction was the time when the autoclave reached operating temperature. The heating rate of the autoclave was 10°C per minute. After the experiment, the reactor was cooled to room temperature the composition of the reaction products was determined by GLC analysis (table 2 and figure 2).

Table 1 – Composition of the fuel oil

#	Component	Time, min	Fraction, %
1	i-octane	4,86	1,40
2	Octane	6,41	2,03
3	1-octene	7,08	1,59
4	1-nonen	9,79	1,10
5	Nonane	10,07	1,97
6	1-decene	13,17	1,13
7	Decane	13,47	2,15
8	1-undecene	16,67	1,35
9	Undecane	16,96	1,84
10	1,2,4,5-tetramethylbenzene	19,09	1,00
11	1-dodecene	20,09	1,01
12	Dodecane	20,37	2,40
13	1-tridecene	23,37	1,08
14	Tridecane	23,62	2,30
15	1-methylnaphthalene	24,16	1,28
16	1-tetradecene	26,47	0,72
17	Tetradecane	26,70	2,55
18	1-pentadecene	29,40	0,74
19	Pentadecane	29,61	2,59
20	1-hexadecene	32,17	0,83
21	Hexadecane	32,36	2,59
22	1-heptadecene	34,81	0,35
23	Heptadecane	34,97	3,27
24	1-octadecene	37,28	0,45
25	Octadecane	37,45	2,58
26	Nonadecane	39,80	2,87
27	Eikozan	42,05	2,84
28	Aneykosan	44,19	2,60
29	Dokozan	46,21	2,32
30	Tricosan	48,22	2,13
31	Tetracosane	50,36	1,79
32	Pentacosane	52,73	1,31
33	Hexacosane	55,58	0,94
34	Heptakosan	58,97	0,62
35	Octacosan	63,08	0,36
36	Nonacosane	68,11	0,34
37	Triacontan	74,42	0,16

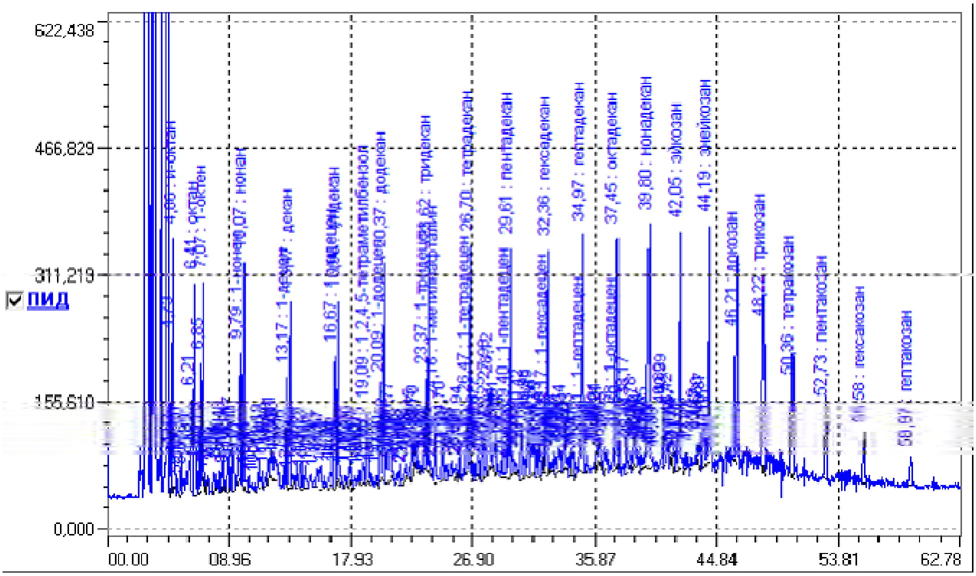


Figure 1 – Chromatogram of the initial fraction of fuel oil

Table 2 – Composition of fuel oil in the hydrogenation at the presence of catalyst Fe_2O_3/CaA

#	Component	Time, min	Fraction, %
1	i-octane	4,87	1,09
2	Octane	6,40	3,892
3	1-octene	7,05	1,8
4	1-nonen	9,73	0,2926
5	Nonane	10,01	2,509
6	1-decene	13,11	0,1329
7	Decane	13,45	1,035
8	1-undecene	16,63	0,6692
9	Undecane	16,90	0,582
10	1,2,4,5-tetramethylbenzene	19,02	0,9559
11	1-dodecene	20,06	0,1592
12	Dodecane	20,31	1,22
13	Tridecene	23,72	0,1928
14	1-tetradecane	26,65	0,7388
15	1-pentadecene	29,56	0,3146
16	Pentadecane	29,74	0,4114
17	1-hexadecene	35,20	0,2119
18	Heptadecane	35,20	0,2119
19	Nonadecane	40,32	0,1373

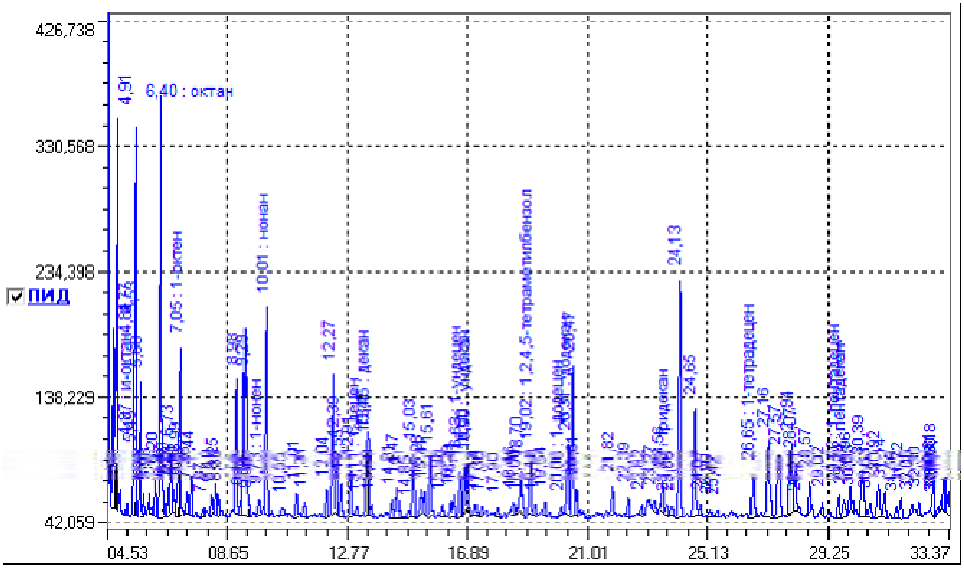


Figure 2 – Chromatogram of fraction
in the hydrogenation of fuel oil at presence of catalyst Fe_2O_3/CaA

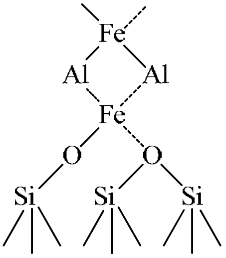
RESULT AND DISCUSSION

Analyzing the chromatogram shown in Figure 2 it was found that there are peaks of saturated hydrocarbon derivatives 12.23%, the amount of iso-derivatives of hydrocarbons was 1.09%. Also tetramethylbenzene is present in an amount of less than 1%.

These data show that at this temperature for all paraffin have stepwise mechanism makes the main contribution to the reaction rate. Relative reaction rate in the range of paraffin in this case changes.

Note that format structures formed by paraffin adsorption on the catalyst surface and decompose sufficiently thermo stable under vacuum at 420^0C. At temperatures above 400^0C the main contribution to the rate of catalysis makes stepwise mechanism. This is consistent with the proposed reaction scheme [8], since the thermal decomposition of the surface structures at temperatures above 400^0C should lead to a decrease in the proportion of the associative mechanism and the stepwise transition to a mechanism that is observed the experiments.

We can assume that in the surface complex coordination number of the iron ion is four. In this case, the surface structure of the complex with the iron coor-dination can be depicted as follows:



In this structure, it is considered that the surface ligands of the iron ion are oxygen, previously associated with a proton carrier and atoms (aluminum silicon). However, this structure may be the dominant, but not the only. It is possible that in the formation of a surface complex, in view of the heterogeneity of the zeolite surface, a certain set of coordination states is realized, the proportion of each of which depends both on the conditions of preliminary dehydration of the carrier and on the amount of the complex. Heterogeneity focal states, apparently increases with increasing temperature and dehydration with increasing concentrations of surface complex; this causes a large number of allowed optical transitions, resulting in a product of almost black color.

Source "cells" size zeolite CaA not more 11,6Ǻ, therefore, should be observed difficulties in penetrating molecules of iron oxide into the inner cavities of the zeolite, especially considering the possibility of adsorption of molecules in the input "cells". Since the nature of the active centers of the zeolite is the same, comparing the results of hydrogenation of fuel oil on iron-containing catalysts on an alumina-silicate substrate allows more clearly to reveal the effects associated with the screening action of the latter.

When Fe_2O_3 converted to aluminosilicate gives less than 1% of the decomposition products, so the depth of hydrogenation was calculated in the weight (%) content of paraffins. Determined amount of gas and coke fraction.For the adopted depth decomposition gas amount + fraction. Reducing the coke yield apparently due to the difficulty of penetration of the molecules of the heavy hydrocarbon feedstock into the inner cavity of the zeolite catalyst Fe_2O_3.Consequently, with the increase in zeolite activity, the more energy-intensive coke production by the condensed mechanism increases more rapidly than by the redistribution-polymerization mechanism.

Conclusion. Thus, analysis of the data leads to the conclusion that the catalytic oxidation of n-paraffin relative reaction speed depends on recent process mechanism. In the case of stepwise mechanism oxidation rate increases with increasing number of carbon atoms per paraffin molecule. Thus, the reaction rate is limited by the interaction of the hydrocarbon with the surface of the catalyst Fe_2O_3/CaA, at which the CH bond in the paraffin molecule.

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Резюме

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МАЗУТ ФРАКЦИЯСЫНЫҢ ГИДРОГЕНИЗАЦИЯ ҮРДІСІНДЕГІ ЦЕОЛИТ НЕГІЗІНДЕ КОМПОЗИТТІ КАТАЛИЗАТОРЛАРДЫҢ ӘСЕРІ

Көмірсутекті шикізат органикалық және минералды заттардың қоспасы болып саналып, конденсирленген ароматикалық көмірсутектерінен және жоғары молекулалық қосылыстардан тұрады. Мақалада ауыр көмірсутегі шикізатының – мазут фракциясының гидрогенизация нәтижелері көрсетілді. Мазут фракциясының цеолит тасымалдағышы қатысында, жоғарыдисперсті темір және кобальт құрамды қосылыстармен импрегнирленген қоспалар қатысындағы гидрогенизация үрдісі нәтижесінде келесі тұжырым жасауға болады, синтезделген катализатор зерттеу нысанының гидрлеу, гидродеструкция үрдістері кезінде жоғары белсенділігін көрсетеді. Газ, фракция мен кокс көлемдері анықталды. Ыдырау тереңдігі ретінде газ+фракциясының қосындысы алынған. Цеолиттің белсенділігінің жоғарлауымен энергоыңғайлы кокс түзілуі қайта бөлу-полимеризациялану механизммен салыстырғанда конденсациялау бойынша тезірек жүреді.

Түйін сөздер: гидрогенизация, мазут фракциясы,температура, сутегі қысымы, катализатор.

Резюме

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А. Т. Ордабаева, М. И. Байкенов, Д. С. Исабекова

ВЛИЯНИЕ КОМПОЗИТНЫХ КАТАЛИЗАТОРОВ НА ОСНОВЕ ЦЕОЛИТА В ПРОЦЕССЕ ГИДРОГЕНИЗАЦИИ ФРАКЦИИ МАЗУТА

Углеводородное сырье состоит из конденсированных ароматических углеводородов и других высокомолекулярных соединений, является сложной смесью органических и минеральных веществ. В работе представлены результаты гидрогенизации тяжелого углеводородного сырья – фракции мазута. В процессе гидрогенизации фракции мазута, в присутствии цеолитного носителя, импрегнированных высокодисперсными железосодержащими добавками, можно констатировать, что синтезированный катализатор проявляет высокую активность в процессах гидрирования, гидродеструкции объекта исследования. Определялось количество газа, фракции и кокса. За глубину разложения принята сумма газ+фракция. С повышением активности цеолита более энергоемкое образование кокса по конденсированному механизму нарастает быстрее, чем по перераспределительно-полимеризационному механизму.

Ключевые слова: гидрогенизация, фракция мазута,температура, давление водорода, катализатор.