ISSN: 2350-0328
International Journal of Advanced Research in Science, Engineering and Technology
Vol. 9, Issue 11 , November 2022

Investigation of the Influence of Various Factors on the Process of Synthesis of High Molecular Hydrocarbons from Synthesis Gas

Kuybokarov Oybek Ergashovich , Fayzullaev Normurod Ibodullaevich, Rahmatov Kh. B.,

Senior Lecturer, Karshi Engineering and Economic Institute, Republic of Uzbekistan, city of Karshi

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

Candidate of Chemical Sciences, Associate Professor.Karshi Engineering and Economic Institute, Karshi, Kashkadarya region, Uzbekistan

ABSTRACT: In this work, the kinetics of the reaction of obtaining high-molecular hydrocarbons from synthesis gas was studied. In the first series of experiments, the initially activated catalyst 15%Co-15%Fe-5%Ni-1%ZrO2/VCC was developed in synthesis gas with the composition CO/H2=1/2 at a pressure of 0.1 MPa and a space velocity of 100 h-1 . The temperature was raised from 150 to 190°C in increments of 10°C. The duration of daily operation at each temperature was 5 hours. At a temperature of 190°C, the volumetric rate of synthesis gas transfer increased from 200 to 400 h-1. The calculated values of E for various gas transfer volumetric rates and the calculated average values of k for each temperature are given. The root-mean-square error in the calculation of the activation energy is 3.24%. At a temperature of 190°C, the average value of the rate constant is 4.59 h-1 with a standard deviation of 8.65%. The activation energy of the reaction at 190 and 210°C can be calculated from two values of the rate constant. It is 89.24 kJ/mol.

KEY WORDS: synthesis gas, rate constant, reaction rate, temperature, activation energy.

I. INTRODUCTION

The aim of the work is to study the reaction kinetics of obtaining high-molecular-weight hydrocarbons from synthesis gas.

Production of lower olefins is growing on a large scale and continuously [1]. Thermal pyrolysis and catalytic cracking processes remain the main method of ethylene and propylene production. The growth rate of consumption of ethylene and propylene significantly exceeds the scale of their production, which makes us look for another, cheaper and more convenient hydrocarbon feedstock. The most popular and studied method of obtaining chemical products from natural gas is their obtaining by preliminary conversion of natural gas into synthesis gas (CO/H_2).

At present time the variant of obtaining of C_2-C_3 olefins from synthesis gas by means of dimethyl ether (DME) which allows to obtain lower olefins with high yield and high selectivity is of great interest [2, 3]. DME can be considered as one of the main possible tools for conversion of non-oil feedstock into valuable chemical products such as olefins [4]. A new catalyst for synthesis of lower olefins from DME is high-silica zeolite of ZSM-5 type. The properties of zeolite catalysts are directly affected by modification with metal compounds [5-9], which can lead to a change in their structure and acidic properties [10-12]. Numerous works have appeared in literature in which the influence of nature of modifying element on properties of zeolite catalysts has been widely studied [13-17], but the concept of understanding the role of nature has not been developed so far. A number of works on the synthesis of lower olefins from DME have been performed [18-28].

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:

$$X_{CO} = \frac{V_{vx}\,{}^{\circ}c(CO)_{vx} - Vvix\,{}^{\circ}c(CO)_{vix}}{V_{vx}\,{}^{\circ}c(CO)_{vx}} \cdot 100\%$$

where Vkir, Vchik are the reactor inlet and reactor outlet gas flow rates, dm^3/h;
c(CO) inlet, c(CO) outlet - CO concentration at the reactor inlet and outlet, units.
Methane selectivity was calculated using the following formula:

$$S_{CH4} = \frac{V(CO)_{CH4}}{V(CO)_{np}} \cdot 100\%$$

where $V(CO)CH_4$ is the volume of CO consumed to produce methane, dm^3; V(CO)mA - is the volume of CO converted to methane, dm^3.
The selectivity for C_{5+} hydrocarbons was calculated by the formula:

$$S_{C5+} = \frac{V(CO)_{C5+}}{V(CO)_{np}} \cdot 100\%$$

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:

$$G_{C5+} = \frac{m_{C5+}}{V_{kam \cdot \tau}}$$

where mC_{5+} - mass of C_{5+} hydrocarbons, kg; Vcat - catalyst volume, m^3; t - time, hour.

Determination of the composition of 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°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.

II.EXPERIMENTAL RESULTS AND THEIR DISCUSSION

Kinetics of synthesis of high-molecular-weight hydrocarbons from synthesis gas.

In order to design Fischer-Tropsch synthesis reactors using mathematical modeling, it is necessary to have information about the reaction kinetics. In doing so, it should not be expressed in the form of a graph or table, but in the form of a kinetic equation. It is desirable that the structure of this equation reflect the chemistry of the process as much as possible, otherwise the inevitable operations of data interpolation and especially extrapolation will become less reliable.

The following equation is widely used in the literature to describe the kinetics of the Fischer-Tropsch process:

$$W_{CO} = k'_{CO} P_{H2}$$

We sought to obtain the dependence of the activity of the catalyst on the conditions - pressure, temperature, volumetric rate and check their compliance with the equation.

Based on the law of acting masses, the expression for the reaction rate can be written in the form:

$$W_{CO} = -k_{CO} C_{H2}^{a} C_{CO}^{b}$$

The rate constants and activation energies were calculated using a computer program.

Several series of experiments were performed, in each of which one of the synthesis parameters - temperature, volume rate, total and partial pressures of the synthesis gas components - was changed in order to check it.

The apparent activation energy was calculated from experimental data using the Arrhenius equation:

$$\ln(k) = \ln(A) - \frac{E}{RT}$$

The calculations of rate constants and activation energies were performed using a computer program.

Several series of experiments were performed, in each of which one of the synthesis parameters - temperature, volume velocity, total and partial pressures of the synthesis gas components - was varied to check the equation.

In the first series of experiments initially activated catalyst 15%Co-15%Fe-5%Ni-1%ZrO_2/VCS was developed in synthesis gas of $CO/H_2=1/2$ composition under pressure 0.1 MPa, volume rate 100 h^{-1}. The temperature was increased from 150 to 190°C in 10°C increments. The duration of daily operation at each temperature was 5 hours. At 190°C the volumetric transfer rate of synthesis gas increased from 200 to 400 h^{-1}. The catalyst loading volume was varied so that the linear rate was the same in all experiments (see the previous section).The obtained values of CO conversion and calculated values of rate constants are summarized in Table 1 according to the equation $W_{CO} = k'_{CO} P_{H2}$. Obviously, the GHSV scores of 100 and 200 h^{-1} should not be considered in the summary table because they have reached full CO development. As can be seen from the calculations, the rate constants change unsatisfactorily - the error is at least 12% in the temperature range 190-210 ° C.. Obviously, the GHSV scores of 100 and 200 h^{-1} should not be considered in the summary table, since they have reached full CO development. As can be seen from the calculations, the rate constants change unsatisfactorily - the error is not less than 12% in the temperature range 190-210°C.

Table 1. Rate constants by equation (R=0.1 MPa, T=190°C)

Volumetric speed hour-1	K_{CO},%	k,
100	78	48.8
200	4	59.6
400	30	59.8

Table 2 Rate constants according to the equation (R=0.1 MPa, T=200 °C)

Volumetric speed hour-1	K_{CO},%	k, $hour^{-1}$
100	89.9	67.9
200	68.8	84.3
400	31.7	66.2

Table 3 Rate constants by equation (R=0.1 MPa, T=210°C)

Volumetric speed hour-1	K_{CO},%	k, $hour^{-1}$
100	99	109.78
200	84	109.38
400	49	102.45

Table 4 Rate constants by equation (R=0.1 MPa, T=230°C)

Volumetric speed hour-1	K_{CO},%	k, hour^{-1}
100	100	109.8
200	100	219.6
400	67	163.4

Based on the obtained temperature dependences of the rate constants we calculated the activation energy of the reaction according to the equation ln(k)=ln(A)-E/RT. The results are summarized in Table 2. The calculated values of E for various volumetric gas transfer rates and the calculated values of the average values of k for each temperature are given. The root-mean-square error of the calculated activation energy is 3.24%. At 190°C, the mean value of the rate constant is 4.59 h^{-1} with a standard deviation of 8.65%. The activation energy of the reaction at 190 and 210°C can be calculated from the two values of the rate constant. It is 89.24 kJ/mol.

$W_{CO} = k'_{CO}P_{H2}$, and the rate constants calculated from the equation, at a synthesis pressure of 2.0 MPa and volume transfer rate of raw materials in the range 180-240°C the temperature dependence of CO conversion is shown in Table 4. According to the Arrhenius equation, the apparent activation energy of the reaction was 74.28 kJ/mol, which is comparable with the value obtained in the previous experiment. In the linear equation, the correlation coefficient is 0.9841, which indicates a good approximation (Fig. 1).

Table 5 Reaction rate constants and activation energy

Volume rate, hour-1	Температура синтеза, °C				E_a kJ/mol
	190	200	210	230	
100	48.8	67.9	109.9	-	74.58
200	59.2	84.3	109.5	-	56.33
400	59.3	66.4	102.5	164.24	55.81

Table 6 According to the equation, the reaction rate constants are R=2.0 MPa, T=190°C.

Volume rate, hour-1	K_{CO}> %	k, hour^{-1}
1000	18	4.42
2000	12	5.29
3000	8	4.85

Table 7 Reaction rate constants according to equation (1), R=2.0 MPa, T=210°C

Volumetric speed hour^{-1}	K_{CO}> %	k, hour^{-1}
1000	35	8.88
2000	26	13.53
3000	19	14.08

Table 8 CO conversions and rate constants at R=2.0 MPa, volume rate 2000 h^{-1}

T, °C	K_{CO}> %	k, hour^{-1}	T, °C	K_{CO}, %	k, hour^{-1}
180	*8*	3.3	215	23	11.93
190	*9*	3.4	220	27	13.84
195	12	5.9	225	30	15.01
200	11	5.9	230	36	18.78
205	14	6.5	235	39	20.93
210	17	8.4	240	52	28.88

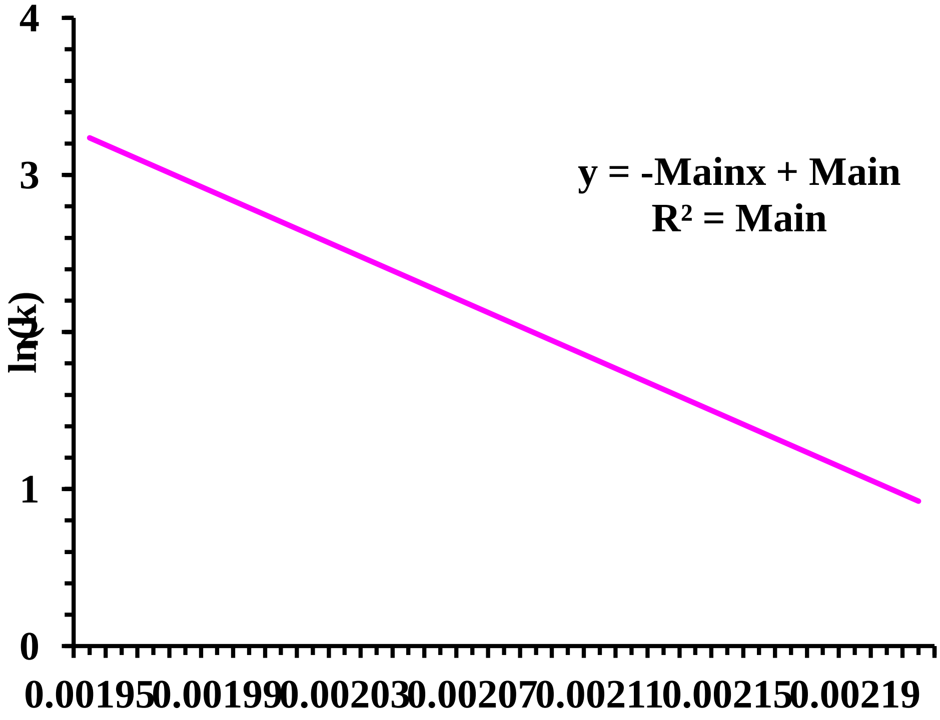

Figure 1. Dependence of the rate constant on temperature. R=2.0 MPa, volume rate 200 h^{-1}

The calculated values of the constants are given in Tables 5 and 6. The scatter of values is very large and the rate constant decreases with increasing pressure. Moreover, the values differ greatly from those obtained at the same temperature but at atmospheric pressure (Table 1). $W_{CO} = k'_{CO}P_{H2}$This means that the adopted kinetic model is not adequate.6

Table 9 Reaction rate constants at full pressure. CO:H2=1:2, T=190°C, high rate 2000 h-1

P, MPa	K_{CO}:	K*10^4, nm^3 CO/(m^{3}kat-h)
0.5	13	22.9
1.0	15	13.6
1.5	18	12.01
2.0	21	9.98

ISSN: 2350-0328
International Journal of Advanced Research in Science, Engineering and Technology
Vol. 9, Issue 11 , November 2022

Table 10 Rate constants by partial pressures T=190°C, volumetric rate 2000 h-1

P_{CO}, MPa	P_{H2}, MPa	K_{CO}, %	к, nm^3 CO/(m^3kat-h)
0.5	0.5	26	57.80
0.5	1.0	18	11.39
0.5	1.5	100	39.53
0.5	2.0	82	18.89
1.0	0.5	26	165.40
1.5	0.5	17	135.67
2.0	0.5	15	111.28

REFERENCES

1. Брагинский О.Б. Нефтехимический комплекс мира. М.: Academia, 2009. 800 с.

2. Hajjar Z., Khodadadi A., Mortazavi Y., Tayyebi S., Soltanali S. // Fuel. 2016. V. 179. P.79.

3. Kolesnichenko N.V., Kolesnikova E.E., Kitaev L.E., Biryukova E.N., Trukhmanova N.I., Khadzhiev S.N. //Petrol. Chemistry. 2012. V. 52. № 3. P. 155.

4. Khadzhiev S.N., Kolesnichenko N.V., Ezhova N.N. //Petrol. Chemistry. V. 48. № 5. P. 325.

5. Tamm S., Ingelsten H.H., Skoglundh M., Palmqvist A.E.C. //J. of Catalysis. 2010. V. 276. P. 402.

6. Миначев Х.М., Дергачев А.А. //Изв. АН СССР. Сер.Хим. 1993. № 6. С. 1018.

7. Seddon D. // Catal. Today. 1998. № 6. P. 351.

8. Choudhary V.R., Banerjee S., Devadas P. // J. Catal.2002. № 2. V. 205. P. 398.

9. Dmitriev R.V., Shevchenko D.P., Shpiro E.S, DergachevA.A.,Tkachenko O.P., MinachevKh.M. // Stud. Surf. Sci.Catal. 1991. V. 69. P. 381.

10. Freeman D., Wells R.P.K., Hutschings G.J. // J. Catal.2002. V. 205. № 2. P. 358.

11. Kolesnichenko N.V., Goryainova T.I., Biryukova E.N.,Yashina O.V., Khadzhiev S.N. // Petrol. Chemistry.
2011. V. 51. № 1. P. 55.

12. Mikhailov M.N., Kazansky V.B., Kustov L.M. // Catal.Lett. 2007. V. 116. P. 81.

13. Zhidomirov G.M., Shubin A.A., Kazansky V.B., VanSanten R.A. // Theoret. Chem. Account. 2005. V. 114.P. 90.

14. Borman S. // Chem. and Eng. News. 2005. V. 83. P. 15.

15. Stewart E. A., Johnson D.W., Shannon M.D. // Innovation in Zeolite Materials Science. 1988. V. 37. P. 57.

16. Vosmerikova L.N., Vagin A.I., Vosmerikov A.V. // Nefteper. iNeftehim. 2002. V. 2. P. 27.

17. Kubasov A.A., Kitaev L.E., Malyshev S.V., NovakovskayaYu.V. // Vest. Mosk. Univer. Khim. 2010. V. 51.P. 339.

11. Aslanov, S.C., Buxorov, A.Q., Fayzullayev, N.I. Catalytic synthesis of C_2-C_4-alkenes from dimethyl ether// International Journal of Engineering Trends and Technology, 2021, 69(4), стр. 67–75

12. F N Temirov, J KhKhamroyev, N I Fayzullayev, G ShHaydarov and M KhJalilov. Hydrothermal synthesis of zeolite HSZ-30 based on kaolin //IOP Conference Series: Earth and Environmental Science. – IOP Publishing, 2021. – Т. 839. – №. 4. – С. 042099.

13. Khamroyev, J.K., Akmalaiuly, 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. – Т. 2432. – №. 1. – С. 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. – Т. 2432. – №. 1. – С. 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. – Т. 2432. – №. 1. – С. 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. – Т. 2432. – №. 1. – С. 050012.

19. Musulmonov N. X., Fayzullaev N. I. Textural characteristics of zinc acetate catalyst //AIP Conference Proceedings. – AIP Publishing LLC, 2022. – Т. 2432. – №. 1. – С. 050015.

20. Bukhorov A. Q., Aslanov S. C., Fayzullaev N. I. Direct extraction of dimethyl ether from synthesis gas //AIP Conference Proceedings. – AIP Publishing LLC, 2022. – Т.2432. – №. 1. – С. 050013.

29.Куйбокаров, О. Э., Бозоров, О. Н., Файзуллаев, Н. И., & Хайдаров, О. У. У. (2021). Синтез высокомолекулярных углеродов из синтетического газа при участии co-fe-ni-zro2/вкц (верхний крымский цеолит). Universum: технические науки, (12-4 (93)), 72-79.

30.Куйбокаров, О. Э., Бозоров, О. Н., Файзуллаев, Н. И., &Нуруллаев, А. Ф. У. (2022). Каталитический синтез высокомолекулярных углеводородов из синтез-газа в полифункциональном катализаторе. Universum: технические науки, (1-2 (94)), 93-103.

31. Куйбокаров, О., Бозоров, О., Файзуллаев, Н., Хайитов, Ж., &Худойбердиев, И. А. (2022, June). Кобальтовые катализаторы синтеза Фишера-Тропша, нанесенные на Al2O3 различных полиморфных модификаций. In E ConferenceZone (pp. 349-351).

32.Куйбоқаров, О. Э., Шобердиев, О. А., Рахматуллаев, К. С., &Муродуллаева, Ш. (2022). Полиоксидные катализаторы переработки метанав синтез газ. Central Asian Research Journal for Interdisciplinary Studies (CARJIS), 2(5), 679-685.