



ISSN: 2350-0328

**International Journal of Advanced Research in Science,
Engineering and Technology**

Vol. 9, Issue 11, November 2022

Study of the Effect of Various Factors on the Process of Synthesis of High-Molecular-Weight Hydrocarbons from Synthesis Gas

Quyboqarov Oybek, Fayzullaev Normurod, Rakhmatov Khudoyor

Senior Lecturer, Department of Oil and Gas Processing Technology, Karshi Institute of Engineering and Economics, Republic of Uzbekistan, Karshi

Doctor of Chemical Sciences, Professor of Samarkand State University, Republic of Uzbekistan Samarkand

Candidate of Chemical Sciences, Associate Professor of the Department "Technology of Oil and Gas Processing" of Karshi Institute of Engineering and Economics, Republic of Uzbekistan, Karshi

ABSTRACT: In this work, the influence of various factors on the process of synthesis of high-molecular hydrocarbons from carbon dioxide and hydrogen was studied. The tests were carried out in a catalytic flow unit under the same conditions: pressure 0.1 MPa, space velocity 100 h^{-1} . The temperature was raised from 160 to 240°C . in steps of $5^\circ/5 \text{ h}$. The results were compared with the readings of samples prepared in 3 soaks. In the entire temperature range, the sample of 3-fold exposure was more active - its CO conversion was 5-10% higher than that of the other two samples. The samples prepared during the 1st and 2nd soaking were practically indistinguishable from each other in this case. Reducing the number of deposition increases the isomeric capacity of the 15%Co-15%Fe-5%Ni-1%ZrO₂/HCC catalyst, despite the absence of a change in the acidity of its surface. The influence of pressure on the synthesis of hydrocarbons from CO and H₂ in the 15%Co-15%Fe-5%Ni-1%ZrO₂/HCC catalyst was studied. The experiments were carried out at a pressure of 0.5 MPa and a space velocity of 2000 h^{-1} , increasing the temperature from 60 to 190°C . When this temperature was reached, the pressure was increased to 2.0 MPa in increments of 0.5 MPa. An increase in catalyst activity was observed with an increase in pressure: the CO conversion increased from 11% at 0.5 MPa to 19% at 2.0 MPa. An increase in activity was observed during the production of liquid hydrocarbons. With an increase in pressure from 0.5 to 2.0 MPa, the yield increased from 28 to 41 g/nm^3 .

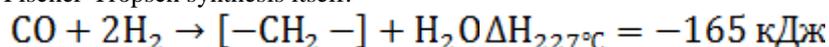
KEY WORDS: synthesis gas, catalyst, pressure, conversion, space velocity, temperature.

I. INTRODUCTION

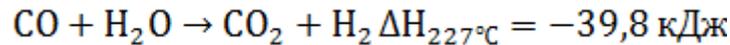
The aim of the work is to study the influence of various factors on the process of synthesis of high-molecular-weight hydrocarbons from gas synthesis.

Widespread conventional hydrocarbon reserves contribute to the widespread search for alternative ways of their extraction [1-2]. Among the possible methods of hydrocarbon synthesis to date, Fischer-Tropsch synthesis and catalytic conversion of methanol should be highlighted [3-5]. Fischer-Tropsch synthesis consists in the sequential conversion of synthesis gas to hydrocarbons with a predominantly linear structure, and the main products of catalytic conversion of methanol/dimethyl ether are aromatic hydrocarbons, olefins, and aliphatic hydrocarbons [6-8]. As catalysts for methanol/dimethyl ether conversion to hydrocarbons, zeolites of various structures, including zeolites with crystal lattices like MFI and SAPO, should be noted [9-10]. Catalytic conversion of methanol/dimethyl ether into hydrocarbons in zeolites consists in sequential conversion of methanol/dimethyl ether into olefins, which, in turn, are converted into methylsubstituted benzene derivatives [11-18].

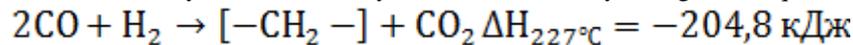
The general reactions of the synthesis of hydrocarbons from carbon and hydrogen oxides can be represented by different equations depending on the catalyst and process conditions, but they all correspond to two main ones. The first basic reaction is the Fischer-Tropsch synthesis itself:



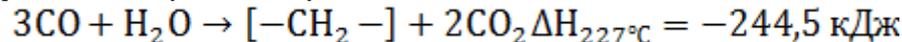
The second important reaction is the equilibration of water gas. As a secondary process, it is easily transferred to iron catalysts:



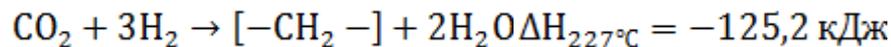
Taking into account this secondary reaction of PT synthesis on iron catalysts, a general equation is obtained:



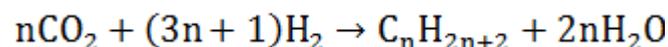
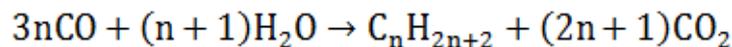
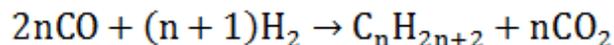
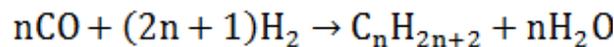
The general equation for the synthesis of hydrocarbons from CO and H₂O is as follows:



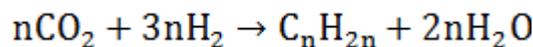
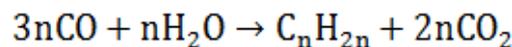
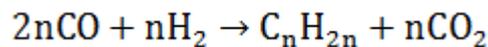
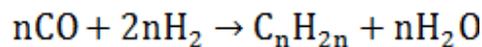
Equation of the reaction of formation of hydrocarbons from CO₂ and H₂:



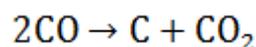
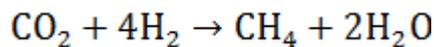
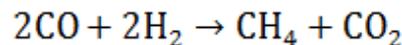
For the synthesis of paraffins



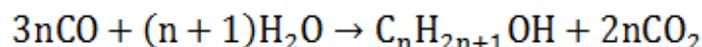
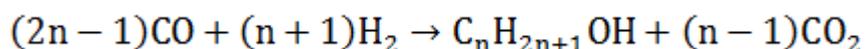
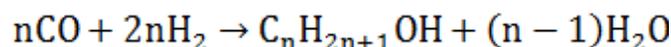
For the synthesis of olefins



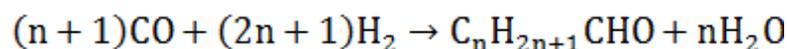
When synthesizing high-molecular-weight paraffins from carbon dioxide and hydrogen, the following additional reactions take place:

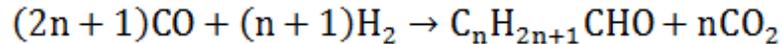


FT-synthesis can lead to the formation of alcohols and aldehydes:



Formation of aldehydes:





II. EXPERIMENTAL PART

Catalytic experiments on the synthesis of high-molecular-weight hydrocarbons were carried out on a laboratory-scale flow-type unit with an integrated reactor. A fixed layer of 5 catalysts was placed in the reactor in the form of a steel tube with an internal diameter of 20 mm. The activity of the hydrocarbon synthesis catalysts was evaluated by the following parameters: CO conversion, selectivity and hydrocarbon productivity. The calculation error did not exceed 2.5%. The CO conversion was calculated by the following formula:

$$X_{CO} = \frac{V_{BX} \cdot c(CO)_{BX} - V_{BbIX} \cdot c(CO)_{BbIX}}{V_{BX} \cdot c(CO)_{BX}} \cdot 100\%$$

where V_{in} , V_{out} are the reactor inlet and reactor outlet gas flow rates, dm^3/h ;
 $c(CO)_{in}$, $c(CO)_{out}$ - CO concentration at the reactor inlet and outlet, units.

Methane selectivity was calculated by the following formula:

$$S_{CH_4} = \frac{V(CO)_{CH_4}}{V(CO)_{np}} \cdot 100\%$$

where $V(CO)_{CH_4}$ is the volume of CO consumed to produce methane, dm^3 ; $V(CO)_{pr}$ is the volume of CO converted to methane, dm^3 .

The selectivity for C_{5+} hydrocarbons was calculated by the formula:

$$S_{C_{5+}} = \frac{V(CO)_{C_{5+}}}{V(CO)_{np}} \cdot 100\%$$

where $V(CO)_{C_{5+}}$ is the volume of CO consumed to form C_{5+} hydrocarbons, dm^3 .

The yield of C_{5+} hydrocarbons was calculated by the following formula:

$$G_{C_{5+}} = \frac{m_{C_{5+}}}{V_{cat} \cdot \tau}$$

where $m_{C_{5+}}$ - mass of C_{5+} hydrocarbons, kg; V_{cat} - catalyst volume, m^3 ; t - time, hour.

Determination of the composition of the synthesis products. The composition of gaseous synthesis products was analyzed by gas adsorption chromatography and two columns with Haysep R active phase and NaX molecular sieves on a Crystal 5000 chromatograph (Chromatec, Russia) with thermal conductivity detector. The analysis mode is programmed by temperature with a heating rate of $8^\circ C/min$.

The composition of C_{5+} hydrocarbons was determined by capillary gas-liquid chromatography-mass spectrometry on a gas chromatograph (Agilent, USA) with MSD 5975C mass-selective detector.

III. EXPERIMENTAL RESULTS AND DISCUSSION

Influence of 15%Co-15%Fe-5%Ni-1%ZrO₂/VCS catalyst preparation method on the yield of reaction of synthesis of high molecular weight hydrocarbons from CO and H₂. The preparation of catalysts by impregnation can be carried out in one or more stages. In the latter case, the active components (catalyst metals and promoters) were introduced onto the carrier surface by sequential impregnation with aqueous solutions of the corresponding salts. In our experiments on the effect of the promoter on the catalyst activity, the samples were prepared by introducing zirconium promoter with three consecutive impregnations. This method does not create difficulties for laboratory tests, which require small amounts of the catalyst.

Tests were performed in a flow-through catalytic unit under the same conditions: pressure 0.1 MPa, volume rate $100h^{-1}$. The temperature was increased from 160 to $240^\circ C$ in steps of $5^\circ/5$ hr. The results were compared with the readings of samples prepared in 3 soaks.

Fig. 1 shows the dependences of carbon monoxide conversion on the synthesis temperature for the samples prepared at durations 1, 2, and 3. As can be seen, the sample prepared by 3-fold soaking over the entire temperature range was more active - its CO conversion was 5-10 % higher than that of the other two samples. The samples prepared by the 1st and 2nd soaking were practically indistinguishable from each other in this case. The temperature

dependences of the methane yield for all three samples are presented in Fig. 2. The methane production in the low temperature region practically did not change for all three samples. Thus, the yield of methane was 1 g/nm³ at 160°C and 5-6 g/nm³ at 180°C. Only the methane yield of the sample obtained for 1 holding at a synthesis temperature of 200°C differed significantly: the methane yield was 30 g/nm³ compared with 20-22 g/nm³ for the other samples. The yields of C₂-C₄ hydrocarbons practically did not change for all three catalyst samples. At 160°C, C₂-C₄ was detected in the exhaust gases in residual amounts. With increasing temperature the yield gradually increased and reached 10-13 g/nm³ at 200°C (Fig.3).

The dependence of the yield of liquid hydrocarbons on the synthesis temperature is shown in Fig. 4. The yield of liquid hydrocarbons increased with increasing temperature and reached its maximum at 190°C. This temperature (optimal synthesis temperature) was the same for all three samples. Further increase of temperature led to decrease of liquid hydrocarbons yield. At optimal temperature the yield of liquid hydrocarbons was 136, 140, 145 g/nm³ of separated gas in the catalysts prepared at 1-, 2- and 3-fold impregnation.

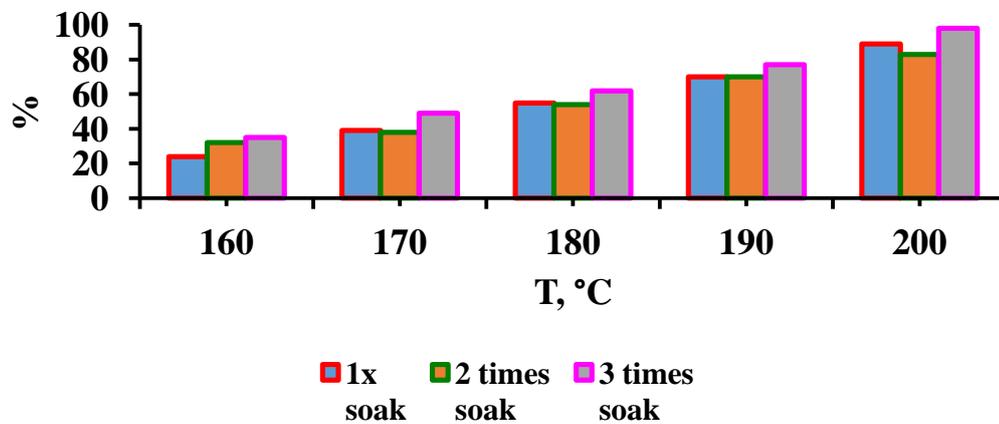


Fig. 1. Dependence of CO conversion on synthesis temperature

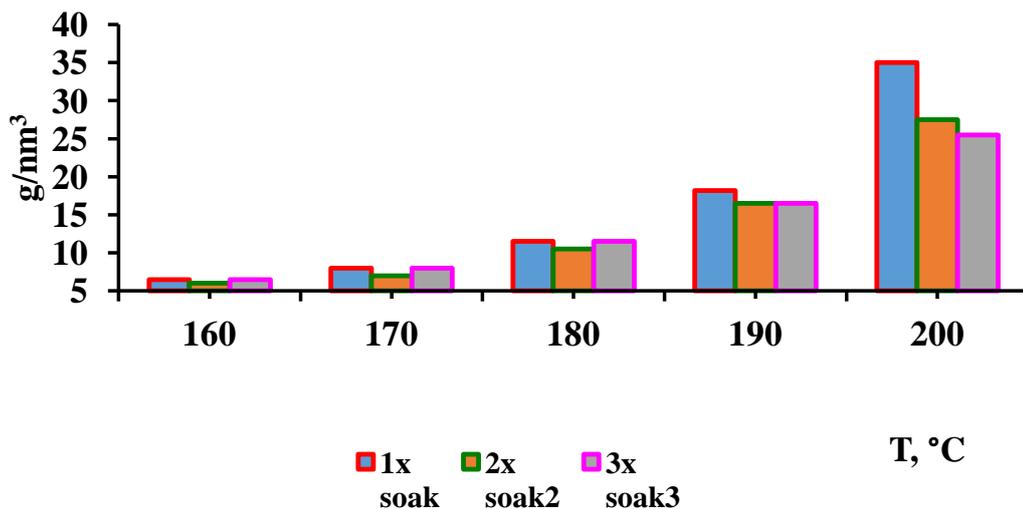


Fig. 2. Dependence of the methane yield on the synthesis temperature

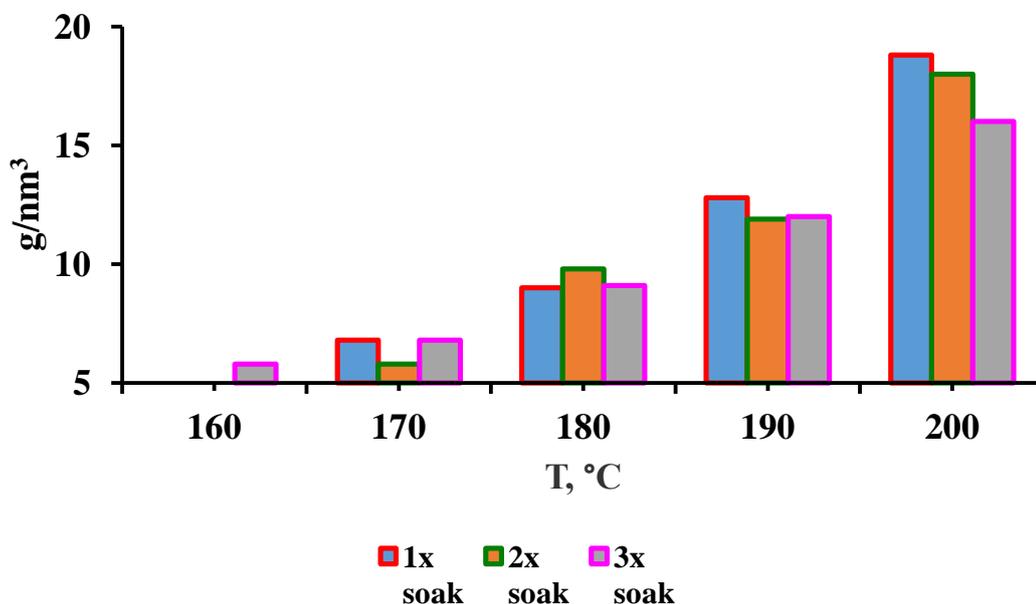


Fig. 3. Dependence of the C2-C4 yield on the synthesis temperature

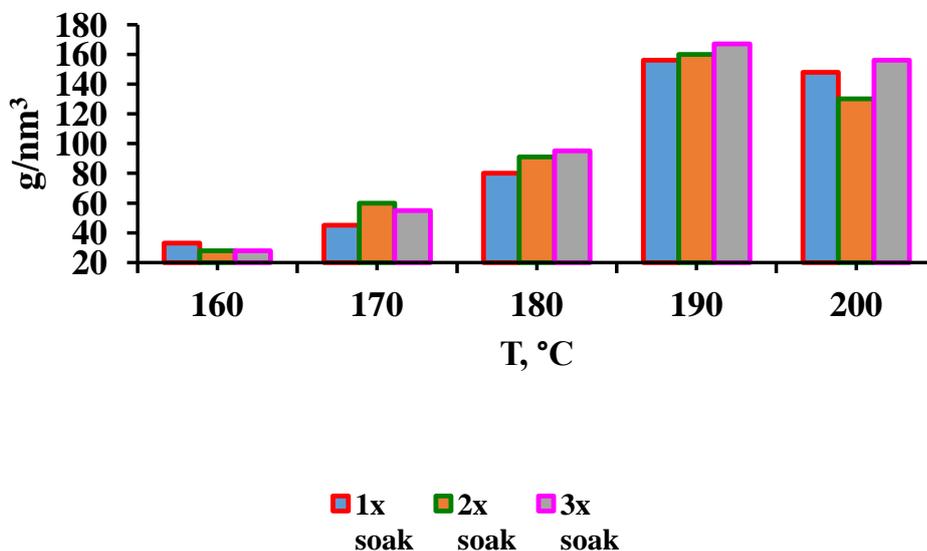


Fig. 4. Dependence of liquid hydrocarbons yield on synthesis temperature

The characteristics of all three samples at the optimal synthesis temperature are presented in Tables 1 and 2. The molar selectivity for the target liquid hydrocarbons decreased with decreasing number of curing and was 88, 87, and 85%, respectively. Methane selectivity practically did not change, at the level of 6-7% (Table 1). It can be noted that the greatest change of indicators is observed when the damping decreased from 3 to 2; at the same time, the difference of catalytic properties of samples prepared at damping 1 and 2 is practically at the level of experimental defect.

The group composition of synthesized liquid hydrocarbons is significantly influenced by the method of preparation. At reduction of number of dwellings the content of isoparaffins in the catalyst increases almost twice and reaches 33 % in the sample prepared for one dwell (Table 2, fig. 1). There is no change in the performance of the

catalyst in this case. Molecular-mass distribution of paraffins shifts toward heavy fractions in accordance with the increase in selectivity for liquid hydrocarbons (Table 2).

TPA NH₃ spectra of all three samples have insignificant differences (Fig. 1). Total acidity is 390-400 mmol/g. In addition, the isomerizing ability of the samples differed slightly.

Table 1

Effect of 15%Co-15%Fe-5%Ni-1%ZrO₂/VCS catalyst preparation method on synthesis rate

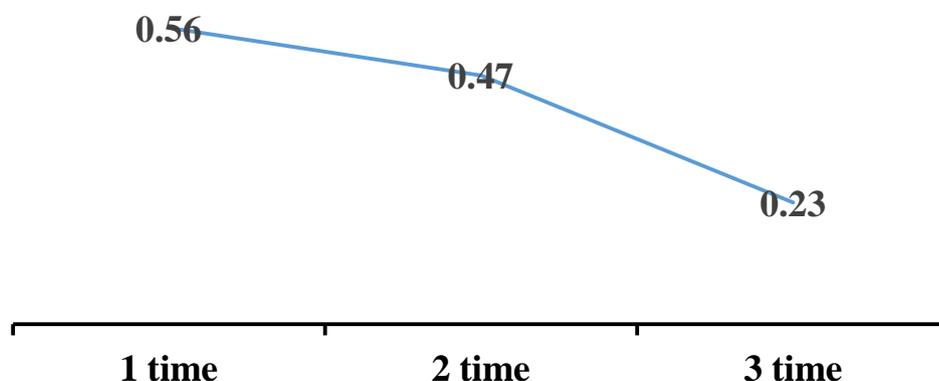
Number of reamers	T, °C	K _{CO} >%					S _{CH₄}	S _{C₅₊}
			CH ₄	C ₂ -C ₄	C ₅₊	CO ₂		
1 paz	190	74	14	10	139	16	8	86
2 paz	190	75	12	9	141	14	7	87
3 paz a	190	81	11	9	147	13	6	88

Table 2

Effect of 15%Co-15%Fe-5%Ni-1%ZrO₂/VKC catalyst preparation method on catalyst composition

Number of reamers	Group composition of liquid HC, %			Paraffin content, %		
	olefins	n-alkanes	i-alkanes	C ₅ —C ₁₀	C ₁₁ -C ₁₈	C ₁₉₊
1	9	60	35	64	36	8
2	9	64	31	59	35	11
3	9	76	19	42	44	19

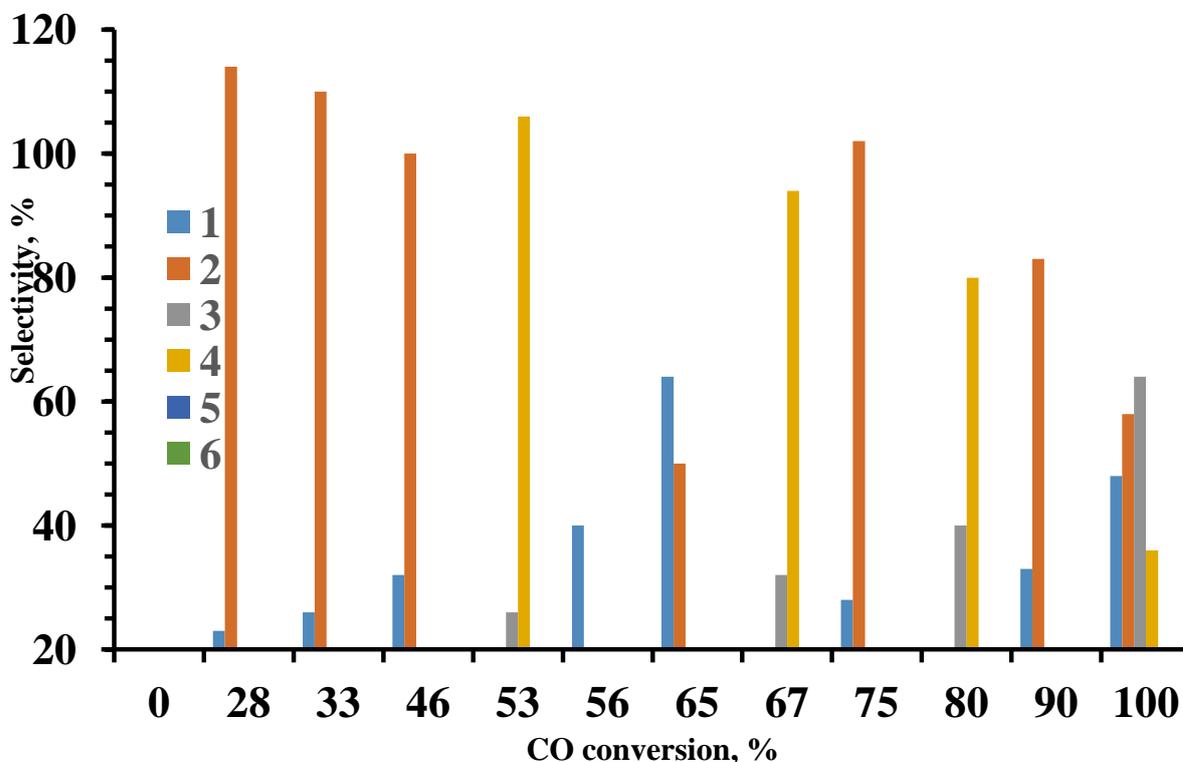
Thus, simplification of preparation procedure slightly reduces catalyst activity, yield of target liquid hydrocarbons and selectivity of their formation. The average molecular weight of hydrocarbons also decreases. The selectivity of methane formation remains unchanged. Reducing the number of sputtering increases the isomeric capacity of the 15%Co-15%Fe-5%Ni-1%ZrO₂/VKC catalyst despite no change in the acidity of its surface.



The partial pressures of synthesis gas components have a great influence on the fractional composition of the obtained hydrocarbons. With increasing of CO:H₂ ratio the value of α increased from 0.78 to 0.86-0.87.

Thus, the partial pressures of synthesis gas components have a significant influence on activity and selectivity of the catalyst for formation of liquid hydrocarbons, as well as on the fractional composition of the products obtained. CO enrichment of synthesis gas enhances selectivity of liquid hydrocarbons, decreases selectivity of methane and formation of products with large molecular weight. In the tubular reactor partial pressures of CO and H₂ decrease as the feed goes through the catalyst bed as the reagents are used up. The lower the volume rate and higher the conversion, the stronger the effect. Indeed, it was observed that the selectivity of methane formation in tube reactors decreased with increasing volume velocity. The dependence of process selectivity on CO conversion was obtained by us in a special series of experiments, in which volumetric rates of synthesis gas transfer were varied. The experiments were carried out at atmospheric pressure in synthesis gas of CO:H₂=1:2 composition. To exclude diffusion factors, the catalyst was loaded in such quantity that the linear gas velocity was constant in all experiments of the series.

Fig.5 shows CO conversion and selectivity coefficients for different volumetric velocities. In the region of low conversions, the dependences of selectivity on conversion are close to linear.



1-S_{CH₄}, volumetric speed 100 h⁻¹; 2-S_{C₅₊}, volumetric speed 100 h⁻¹; 3-S_{CH₄}, volumetric speed 200 h⁻¹; 4-S_{C₅₊}, volumetric speed 200 h⁻¹; 5-S_{CH₄}, volumetric speed 400 h⁻¹; 6-C₅₊, volumetric speed 400 h⁻¹

Fig.5. Dependence of selectivity of conversion of CO to methane and liquid hydrocarbons

REFERENCES

- Zhang J., Xu L., Zhang Y., Huang Z., Zhang X., Zhang X., ... et Xu L. Hydrogen transfer versus olefins methylation: On the formation trend of propene in the methanol-to-hydrocarbons reaction over Beta zeolites // *Journal of Catalysis*. 2018. V. 368. P. 248-260. <https://doi.org/10.1016/j.jcat.2018.10.015>
- Doluda V. Yu., Sulman M. G., Matveeva V. G., Lakina N. V., Bykov A. V., Sulman E. M. Catalytic transformation of methanol into hydrocarbons // *Bulletin of the Tver State University. Series: Chemistry*. 2015. No. 4. pp. 60-66.
- Chotiwan S., Somwongsa P., Laoubol S., Laoauporn P., Attanatho L., Laosombut T., Larpiattaworn S. Two-step catalytic hydrogenation of methanol to hydrocarbons conversion // *Materials Today: Proceedings*. 2019. V. 17. P. 1362-1369. <https://doi.org/10.1016/j.matpr.2019.06.156>
- Arora S. S., Bhan A. The critical role of methanol pressure in controlling its transfer dehydrogenation and the corresponding effect on propylene-to-ethylene ratio during methanol-to-hydrocarbons catalysis on H-ZSM-5 // *Journal of Catalysis*. 2017. V. 356. P. 300-306. <https://doi.org/10.1016/j.jcat.2017.10.014>
- Doluda V. Yu., Lakina N. V., Brovko R. V. Catalytic transformation of dimethyl ether into hydrocarbons on iron-modified zeolite H-ZSM-5 // *Bulletin of science and practice*. 2019. V. 5. No. 12. pp. 12-19. <https://doi.org/10.33619/2414-2948/49/01>
- Lee S., Choi M. Unveiling coke formation mechanism in MFI zeolites during methanol-to-hydrocarbons conversion // *Journal of catalysis*. 2019. V. 375. P. 183-192. <https://doi.org/10.1016/j.jcat.2019.05.030>
- Zhang Z., Liu B., Liu F., Zhao Y., Xiao, T. Effect of nickel loading on the performance of nano- and micro-sized ZSM-5 catalysts for methanol to hydrocarbon conversion // *Catalysis Today*. 2018. V. 317. P. 21-28. <https://doi.org/10.1016/j.cattod.2018.03.044>
- Li L. P., Ling G. U., Chun J. I. N., Peng, F. E. I. Synthesis of SiGeAl-ITQ-13 and SiAl (B)-ITQ-13 and their catalytic performance in the conversion of methanol to hydrocarbons // *Journal of Fuel Chemistry and Technology*. 2017. V. 45. №10. P. 1244-1250. [https://doi.org/10.1016/S1872-5813\(17\)30056-7](https://doi.org/10.1016/S1872-5813(17)30056-7)
- Grahn M., Faisal A., Öhrman O. G., Zhou M., Signorile M., Crocellà V., ..., Hedlund J. Small ZSM-5 crystals with low defect density as an effective catalyst for conversion of methanol to hydrocarbons // *Catalysis Today*. 2020. V. 345. P. 136-146. <https://doi.org/10.1016/j.cattod.2019.09.023>
- Kim S., Park G., Kim S. K., Kim Y. T., Jun K. W., Kwak G. Gd/HZSM-5 catalyst for conversion of methanol to hydrocarbons: effects of amounts of the Gd loading and catalyst preparation method // *Applied Catalysis B: Environmental*. 2018. V. 220. P. 191-201.
- Aslanov S.C., Buxorov A.Q., Fayzullayev N.I. Catalytic synthesis of C₂-C₄-alkenes from dimethyl ether // *International Journal of Engineering Trends and Technology*, 2021, 69(4), стр. 67-75



ISSN: 2350-0328

International Journal of Advanced Research in Science, Engineering and Technology

Vol. 9, Issue 11, November 2022

12. F.N.Temirov, J.Kh.Khamroyev, N.I.Fayzullayev, G.Sh.Haydarov and M Kh Jalilov. Hydrothermal synthesis of zeolite HSZ-30 based on kaolin //IOPConference Series: Earth and Environmental Science. – IOP Publishing, 2021. – T. 839. – №. 4. – C. 042099.
13. Khamroyev J.K., Akmalov K., Fayzullayev N.Mechanical activation of navbahorsk bentonite and its textural and adsorption characteristics//News of the National Academy of Sciences of the Republic of Kazakhstan, Series of Geology and Technical Sciences, 2022, 1(451), стр. 167–174.
14. Xolmirzayeva H.N., Fayzullayev N.I. Obtaining Nanocarbon from Local Raw Materials and Studying Its Textural and Sorption Properties //International Journal of Engineering Trends and Technology, 2022 Volume 70 Issue 2, 163-171. ISSN: 2231 – 5381 /doi:10.14445/22315381/IJETT-V70I2P219
15. Buronov F., Fayzullayev N. Synthesis and application of high silicon zeolites from natural sources //AIP Conference Proceedings. – AIP Publishing LLC, 2022. – T. 2432. – №. 1. – C. 050004.
16. Bukhorov A.Q., Aslanov S.C., Fayzullaev N.I. Catalyst deactivation in synthesis of olefins below methanol //AIP Conference Proceedings. – AIP Publishing LLC, 2022. – T. 2432. – №. 1. – C. 050010.
17. Bukhorov A.Q., Aslanov S.C., Fayzullaev N.I. Conversion of dimethyl ether to lower olefines //AIP Conference Proceedings. – AIP Publishing LLC, 2022. – T. 2432. – №. 1. – C. 050011.
18. Bukhorov A. Q., Aslanov S.C., Fayzullaev N. I. Kinetic laws of dimethyl ether synthesis in synthesis gas //AIP Conference Proceedings. – AIP Publishing LLC, 2022. – T. 2432. – №. 1. – C. 050012.
19. Kuibokarov O.E., Bozorov, O.N., Faizullaev, N.I., & Khaidarov, O.U.U. (2021). Synthesis of high-molecular carbons from synthetic gas with the participation of Co-Fe-Ni-ZrO₂/VCC (Upper Crimean zeolite). *Universum: Engineering Sciences*, (12-4(93)), 72-79.
20. Kuibokarov O. E., Bozorov O. N., Faizullaev N. I., & Nurullaev A. F. U. (2022). Catalytic synthesis of macromolecular hydrocarbons from synthesis gas in a polyfunctional catalyst. *Universum: Engineering Sciences*, (1-2 (94)), 93-103.
21. O. Kuibokarov, O. Bozorov, N. Fayzullaev, J. Khaitov, & I. Khudoiberdiev (2022, June). Cobalt catalysts for the Fischer-Tropsch synthesis supported on Al₂O₃ of various polymorphic modifications. In *E Conference Zone* (pp. 349-351).
22. Kuyboqarov O.E., Shoberdiev O.A., Rakhmatullaev K.S., & Murodullaeva Sh. (2022). Polyoxide catalysts for the processing of methane into synthesis gas. *Central Asian Research Journal for Interdisciplinary Studies (CARJIS)*, 2(5), 679-685.