

NEWS

OF THE NATIONAL ACADEMY OF SCIENCES OF THE REPUBLIC OF KAZAKHSTAN

SERIES OF GEOLOGY AND TECHNICAL SCIENCES

ISSN 2224-5278

Volume 2, Number 428 (2018), 112 – 117

UDC 662.67, 661.715, 541.128.13

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COBALT CATALYST ON THE BASIS OF THE KENDYRLIK SHALE AND ITS APPROBATION IN FISHER-TROPSH SYNTHESIS

Abstract. The method of preparation of the cobalt catalyst and the results of the Fischer-Tropsch synthesis on the resulting catalyst, in which the shale of the Kendyrlík deposit was used as the support, zirconia was used as the promoter. The shale was pretreated by carbonization in an inert argon medium in the temperature range of 25-700°C and activation by steam at 850-900°C for 60 minutes. The catalyst (composition of 10%Co/1%ZrO₂/89%slate) in a volume of 100 ml was prepared by double impregnation, wherein salts hexahydrate of cobalt nitrate Co(NO₃)₂·6H₂O and zirconium oxonitrate ZrO(NO₃)₃·2H₂O were used. Further, the resulting catalyst was tested in Fischer-Tropsch synthesis in order to produce synthetic hydrocarbons. The catalyst was preliminarily reduced in a hydrogen atmosphere at 350°C for 1 hour, at a hydrogen space velocity of 1000 h⁻¹ and a pressure of 0.2 MPa. The synthesis was carried out (at a molar ratio of H₂/CO/N₂ = 2/1/0.2) in the temperature range 160-220°C, at a space velocity of 500 h⁻¹, and a pressure of 1.0 MPa. Chromatographic analysis of the hydrocarbons C₆-C₂₁ obtained showed that mainly alkanes and arenes are formed during the synthesis.

Keywords: catalyst, cobalt, shale, Kendyrlík, activation, Fischer-Tropsch synthesis, hydrocarbons.

Introduction. At present, much attention is paid to the implementation of selective Fischer-Tropsch synthesis (FT synthesis), in particular, to the synthesis of linear alkanes C₁₁-C₁₈, C₅-C₁₀ isoalkanes, solid linear paraffins [1]. This catalytic process occurs by hydrogenation of the carbon monoxide with hydrogen and includes the steps of polymerization, oligomerization, alkylation.

In FT synthesis, iron-containing and cobalt-containing catalysts are commonly used. In addition, Ni and Ru catalysts are also active, but their use seems ineffective due to low selectivity to higher hydrocarbons (Ni) and higher costs (Ru) [2].

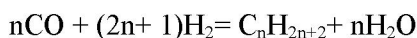
To maintain high activity and selectivity of FT synthesis catalysts, in addition to varying the composition and conditions of preparation, a special organization of the catalytic layer is necessary in order to reduce the probability of overheating and reduce the gas-dynamic resistance. Particularly negatively affect the catalyst overheating, accompanied by coking and deactivation of the catalyst [3].

The main requirements for the organization of the catalytic layer for FT synthesis are: high concentration of the catalytically active component in the reaction volume, small characteristic particle size of the catalyst, high effective thermal conductivity of the catalyst layer, thermal stability and high mechanical strength of the catalyst, low hydraulic resistance [4].

However, these requirements do not always correspond to the requirements of existing process schemes using conventional catalysts in a suspended, fixed or fluidized bed [5]. In this regard, increasing the efficiency of the process of obtaining hydrocarbons from synthesis gas requires the development of new catalysts.

Products of FT-synthesis are of great practical importance as carbon-chemical raw materials, especially in connection with the fact that they contain many olefins, mainly of normal structure. The development of catalysts with improved catalytic properties and directional selectivity is of particular practical

interest and includes the study of new supports, catalytic compositions, and the conditions for their formation. Promising catalysts for the synthesis of hydrocarbons from CO and H₂ include cobalt systems that allow selective production of linear alkanes [1]:



Usually, Al₂O₃, SiO₂, TiO₂ are used as support for cobalt catalysts [6]. Their main disadvantage is the intensive interaction with the metal, leading to the formation of mixed compounds, which lose the active phase and have a very high reduction temperature. One way to solve this problem is to use carbon supports that have little interaction with metal catalysts. Carbon supports have a number of unique structural properties and are of interest for catalysts in heterogeneous catalysis [6]. Carbon materials used as supports can be divided into several groups: activated carbon, carbon black, graphite, carbon nanotubes [7].

Especially it is necessary to allocate catalysts on cement (alumo-calcium) basis, which are characterized by high activity and productivity, mechanical strength, and also the ability to prevent them from carbonization [8].

The source of carbonaceous catalyst carriers can be shale rocks, which are available in Kazakhstan in sufficient quantities for their industrial use. Thus, the creation of fundamental and technological fundamentals for the production of new materials for gas-phase synthesis becomes particularly relevant.

The aim of this work is to prepare Co catalysts in which the shale of the Kendyrlík deposit was used as the support, followed by their testing in the Fischer-Tropsch synthesis to produce liquid hydrocarbons.

Experimental part. For the catalyst preparation (10%Co/1%ZrO₂/89%shale), the following reagents were used: cobalt nitrate Co(NO₃)₂·6H₂O six-water salt, zirconium oxonitrate ZrO(NO₃)₃·2H₂O. Table 1 shows the main characteristics of the reagents.

Table 1 – Characteristics of reagents

Reagents	Content, %
Co(NO ₃) ₂ ·6H ₂ O	Co.....99.000 not less
	Ni0.010 not more
	Sulfates.....0.003 not more
	Chlorides.....0.001 not more
ZrO(NO ₃) ₃ ·2H ₂ O	99.95
CO	99.999
H ₂	99.95

To use Kendyrlík shale as a carrier, it was preliminarily ground on a hammer mill (Molot-200) to a fraction of 0.1 mm and granulated samples with a diameter of 0.8 cm were obtained from the obtained powder on a tablet press (model 1000). The samples were then subjected to processes of carbonization in an inert argon medium in the temperature range 25-700 ° C and then activation by steam at 850-900 ° C for 60 minutes.

The quantity of ingredients for the preparation of catalysts in a volume of 100 ml (weight 77 g) was: shale support– 68,53 g, metal Co - 7.7 g, zirconium Zr - 0.77 g, salt (for dissolution with water) - 2.22 g, distilled water - 13,23 ml.

The catalysts were prepared by the double impregnation method as follows. The metal salts of ZrO(NO₃)₂·2H₂O, Co (NO₃)₂·6H₂O were dissolved in distilled water in a certain proportion. The concentration of solutions was selected based on the desired content of the active metal and the promoter in the catalyst. The resulting solution was gradually added to the support, continuously mixing it. Then, it was left at room temperature for 1 hour, so that the solution completely absorbed onto the support. The sample was then dried at 100 °C for 12 hours, followed by calcination in a Thermogravimetric Analyzer "ThermosterEltra" at 350 °C for 1 hour in an inert argon medium. The prepared catalysts were stored in desiccators.

Catalytic tests of the obtained Co catalyst were carried out in a laboratory flow-through installation with a tubular reactor with a fixed catalyst bed at atmospheric pressure (figure 1). For the synthesis, cylinders with gases (CO, H₂, N₂) were used, the degree of purity was not less than 99%.

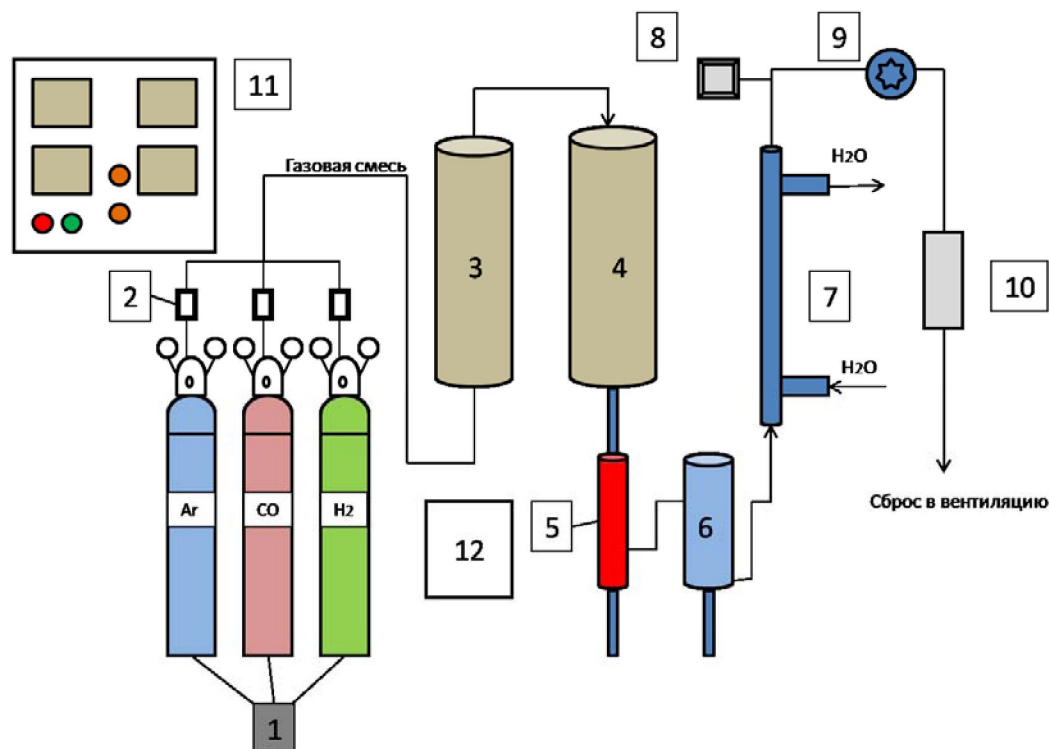


Figure 1 – Scheme of the Fischer-Tropsch bench installation:

1 – cylinders with gas; 2 – gas flow regulator; 3 – oven; 4 – tubular reactor; 5 – hot separator; 6 – cold separator; 7 – refrigerator; 8 – pressure sensor; 9 – pressure regulator "up to itself"; 10 – gas meter; 11 – control unit; 12 – thermostat

Reactor (4), an inner diameter of 20 mm with a thermocouple inlet, was filled with 100 cm³ of a catalyst diluted with 30 cm³ of quartz.

Prior to the synthesis, the apparatus was purged with an inert gas of N₂ for 30 minutes, at a space velocity of 500 h⁻¹. The reduction of the catalyst was carried out at a temperature of 350 °C in hydrogen medium for 3 hours, at a hydrogen space velocity of 1000 h⁻¹, pressure 0.2 MPa.

The synthesis of liquid products was carried out as follows. In the first stage, the temperature was raised to 100 °C and held for 30 minutes to remove moisture. In a second step, the reactor was gradually heated to a temperature of 300 °C at a rate of 1 °C/min. At this stage, hydrogen was fed into the system at a space velocity of 100 h⁻¹. The third stage is directly the catalyst reduction process described above. The fourth stage is cooling the reactor to the synthesis temperature (160-220 °C). When the predetermined synthesis temperature (160 °C) was reached, CO was supplied. The pressure in the system is created by the pressure regulator "up to itself" (9), and the indicators are fixed by the pressure sensor (8). The required gas flow was set using the flow regulators (2). The gas mixture, at a molar ratio of H₂/CO/N₂ = 2/1/0.2, was sent to the preheating furnace (3) and then to the tubular reactor (4). Further, the mixture consisting of reaction products and unreacted synthesis gas passes hot and cold separators (5) and (6). In the refrigerator (7) condensation of gaseous products occurs. The total gas flow was determined by the gas meter. The temperature in the reactor and furnace was recorded with Pt-100 thermocouples. The temperature in the reactor was maintained with an accuracy of ± 0.5 °C. The synthesis was carried out at a pressure of 1.0 MPa and a space velocity of 500 h⁻¹.

Thermalan (Silica S4) was used as a coolant. Circulation of the coolant through the system was carried out using a thermostat. The liquid synthesis products condensed sequentially in the hot separator (5) and in the cold separator (6) were collected and extracted with diethyl ether. Unreacted gases and light hydrocarbons that do not condense in the separators were sent to the vent.

The element composition, structure and dimension of the Co catalyst were studied by energy dispersive X-ray spectroscopy using a SEM device (Quanta 3D 200i) with an attachment for energy-dispersive analysis from EDAX.

An analysis of the component composition of the liquid products of FT synthesis was carried out on a chromatograph called Chromos GC-1000.

Electron microscopic images (with magnitudes x30000 and x100000) and elemental composition of Co catalyst are presented in figures 2 and 3. Analysis of the obtained data showed that the structure of the catalyst is represented by large aggregation of metal particles (Co, Zr) of various geometric shapes deposited on the surface of shale supports, the sizes of which are 200-350 nm.

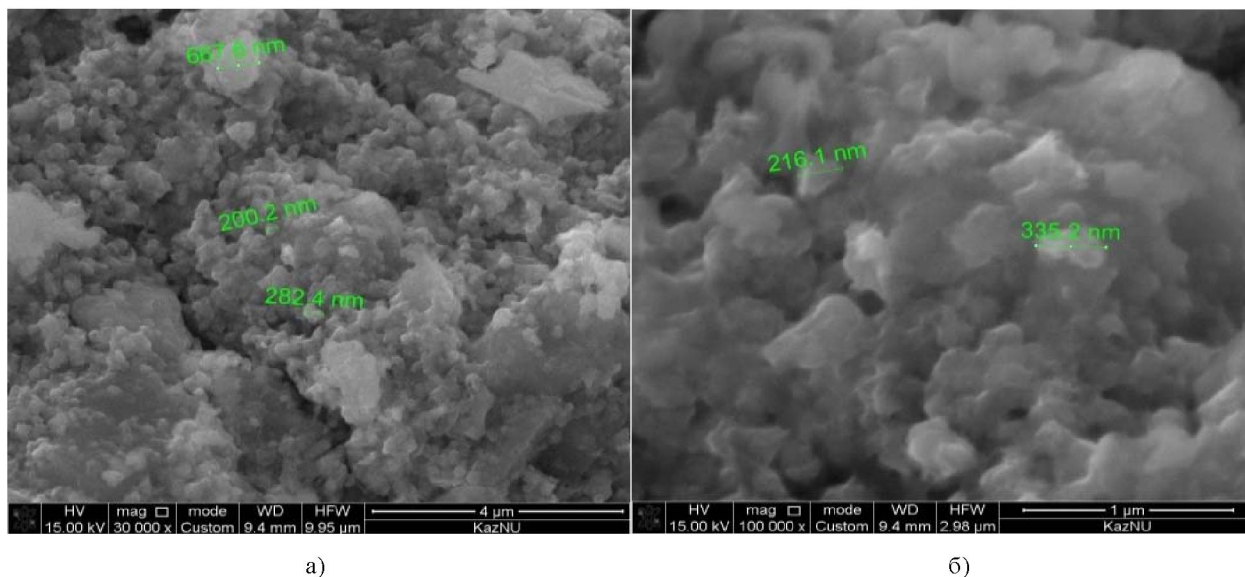
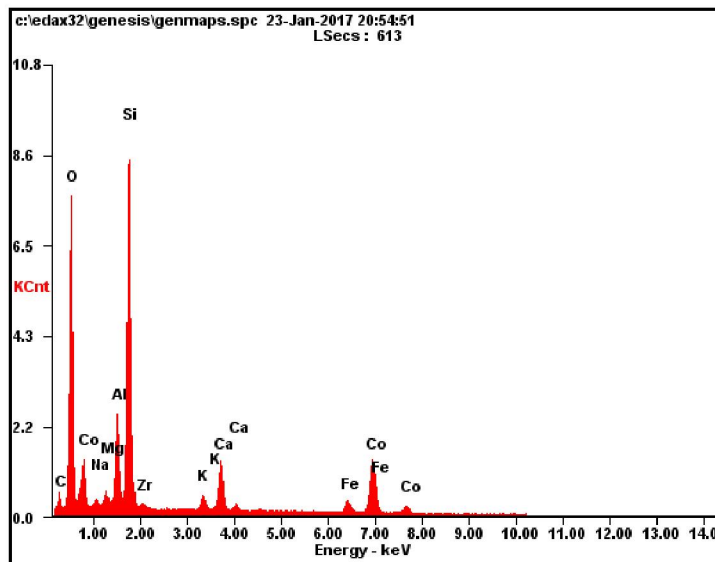


Figure 2 – SEM-image of Co-catalyst magnifications:
a) x30 000; b) 100 000



Element	W, %
C	5.02
O	30.27
Na	0.62
Mg	0.95
Al	4.84
Si	20.26
Zr	1.07
K	1.56
Ca	5.45
Fe	4.28
Co	10.23

Figure 3 – Elemental composition of Co-catalyst

As can be seen from figure 3, the elemental composition of the prepared catalysts, with satisfactory accuracy, corresponds to their assigned composition (10%Co/1%ZrO₂/89%shale). The deviation for cobalt and zirconium is, respectively: +2.3% and +7%.

The results of the Fischer-Tropsch synthesis are presented in table 2. The component composition of the liquid hydrocarbon fractions formed is represented by a set of compounds C₆-C₂₁ (alkanes, isoalkanes, isoalkenes, arenes, isocycloalkanes). Alkanes and arenes are predominantly formed during the synthesis, among which the main share is 1-methyl-2,4-diethylbenzene, n-tridecane, n-oscadecane, i-butylcyclohexane.

Table 2 – Component composition of liquid products of FT-synthesis

Components	Concentration, wt. %
n-hexane	1.580
n-undecane	0.570
1-methyl-2,4-diethylbenzene	9.078
n-dodecane	0.331
c6-Benzene-2	0.453
tridecene-1	1.270
n-tridecane	8.744
n-okadekan	6.363
2,4-dimethylhexane	0.093
1,2,4-trimethylbenzene	1.346
t-butylbenzene	0.884
i-butylcyclohexane	10.194
1.2.3-trimethylbenzene	2.873
butylcyclohexane	0.440
2-methyl-n-butylbenzene	1.291
1.2.3.4-Tetramethylbenzene	0.667
Naphthalene	2.172
1.2.4-triethylbenzene	0.694
n-tetradecane	0.670
n-C ₁₉	4.876
n-C ₂₀	4.649
n-C ₂₁	4.284

Conclusions. A distinctive feature of the new cobalt-containing catalysts obtained in comparison with many catalysts used in petrochemistry (based on Al₂O₃, SiO₂, etc.) is that Kendyrylyk shale was chosen as the carrier, which was previously activated in the process of high-temperature treatment in a water vapor medium. Such an influence promotes the formation of a developed microporous structure, an increase in the specific surface and other adsorption characteristics [9, 10]. This directly affects the increase in the activated properties of the catalyst and the selectivity with respect to the formation of synthetic hydrocarbons, in this case C6-C21. Thus, the use of activated shale (when modified with Co and Zr metal ions) as a catalyst support can be a promising direction in catalysis.

The present work was carried out within the framework of the scientific and technical program No. 0020/PTF-15 on the topic: "Development of technologies and creation of a pilot complex for deep processing of Kazakh shales with a feedstock capacity of 250 tons per year", funded by the Science Committee of the Ministry of Education and Science of the Republic of Kazakhstan.

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КЕНДІРЛІК СЛАНЕЦ НЕГІЗІНДЕ КОБАЛЬТ КАТАЛИЗАТОРЫН АЛУ ЖӘНЕ ОНЫ ФИШЕР-ТРОПШ СИНТЕЗІНДЕ АПРОБАЦИЯДАН ӨТКІЗУ

Аннотация. Жұмыста «Кендірлік» кенішінен алынған сланец негізінде кобальт катализаторын дайындау әдісі және Фишер-Тропш синтезінде апробация нәтижелері келтірілген, промотор ретінде цирконий диоксиді қолданылды. Сланец алдымен аргон қатысында, инертті ортада 25-700 °С температура интервалында карбонизация және 850-900 °С аралықта 60 минут көлемінде су буымен активация әдісімен өңделді. Катализатор (құрамы 10%Co/1%ZrO₂/89%сланец) екі рет сіңіру әдісімен дайындалды, алты сулы кобальт нитратының Co(NO₃)₂·6H₂O және цирконидің оксонитрат ZrO(NO₃)₃·2H₂O тұздары қолданылды. Алынған катализатор синтетикалық көмірсутектер алу үшін Фишер-Тропш синтезінде апробацияланды. Алдын ала катализатор 350 °С-та 3 сағат көлемінде тотықсыздандырылды, сутегінің көлемдік жылдамдығы 1000 сағ⁻¹ және қысым 0,2 МПа құрады. Синтез (H₂/CO/N₂=2/1/0,2 мольдік қатынаста) 160-220 °С температура интервалында, 500 сағ⁻¹ көлемдік жылдамдықта және 1,0 МПа қысымда жүргізілді. Түзілген көмірсутектердің C₆-C₂₁ хроматографиялық талдауы негізінен алкандар мен арендердің түзілгенін көрсетті.

Түйін сөздер: катализатор, кобальт, сланец, Кендірлік, активация, Фишер-Тропш синтезі, көмірсутектер.

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ПОЛУЧЕНИЕ КОБАЛЬТОВОГО КАТАЛИЗАТОРА НА ОСНОВЕ КЕНДЫРЛЫКСКОГО СЛАНЦА И ЕГО АПРОБАЦИЯ В СИНТЕЗЕ ФИШЕРА-ТРОПША

Аннотация. В работе приведены метод приготовления кобальтового катализатора и результаты синтеза Фишера-Тропша на полученном катализаторе, в котором в качестве носителя использовали сланец месторождения «Кендырлык», промотором служил диоксид циркония. Сланец предварительно обрабатывали путем карбонизации в инертной среде аргона в интервале температур 25-700 °С и активации водяным паром при 850-900 °С в течение 60 минут. Катализатор (состава 10%Co/1%ZrO₂/89%сланец) готовили методом двойной пропитки, где использовали шестиводную соль нитрата кобальта Co(NO₃)₂·6H₂O и оксонитрат циркония ZrO(NO₃)₃·2H₂O. Далее полученный катализатор апробировали в синтезе Фишера-Тропша для получения синтетических углеводородов. Предварительно катализатор восстанавливали в среде водорода при температуре 350 °С в течение 3 часов, при объемной скорости водорода 1000 ч⁻¹ и давлением 0,2 МПа. Синтез проводили (при мольном отношении H₂/CO/N₂ = 2/1/0,2) в интервале температур 160-220 °С, при объемной скорости 500 ч⁻¹, давлении 1,0 МПа. Хроматографический анализ полученных углеводородов C₆-C₂₁ показал, что в процессе синтеза образуются преимущественно алканы и арены.

Ключевые слова: катализатор, кобальт, сланец, Кендырлык, активация, синтез Фишера-Тропша, углеводороды.

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