МРНТИ 61.51.29 **https://doi.org/10.58805/kazutb.v.2.23-484**

PRODUCTION OF SYNTHETIC HYDROCARBONS USING COBALT CATALYSTS BASED ON ZSM-5 ZEOLITE

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In this work, cobalt catalysts based on zeolite ZSM-5 were prepared by the triple impregnation method and chemically analyzed. Zirconium dioxide was used as a promoter (3 wt. %). Chemical analysis of the elemental composition and structure of the obtained catalysts was carried out using scanning electron microscopy. It is shown that the elemental composition of the catalysts with satisfactory accuracy corresponds to their given composition. Experiments for catalytic tests of the prepared catalysts were carried out on a laboratory Fischer-Tropsch synthesis unit and synthetic hydrocarbons were obtained. Comparative characterization of activity of the obtained catalysts with cobalt content of 10 % and 20 % has been carried out, dependence of carbon monoxide conversion and selectivity with respect to formation of gas hydrocarbons and yield of liquid products on temperature has been studied.

Keywords: synthesis gas, cobalt catalysts, promoter, Fischer-Tropsch synthesis, conversion, selectivity, hydrocarbons

ZSM-5 ЦЕОЛИТ НЕГІЗІНДЕГІ КОБАЛЬТ КАТАЛИЗАТОРЛАРЫН ҚОЛДАНУ АРҚЫЛЫ СИНТЕТИКАЛЫҚ КӨМІРСУТЕКТЕРДІ АЛУ

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Жұмыста үш есе сіңдіру әдісімен ZSM5 цеолитіне негізделген кобальт катализаторлары дайындалды және олардың химиялық талдауы жүргізілді. Промотор ретінде цирконий диоксиді қолданылды (3 мас. %). Растрлық электронды микроскопияны қолдана отырып, алынған катализаторлардың элементтік құрамы мен құрылымына химиялық талдау жасалды. Катализаторлардың элементтік құрамы олардың берілген құрамына қанағаттанарлық дәлдікпен сәйкес келетіні көрсетілген. Фишер-Тропш синтезінің зертханалық қондырғысында дайындалған катализаторларды каталитикалық сынау үшін эксперименттер жүргізілді және синтетикалық көмірсутектер алынды. Кобальт мөлшері 10% және 20 болатын алынған катализаторлардың белсенділігіне салыстырмалы сипаттама жасалды %, газ көмірсутектерінің түзілуіне және сұйық өнімдердің шығымына қатысты көміртегі тотығының конверсиясы мен селективтілігінің температураға тәуелділігі зерттелді.

Түйін сөздер: синтез-газ, кобальт катализаторлары, промотор, Фишер-Тропш синтезі, конверсия, селективтілік, көмірсутектер.

ПОЛУЧЕНИЕ СИНТЕТИЧЕСКИХ УГЛЕВОДОРОДОВ С ПРИМЕНЕНИЕМ КОБАЛЬТОВЫХ КАТАЛИЗАТОРОВ НА ОСНОВЕ ЦЕОЛИТА ZSM-5

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В работе приготовлены кобальтовые катализаторы на основе цеолита ZSM-5 методом тройной пропитки и проведен их химический анализ. В качестве промотора использовали диоксид циркония (3 мас. %). С применением растровой электронной микроскопии проведен химический анализ элементного состава и структуры полученных катализаторов. Показано, что элементный состав катализаторов с удовлетворительной точностью соответствует их заданному составу. Проведены эксперименты для каталитических испытаний приготовленных катализаторов на лабораторной установке синтеза Фишера-Тропша и получены синтетические углеводороды. Проведена сравнительная характеристика активности полученных катализаторов с содержанием кобальта 10 % и 20 %, изучена зависимость конверсии оксида углерода и селективность в отношении образования газовых углеводородов и выхода жидких продуктов от температуры.

Ключевые слова: синтез-газ, кобальтовые катализаторы, промотор, синтез Фишера-Тропша, конверсия, селективность, углеводороды.

Introduction. One of the typical heterogeneous catalytic processes is the Fischer-Tropsch synthesis, which serves as the basis for technologies for the production of hydrocarbons from various organic raw materials and is of great importance for the use of alternative types of motor fuels and environmental protection [1, 2].

Fischer-Tropsch synthesis is a key stage in the technology for producing synthetic oil and high-quality fuel components from carbon-containing raw materials. In recent years, the technology has received increasing attention as an alternative to tapping dwindling oil reserves. The solution of environmental problems, for example, such as the utilization of associated gas, adds relevance [3-5].

In recent decades, a large number of studies have been carried out in the field of developing new catalysts for FT synthesis [6-9]. At the same time, individual oxides and mixed oxide systems that are prone to the formation of solid solutions or spinel structures are usually used as supports for Fischer-Tropsch synthesis catalysts (especially cobalt ones) [10]. Typical carriers of Co-catalysts are: silica gel, kieselguhr, oxides of aluminum, silicon, titanium, magnesium and zirconium, amorphous aluminosilicates, zeolites. The nature of the carrier and its physicochemical characteristics can have a strong impact on the activity and selectivity of contacts. The carrier can also enter into a chemical interaction with the metal; the carrier participates in the formation of new compounds or new phases. Strong interaction between a metal and a carrier can occur through the charge transfer mechanism with the appearance of a partial positive charge on the metal [11]. Basically, with increasing carrier acidity, the yield of liquid and solid hydrocarbons increases [12].

Promising catalysts for the Fischer-Tropsch synthesis are cobalt catalysts, in the presence of which oxygen-containing and aromatic hydrocarbons are practically not formed [13,14]. Cobalt catalysts have become widespread due to their high activity, durability, and high selectivity to saturated linear paraffins. In addition, Co-catalysts are considered the optimal choice for the production of long-chain hydrocarbons (C_{5+}), at moderate temperatures and pressures [15,16].

The objectives of this work are: obtaining synthetic hydrocarbons from carbon monoxide and hydrogen on cobalt catalysts based on ZSM-5 zeolite (promoted with zirconium dioxide); study of the temperature dependence of carbon monoxide conversion and the yield of hydrocarbon products; study of the influence of cobalt content on the main parameters of Fischer-Tropsch synthesis.

Materials and methods. Granular zeolite ZSM-5 was used as a cobalt catalyst carrier, and zirconium dioxide ZrO_2 served as a promoter, which was used to increase the activity of the catalyst and selectivity in the formation of synthetic hydrocarbons. To prepare cobalt catalysts, the following reagents were used: cobalt nitrate hexahydrate ($Co(NO_3)_2{\cdot}6H_2O$) and zirconium nitrate hexahydrate ($ZrO(NO_3)_2{\cdot}2H_2O$).

Cobalt catalysts were prepared by the triple impregnation method. Previously, the carrier was pierced in a muffle furnace at a temperature of 450 ^{0}C for 5 hours to remove foreign substances (including especially carbon).

Cobalt catalysts of the following compositions were prepared: 10% Co/3% ZrO_2/87%zeolite ZSM-5 and 20% Co/3% ZrO_2/77%zeolite ZSM-5. Previously, the cobalt catalysts were pre-activated (reduced) in a stream of hydrogen at atmospheric pressure and a temperature of 350 ^{0}C with a volumetric flow rate of synthesis gas of 1000 h^{-1} for 1 hour.

Catalytic tests on these catalysts were carried out in a laboratory Fischer-Tropsch synthesis unit at a pressure of 15 atm. in the temperature range 180-220 ^{0}C. Synthesis gas with a molar ratio of $H_2/CO = 2/1$ was supplied at a successively increased temperature in increments of 10 ^{0}C. The duration of the Fischer-Tropsch synthesis under isothermal conditions at a volumetric flow rate of synthesis gas of 500 h^{-1} was about 12 hours.

The study of the elemental composition and structural features of the catalysts was carried out using a Hitachi TM3030 scanning electron microscope with a Bruker XFlash MIN SVE microanalysis system at an accelerating voltage of 15 kV.

Results and Discussion. Figure 1, using the scanning electron microscopy (SEM) method, shows the results of an analysis of the composition and structural features of the prepared cobalt catalyst 20%Co/3%ZrO_2/77%zeolite ZSM-5, which shows the atomic and weight fraction of the element in the cobalt catalyst based on zeolite This EDS spectrum contains information about the characteristic peaks of the sample and the chemical elemental composition of the cobalt catalyst with the composition 20%Co/3%ZrO_2/77%zeolite ZSM-5.

Analysis of SEM images showed that the resulting catalyst with the composition 20% Co/3%ZrO2/77%zeolite ZSM-5 had pore sizes from 0.3 to 0.7 μm (Figure 2, A). As can be seen from Figure 2 (B), the particle size of the cobalt catalyst is approximately ≈13-16 μm.

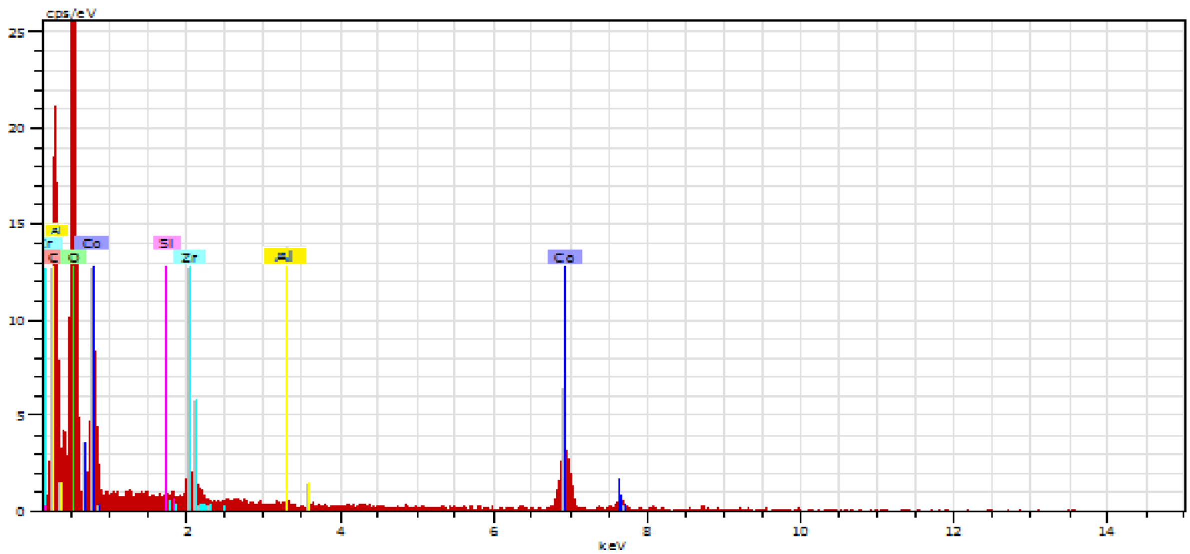


Figure 1 – EDS spectrum of a cobalt catalyst based on zeolite (20%Co/3%ZrO2/77%zeolite ZSM-5)

Spectrum: Point

Element AN Series Net unn. C norm. C Atom. C Error

[wt.%] [wt.%] [at.%] [%]

Oxygen 8 K–series 4029 64.34 48.88 49.39 8.5

Carbon 6 K–series 2380 45.13 34.29 46.15 6.4

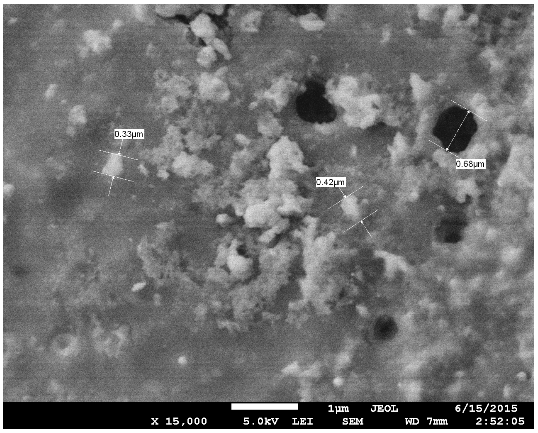
Cobalt 27 K–series 1002 19.21 14.59 4.00 0.6

Zirconium 40 L–series 448 2.73 2.07 0.37 0.1

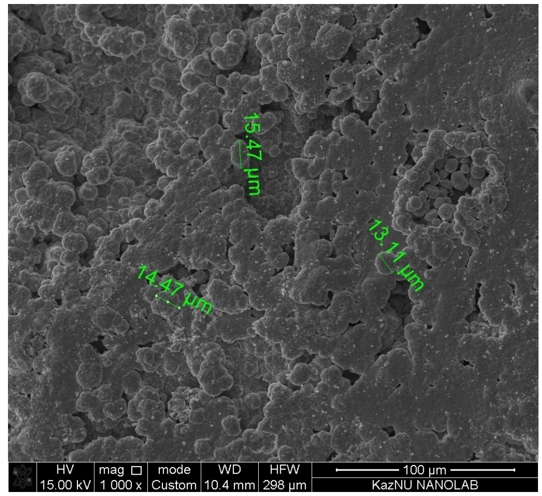
Silicon 14 K–series 36 0.13 0.10 0.06 0.0

Aluminium 19 K–series 17 0.08 0.06 0.03 0.0

Total: 131.62 100.00 100.00



A



B

Figure 2 – SEM images of a cobalt catalyst based on zeolite
20% Co/3% ZrO2/77%zeolite ZSM-5

A more detailed study revealed that large fractions of particles of the catalyst under study were coated with a layer of cobalt and zirconium in a percentage ratio of 7:1.

Analysis of the data obtained showed that the elemental composition of the prepared catalysts, determined using scanning electron microscopy, corresponds with their specified composition with satisfactory accuracy.

Figures 3 and 4 show chromatograms, respectively, of gaseous (at a temperature of 210^0 C) and liquid products (at a temperature of 200 ^{0}C) of synthesis on the catalyst 20% Co/3% ZrO_2/77% zeolite ZSM-5 (at their highest concentrations).

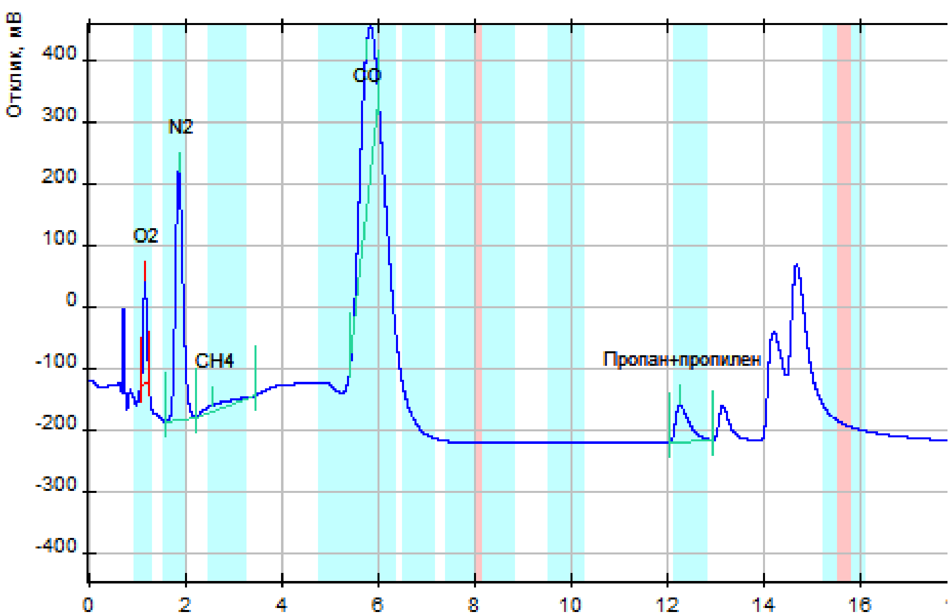


Figure 3 – Chromatogram of gaseous synthesis products on the catalyst 20%Co/3%ZrO_2/77%zeolite ZSM-5 at a temperature of 210 ^{0}C

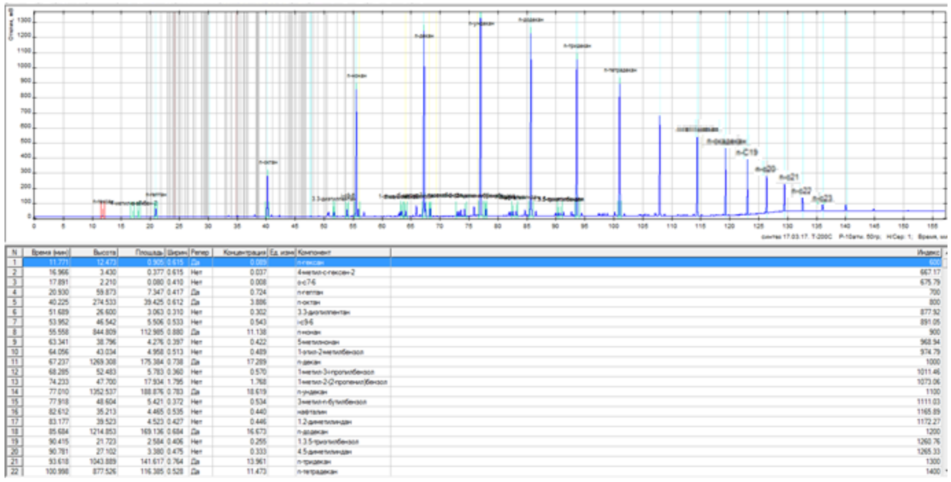


Figure 4 – Chromatogram of liquid synthesis products on the catalyst 20%Co/3%ZrO_2/77%zeolite ZSM-5 at a temperature of 200 ^{0}C

The results of the studies on the production of synthetic hydrocarbons are presented in Tables 1-3, which show the corresponding dependences of the conversion of carbon monoxide and the concentration of C_1-C_4 products on the synthesis temperature on catalysts 10% Co/3% ZrO_2/87%zeolite ZSM-5 and 20% Co/3%ZrO_2/77%zeolite ZSM-5 with cobalt content of 10 and 20 wt.%.

In Table 3, the yield of liquid C_{5+} products (g/m^3) of the FT synthesis process on the catalysts under study was obtained throughout the entire duration of the synthesis.

Table 1 - Main parameters of the Fischer-Tropsch synthesis on the catalyst 10%Co/3% ZrO_2/87%zeolite ZSM-5

Температура, ^{o}C	Конверсия CO, %	$C_1 - C_4$%
180	*21,5*	*3,7*
185	*27,4*	*7,3*
190	*31,6*	*9,4*
195	*35,5*	*15,2*
200	*42,1*	*19,3*
205	*48,2*	*22,1*
210	*58,8*	*19,8*
220	*62,7*	*17,3*

Table 2 - Main parameters of the Fischer-Tropsch synthesis on the catalyst 20%Co/3% ZrO_2/77%zeolite ZSM-5

Температура, 0C	Конверсия CO, %	C1 – C4%
180	*28,7*	*4,9*
185	*31,6*	*8,1*
190	*37,4*	*11,8*
195	*45,9*	*18,7*
200	*54,8*	*20,6*
205	*67,1*	*26,9*
210	*70,2*	*28,4*
220	*79,2*	*25,3*

Table 3 - Yield of liquid products of the Fischer-Tropsch synthesis process on the catalysts under study

Catalysts	Temperature, °C	Yield C_{5+}, g/m^3
10%Co/3%ZrO2/87% zeolite ZSM-5	210	75
20%Co/3%ZrO2/77% zeolite ZSM-5	200	89

Analysis of the data obtained showed that during the synthesis on the catalyst
10% Co/3% ZrO_2/87%zeolite ZSM-5 with an increase in temperature from 180 ^{0}C to 220 ^{0}C, the main indicators of the process significantly increase: conversion of carbon monoxide (21.5-62.7 %), selectivity for the formation of C_1-C_4 hydrocarbons (3.7-22.1%) and the yield of C_{5+} liquid products. At the same time, the optimal temperatures at which the largest amount of hydrocarbons are formed are 205 ^{0}C and 210 ^{0}C for gas and liquid products, respectively.

Using the catalyst 20%Co/3%ZrO_2/77%zeolite ZSM-5, with increasing temperature (180-220^{0}C), the conversion of carbon monoxide (28.7-79.2%) and the selectivity of C_1-C_4 hydrocarbons (4.9-28.4) and the yield of liquid C_{5+} products. At temperatures of 210 ^{0}C and
200^{0}C, the largest amounts of gas and liquid hydrocarbons are formed, respectively.

The obtained experimental results showed that the addition of cobalt from 10% to 20% (wt.) to the promoted catalyst leads to an increase in the highest values of carbon monoxide conversion from 62.7% to 79.2%, an increase in the highest selectivity for the formation of gas hydrocarbons C_1-C_4 with 22.1% to 28.4% and the yield of liquid products from 75 g/m^3 to 89 g/m^3. Also, when cobalt is added, a decrease in temperature is observed from 210 to 200 ^{0}C.

It should also be noted that by-products such as H_2O and CO_2 were formed in the gas leaving the reactor during the FT synthesis process. The formation of the latter can occur as a result of disproportionation reactions of CO (Bella-Boudoir) and water gas:

$$2CO \leftrightarrow CO_2 + C; CO + H_2O \leftrightarrow CO_2 + H_2$$

As the synthesis temperature increased, in virtually all experiments an increase in the proportion of CO_2 in the gas was observed. At the same time, the carbon released during the reaction (simultaneously with CO_2) leads to “carbonization” of the catalyst (as well as the reactor), which significantly reduces the activity and selectivity of the catalyst. Therefore, an increase in the carbon dioxide content in the resulting gas has a negative effect.

Conclusions. When carrying out the Fischer-Tropsch synthesis with different cobalt additions, the catalyst 20%Co/3%ZrO_2/77%zeolite ZSM-5 showed the greatest activity and selectivity with respect to the formation of gaseous and liquid products compared to the catalyst 10%Co/3%ZrO_2/87%zeolite ZSM-5. Cobalt catalysts based on ZSM-5 zeolite with a cobalt content of 20% showed sufficient activity and selectivity in the Fischer-Tropsch synthesis in the formation of synthetic hydrocarbons.

References

1. Song H. Qingzhu Zhao, Xing Zhou, Ziye Cao, Mingsheng Luo Selection of highly active and stable Co supported SiC catalyst for Fischer-Tropsch synthesis: Effect of the preparation method. //Fuel, 2018.-Vol.229.- P.144-150. https://doi.org/10.1016/j.fuel.2018.05.025

2. Munnik P., Jongh P.E., Jong K.P. Control and Impact of the Nanoscale Distribution of Supported Cobalt Particles Used in Fischer–Tropsch Catalysis// Journal of the American Chemical Society,2014. – Vol.136(20).- P.7333-7340. DOI: 10.1021/ja500436y.

3. A. P. Steynberg, “Introduction to Fischer-Tropsch Technology,” In: A. P. Steynberg and M. Dry, Eds., Studies in Surface Science and Catalysis: Fischer-Tropsch Technology, Elsevier B.V., Amsterdam, 2004 – P.1-63.

http://dx.doi.org/10.1016/S0167-2991(04)80458-0

4. Baliban R.C., Elia J.A., Floudas C.A. Novel natural gas to liquids processes: process synthesis and global optimization strategies // AIChE Journal,2013. - Vol. 59(2). - P.505-531.

DOI: 10.1002/aic.13996

5. Song D., Li J. Effect of catalyst pore size on the catalytic performance of silica supported cobalt Fischer–Tropsch catalysts // Journal of Molecular Catalysis A: Chemical, 2006.-Vol. 247(1-2)- P.206-212.

https://doi.org/10.1016/j.molcata.2005.11.021

6. Patent RF №2389548. Riz Deivid K. The promoted catalyst of synthesis of Fischer-Tropsh, way of his production and way of synthesis of hydrocarbons of Fischer-Tropsh., 2010.

7. Saib A.M., Moodley D.J., Ciobic I.M., Hauman M.M., Sigwebela B.H., Weststrate C.J., Niemantsverdriet J.W., van de Loosdrecht J. Fundamental understanding of deactivation and regeneration of cobalt Fischer-Tropsch synthesis catalysts // Catalysis Today. – 2010. –Vol.154(3-4).- P.271-282. DOI:10.1016/j.cattod.2010.02.008

8. Borg O., Eri S., Blekkan E.A., Storsoter S., Wigum H., Rytter E., Holmen A. Fischer-Tropsch synthesis over γ-alumina-supported cobalt catalysts: Effect of support variables // Journal of Catalysis, 2007.- Vol.248.- P.89-100. http://dx.doi.org/10.1016/j.jcat.2007.03.008

9. Lohitharn N., Goodwin Jr. J.G. Impact of Cr, Mn and Zr addition on Fe Fischer-Tropsch synthesis catalysis: Investigation at the active site level using SSITKA // Journal of Catalysis, 2008.- Vol.257(1). - P.142-151. DOI:10.1016/j.jcat.2008.04.01

10. Zare A., Shiva M., Mirzaei A.A**.** Effect of calcination and reaction conditions on the catalytic performance of Co-Ni/Al2O3 catalyst for CO hydrogenation **//** Journal of industrial and engineering chemistry, 2013.- Vol.19 (6) - P.1858-1868. DOI:10.1016/j.jiec.2013.02.032

11. Wenping P., Jacobs G., Kang J., Sparks D., Gnanamani M.K., Pendyala V.R.R., Shafer W.D., Keogh R.A., Graham U.M., Thomas G.A. Fischer-Tropsch synthesis. Effect of alkali, bicarbonate and chloride addition on activity and selectivity // Catalysis today, 2013.-Vol.215. - P.73-79.

https://doi.org/10.1016/j.cattod.2013.03.003

12. Dachuan Shi, Jimmy A. Faria, Ali A. Rownaghi, Raymond L. Huhnke, Daniel E. Resasco. Fischer-Tropsch Synthesis Catalyzed by Solid Nanoparticles at the Water/Oil Interface in an Emulsion System // Energy & fuels, 2013.-Vol.27(10)- P.6118-6124. DOI:10.1021/ef401198m

13. Maitlis P.M., de Klerk A. (eds.) Greener Fischer-Tropsch Processes. Weinheim: Wiley–VCH, 2013. ISBN: 978-3-527-32945-8. - 390 p.

14. Arno de Klerk A., Furimsky E. Catalysis in the refining of Fischer-Tropsch syncrude. Cambridge: RSC Publishing, 2010. - 274 p. ISBN: 978-1-84973-080-8, £121.99

15. Huang X., Hou B., Wang J., Li D., Jia L., Chena J., Suna Y. CoZr/HZSM-5 hybrid catalysts for synthesis of gasoline-range isoparaffins from syngas//Appl. Catal., A: Gen, 2011.Vol.408(1)- P.38-46.

DOI:10.1016/j.apcata.2011.09.004

16. Zhang Y., Nagamori S., Hinchiranan S., Vitidsant T., Tsubaki N. Promotional Effects of Al2O3 Addition to Co/SiO2 Catalysts for Fischer-Tropsch Synthesis// Energy & Fuels, 2006- Vol.20(2). - P.417-421.

https://doi.org/10.1021/ef050218c

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