

Research of the catalytic properties of a catalyst selected for the production of high-molecular weight liquid synthetic hydrocarbons from synthesis gas

Ganisher Rakhimov^{1*}, *Oybek Kuybokarov*¹, and *Muradulla Karshiyev*¹

¹Karshi Engineering-Economic Institute, Kashkadarya region, Republic of Uzbekistan

Abstract. The purpose of the research: consists of developing a technology for producing high-molecular synthetic hydrocarbons from pentane to nonadecane from synthesis gas based on local raw materials. The article covers the process of catalytic synthesis of high-molecularweight from synthetic hydrocarbons from the pentane to nonadecanefrom carbon monoxideand hydrogen, which was carried out in a flow reactor operating in differential mode.

1 Introduction

Samples of selected catalysts for obtaining high-molecular weight synthetic hydrocarbons from pentane to nonadecane from synthesis gas, that is, from a mixture of carbon monoxide and hydrogen, were prepared by thermal decomposition of appropriate salts of the starting materials or their solutions in a wide temperature range [1].

At 120°C, below the decomposition temperature, the decomposition of iron (III) nitrate crystal hydrate, cobalt (II) nitrate crystal hydrate, nickel (II) nitrate crystal hydrate, and zirconyl (IV) nitrate crystal hydrate results separation of liquid into hydrocarbon part and dissolution of iron (III) nitrate crystal hydrate, cobalt (II) nitrate crystal hydrate, nickel (II) nitrate crystal hydrate and zirconyl (IV) nitrate crystal hydrate in its water of crystallization, and a dark red solution formed was observed [2].

At 150-170°C, decomposition of iron (III) nitrate crystal hydrate, cobalt (II) nitrate crystal hydrate, nickel (II) nitrate crystal hydrate and zirconyl (IV) nitrate crystal hydrate was observed with the release of brown gas-nitrogen oxide (IV). A light brown suspension of iron (III) oxide, cobalt (II) oxide, nickel (II) oxide and zirconium (IV) oxide were formed. However, it is unstable due to the large size of the particles formed by iron (III) oxide, cobalt (II) oxide, nickel (II) oxide and zirconium (IV) oxide. Almost complete sedimentation of iron (III) oxide, cobalt (II) oxide, nickel (II) oxide and zirconium (IV) oxide particles were observed a few minutes after the end of mixing [3].

At 200-250°C, the decomposition of iron (III) nitrate crystal hydrate, cobalt (II) nitrate crystal hydrate, nickel (II) nitrate crystal hydrate and zirconyl (IV) nitrate crystal hydrate

* Corresponding author: ganisher.raximov@inbox.ru

occurs more rapidly than at 150-170°C. The resulting colloidal solution has a darker color and is characterized by greater stability, and sedimentation is not observed for a long time [4].

Chromatographic analysis of starting materials and reaction products.

2 Materials and methods

Qualitative and quantitative analysis of liquid and gaseous products of the reaction of obtaining hydrocarbons from synthetic pentane to nonadecane from carbon monoxide and hydrogen was carried out by the gas-adsorption chromatography method in the “Krystallyuks-4000M” chromatograph under the following optimal conditions: detector-catarometer, number of chromatographic columns 2, temperature the mode is isothermal and is equal to 80°C, the carrier gas is helium, and its consumption is equal to 20 ml/minute. A column filled with CaA (3m x 3mm) was used to separate the carbon monoxide and hydrogen. Separation of hydrocarbons from carbon monoxide and methane to butene was carried out in a column filled with HayeSep (3 m x 3 mm) with a flow rate of 20 ml/min, carrier-gas-helium, temperature regime programmed between 80-200°C at a rate of 8°C/min. A typical chromatogram of the reaction mixture is shown [6].

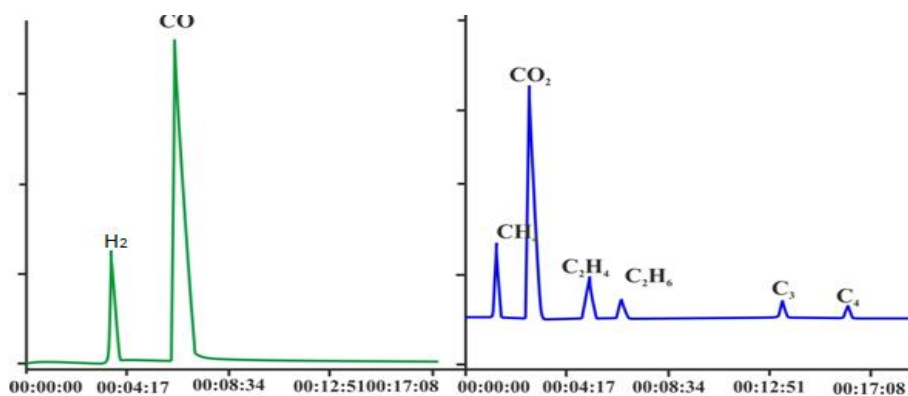


Fig. 1. Typical chromatogram of gaseous compounds. Determination of composition of synthesis products.

Figure 2 shows a chromatogram obtained as a result of the chromatographic analysis of the products of the water layer formed by the interaction of a mixture consisting of carbon monoxide and hydrogen.

Figure 1. Aqueous layer typical chromatogram of synthesis products of high-molecular weight synthetic hydrocarbons from pentane to nonadecane from carbon monoxide and hydrogen

Figure 2. Surface morphology of catalysts selected for the production of high-molecular weight synthetic hydrocarbons from pentane to nondecane from synthesis gas, that is, a mixture of carbon monoxide and hydrogen

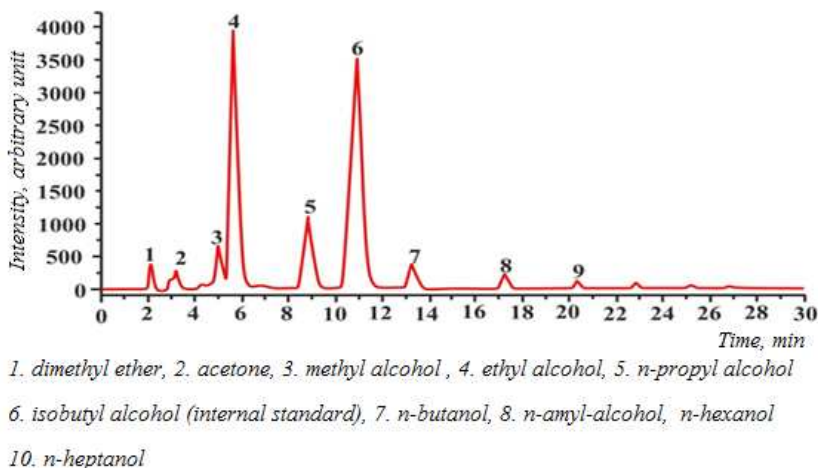


Fig. 2. Chromatogram obtained as a result of chromatographic analysis of the products of the aqueous layer.

3 Results

Preparation of selected catalysts by absorption method in order to obtain high-molecular weight liquid synthetic hydrocarbons from syngas, i.e., mixture consisting of carbon monoxide and hydrogen, can be done in one or more steps [8-9]. In the latter case, the active components were introduced to the surface of the carrier by successive absorption with aqueous solutions of the respective salts. In our experiments on the effect of the catalyst activity enhancer on the activity of the selected catalyst for obtaining high-molecular liquid synthetic hydrocarbons from synthesis gas, i.e., a mixture consisting of carbon monoxide and hydrogen, the samples were prepared by introducing the activity enhancer of the zirconium catalyst with three successive absorptions. Such a method does not pose difficulties for laboratory tests, for which small amounts of the selected catalyst are required to obtain high-molecular weight liquid synthetic hydrocarbons from synthesis gas, that is, a mixture consisting of carbon monoxide and hydrogen [10].

Tests were conducted under the following optimal conditions: pressure 0.1 MPa, volume speed 100 h⁻¹. The results were compared with the sample values prepared in 3-fold [11].

As can be seen in Figure 3, the sample prepared in 3-fold digestion was more active in the entire temperature range - the greenhouse gas conversion in it was 5-10% higher than that of the other two samples. In this case, the samples prepared in 1 and 2 times were almost indistinguishable from each other [12].

Temperature dependences of methane yield for all three samples are shown in Fig. 4. Methane production in the lower temperature range was not significantly different for all three samples. Thus, the yield of methane was 1 g/m³ at 160°C and 5-6 g/m³ at 180°C. Only from synthesis-gas, the production of methane in the sample prepared in 1-fold at a temperature of 200°C, that is, from synthesis-gas, was significantly different: the yield of methane in it was 30 g/m³ compared to 20-22 g/m³ for the remaining samples did [13].

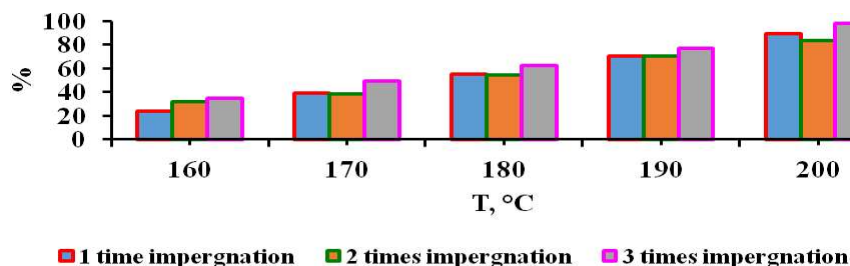


Fig. 3. Dependence of carbon monoxide conversion on synthesis temperature.

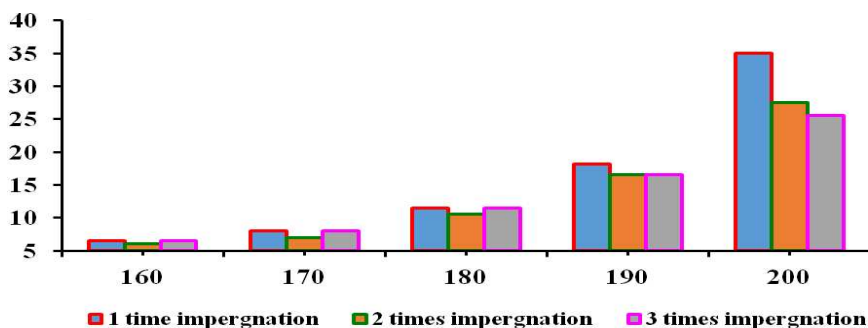


Fig. 4. Dependence of methane yield on synthesis temperature.

4 Discussion

Effect of Ni and Zr properties in 15% Co -15% Fe -5% Ni- 1% ZrO₂/ZCC catalytic system on the synthesis of high-molecular weight liquid synthetic hydrocarbons from carbon monoxide and hydrogen

Table 1. Influence of Ni and Zr properties.

Me	T _{opt} , °C	K _{opt}	Yield, g/m ³			C ₄₊ %	Yield, C ₅₊ /kg•cat,h	Content C ₅₊ , %		
			CH ₄	C ₂ -C ₄	C ₅₊			olefins	n-paraffins	isoparaffins
•	200	73	17	17	118	76	12	7	58	35
Ni	200	82	23	23	124	72	11	4	74	22
Zr	200	84	26	27	129	77	14	7	71	22
Ni, Zr	190	83	16	19	139	81	15	7	64	29

The introduction of Ni and Zr metals into the 15% Co -15% Fe/ZCC catalytic system also affected the composition of the resulting liquid synthetic hydrocarbons (Table 1). Polyfunctional catalytic systems are more selective towards linear saturated hydrocarbons. The ratio of n-paraffins/isoparaffins increased from 1.7 to 2.2-4.1 in the liquid products of obtaining high-molecularweight liquid synthetic hydrocarbons from synthesis-gas, i.e., from carbon monoxide and hydrogen. Liquid products were mainly characterized by lower molecular mass [14].

5 Conclusion

In order to obtain a catalyst with high catalytic activity and selectivity for the production of liquid hydrocarbons from CO and H₂ and to establish relationships between the catalytic and physical and chemical properties of these systems, in this work, the effect of promoting the 15%Co-15%Fe/ZCC catalytic system with nickel and zirconium metals was studied.

It should be noted that there are few studies in the literature devoted to the systematic research of 15% Co-15%Fe-5%Ni-1%ZrO₂/ZCC containing polyfunctional catalytic systems for the synthesis of hydrocarbons from CO and H₂.

It is known that metals such as nickel and zirconium have the ability to adsorb hydrogen and dissociatively convert it into atomic hydrogen. As a result, when adding them to the catalysts storing Co and Fe, as a result of the chemisorption of hydrogen, the basic phases of cobalt and iron oxide on the surface of the catalytic system are more easily regenerated, which led to an increase in the number of active centers, and as a result, the catalytic activity of these catalytic systems increased.

The activity of Fischer-Tropsch synthesis catalysts depends on the process conditions: synthesis temperature, pressure, volume rate of synthesis gas transfer, etc. affects. In this work, the experiments were conducted at atmospheric pressure.

The trends of the effect of the reaction temperature on the main indicators of hydrocarbon synthesis from CO and H₂ are shown in the example of the 15%Co-15%Fe/ZCC sample, and they remained constant for all Co and Fe retaining catalysts. An increase in temperature led to an increase in the conversion of CO, while the yield of the synthesis products increased. However, while the yield of C₁-C₄ hydrocarbons and carbon monoxide increased with increasing synthesis temperature, the yield of liquid hydrocarbons passed through a maximum corresponding to the optimum temperature for obtaining these products. The selectivity towards the formation of liquid hydrocarbons decreased with increasing temperature.

References

1. O.E. Kuybokarov, Catalytic synthesis of high-molecular weight hydrocarbons from synthesis gas in a polyfunctional catalyst, *Universum: technical sciences*, **1-2**, **94**, 93-103 (2022)
2. A.N. Saliev, Technology of a cobalt zeolite-containing catalyst for the selective synthesis of liquid hydrocarbons from CO and H₂: dissertation of candidate of technical sciences: 05.17.01, Novocherkassk (2018)
3. S. Cheng, N. Shang, C. Feng, S. Gao, C. Wang, Z. Wang, Efficient multicomponent synthesis of propargylamines catalyzed by copper nanoparticles supported on metal-organic framework derived nanoporous carbon, *Catalysis Communications*, **89**, 91-95. (2017)
4. X. Wang, F. Meng, H. Chen, F. Gao, Y. Wang, X. Han, C. Fan, C. Sun, S. Wang, L. Wang, Synthesis of a hierarchical ZSM-11/5 composite zeolite of high SiO₂/Al₂O₃ ratio and catalytic performance in the methanol-to-olefins reaction, *Comptes Rendus Chimie*, **20**, **11**, 1083-1092 (2017)
5. I.K. Kobrakov, Synthesis of hydrocarbons from CO and H₂ on promoted cobalt-containing catalysts, dissertation of candidate of technical sciences, 126 (2007)
6. H. Huang, X. Meng, C. Chen, M. Zhang, Z. Meng, C. Li, Q. Cui, Effect of Phosphorus Addition on the Performance of Hierarchical ZSM-11 Catalysts in Methanol to Propene Reaction, *Catalysis Letters*, **146**, **11**, 2357-2363 (2016)

7. E. Catizzone, Z. Cirelli, A. Aloise, P. Lanzafame, M. Migliori, G. Giordano, Methanol conversion over ZSM-12, ZSM-22 and EU-1 zeolites: from DME to hydrocarbons production, *Catalysis Today*, **304**, 39-50 (2018)
8. X. Zhao, L. Wang, J. Li, S. Xu, W. Zhang, Y. Wei, X. Guo, P. Tian, Z. Liu, Investigation of methanol conversion over high-Si beta zeolites and the reaction mechanism of their high propene selectivity, *Catalysis Science & Technology*, **7**, **24**, 5882-5892 (2017)
9. K. Terasaka, H. Imai, X. Li, Control of Morphology and Acidity of SAPO-5 for the Methanol-To-Olefins (MTO) Reaction, *J Adv Chem Eng*, **5**, 4 (2015)
10. M. Sanchez-Sanchez, A.A. Romero, I. Pinilla-Herrero, E. Sastre, Ionothermal preparation of triclinic SAPO-34 and its catalytic performance in the MTO process, *Catalysis Today*, **296**, 239-246 (2017)
11. F. Buronov, N. Fayzullayev, *Synthesis and application of high silicon zeolites from natural sources*, In AIP Conference Proceedings, AIP Publishing, **2432**, **1** (2022)
12. F. E. Buronov, N. I. Fayzullaev, *Mathematical modeling of ethylene oxidative acetylation process*, In E3S Web of Conferences, EDP Sciences, **411**, 01037 (2023)
13. G. B. Rakhimov, F. I. Murtazayev, *Increasing the efficiency of heat exchange by changing the construction of a shell-and-tube heat exchanger*, In E3S Web of Conferences, **443**, 03008 (2023)
14. A. Khurmamatov, G. Rakhimov, F. Murtazayev, *Intensifications of heat exchange processes in pipe heat exchangers*, In AIP Conference Proceedings, AIP Publishing, **2432**, **1** (2022)