CATALYTIC SYNTHESIS OF DIMETHYLPHYR FROM IS GAS

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***Abstract**. At present, obtaining dimethyl ether from syngas in one step is an actual issue, and the effect of various factors on the process of direct synthesis of dimethyl ether from syngas in one step was studied in $Cu_2O·ZnO·ZrO_2$/YuKTs catalyst. As a result of studies conducted on the effect of various factors on the yield of target products in the process of obtaining dimethyl ether from synthesis gas, it was found that the increase of pressure, temperature, mole ratio of hydrogen to hot gas, and the mole ratio of hydrogen:hot gas leads to an increase in conversion of hot gas. An increase in the volume velocity reduces the conversion of the is gas, because the reaction between the reactants in the gas phase and the methanol catalyst surface does not have time to occur due to the low contact time. It has been proven that the increase in the ratio of gas to hydrogen moles leads to an increase in the yield of dimethyl ether and the conversion of gas. As a result of the research, the following optimal conditions for obtaining dimethyl ether from hydrogen gas in one step were determined: R=1 MPa, T=300℃, hydrogen:gas gas=2, volumetric speed 1000 hour^{-1}. In this case, the conversion of exhaust gas does not decrease for 220 hours. At the same time, the physicochemical and textural characteristics of the $Cu_2O·ZnO·ZrO_2$/YuKTs catalyst were studied.*

***Keywords**: natural gas, synthesis gas, conversion, dimethyl ether, catalyst, synthesis, kinetic law.*

Purpose of work - consists in studying the kinetic laws of the synthesis reaction of dimethyl ether in one step from syngas and the textural characteristics of the catalyst.

INTRODUCTION

The deep processing of natural gas, petroleum satellite gas, biogas, etc. into valuable petrochemical products is one of the most important processes of the chemical industry[1,2], and the conversion of natural and petroleum satellite gas into easily transportable products makes it possible to transfer these natural resources into universal energy reserves[3-7].

In recent years, the process of processing synthesis gas into dimethyl ether in one step has attracted great interest among world scientists. The composition and characteristics of ethylene series hydrocarbons obtained from dimethyl ether depend on the physical and chemical properties of the zeolite catalyst used for this process, textural characteristics, production methods and process conditions, as well as the proportion of carbon dioxide and hydrogen in the synthesis gas. Controlling the acidic properties of high-silica zeolites and the composition of the initial synthesis gas allows obtaining light sulfur-free synthetic oil from methanol and dimethyl ether [8-10]. It is known that acidic properties of zeolites depend on the nature of exchangeable cations [11-25] and the method of their introduction [22-29].

EXPERIMENTAL PART

In the work, a Cu2O·ZnO·ZrO2/YuKTs catalyst was used to obtain dimethyl ether from synthesis gas.

The study of the catalytic activity of the samples was carried out in a device with a fixed layer catalyst (quartz particles mixed into the catalyst) in a flow reactor at a pressure of 0.1-2 MPa and a temperature range of 220-300°C.

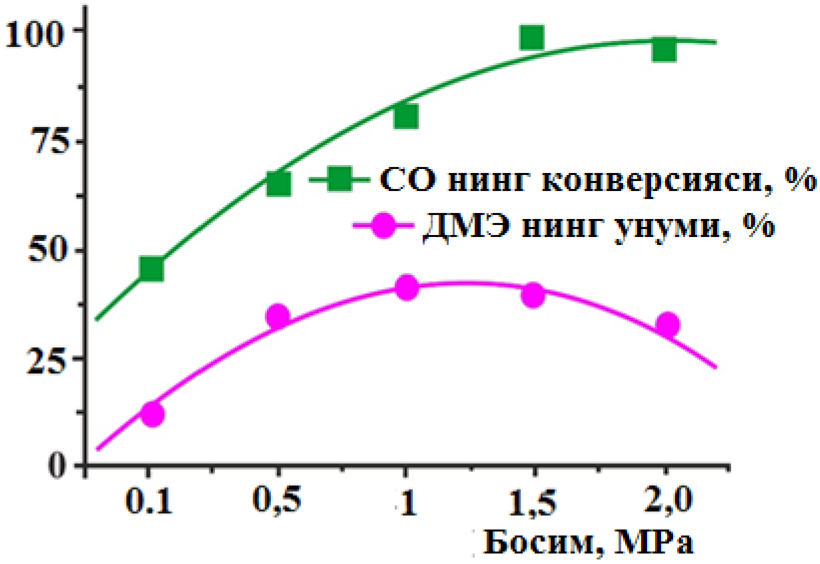
Quantitative and qualitative analysis of the products was carried out on the "Krystal 5000.2" gas chromatograph.

The phase composition of the studied samples before and after the catalytic tests was determined by X-ray phase analysis using unfiltered CuKα-radiation (l=1.5418 Å) on a Shimadzu XRD-6000 diffractometer. Brunauer-Emmet-Teller and Barrett-Joyner-Haland methods were used to determine the textural characteristics of the samples. The comparison was calculated from the data of nitrogen adsorption isotherms observed at surface area minus 197°C. The pore volume was determined at a relative pressure of R/R_0=0.99. The acidity properties of the samples were determined by the "Nicolet IR200" IR-spectrometer.

EXPERIMENTAL RESULTS AND THEIR DISCUSSION

As a result of studying the influence of different proportions of the mixture of initial gases on the yield of dimethyl ether, it was found that the yield of dimethyl ether has the highest value when the mixture of initial gases is in a ratio of 1:2. The participation of carbon dioxide also plays an important role in the synthesis of dimethyl ether. As a result of the experiments, it was proved that the yield of dimethyl ether increases with the concentration of carbon dioxide. A number of experimental studies were carried out to determine the optimal amount of carbon dioxide added to the mixture used for the synthesis of dimethyl ether, and it was found that the yield of dimethyl ether is the highest in the conditions where the molar ratio of gases is 2:1:2.

In the synthesis of dimethyl ether from is gas and hydrogen, the volume decreases, so the process was carried out at high temperature, the effect of temperature on the yield of dimethyl ether is shown in Figure 1. It can be seen that the conversion of carbon dioxide increases with increasing pressure, with the dimethyl ether yield having the highest value at a pressure of 1 MPa.



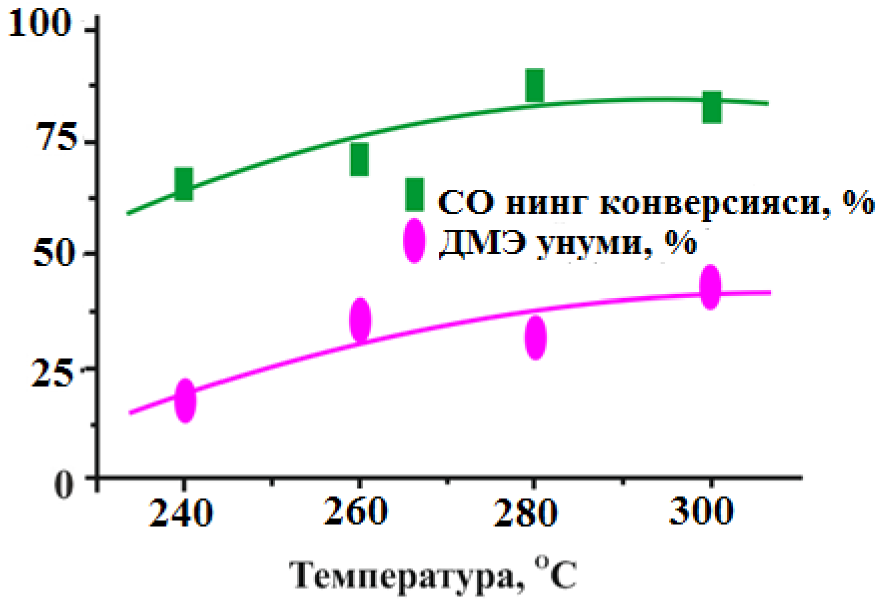
T=300°C, hydrogen: carbon dioxide =2, volumetric rate 1000 h^{-1}.

Figure 1. Effect of pressure on SO gas conversion and dimethyl ether yield

The decrease in the yield of dimethyl ether can be explained by its decomposition

$CH_3OCH_3 \leftrightarrow CH_4 + CO + H_2$.

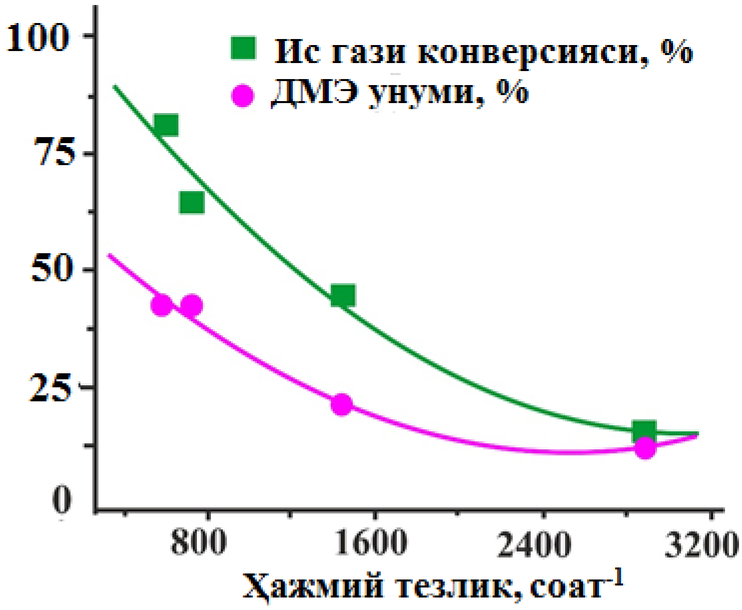
As the temperature increases, soot gas conversion and dimethyl ether yield increase (Figure 2).



T=300°C, hydrogen: carbon dioxide =2, volumetric rate 1000 h^{-1}.

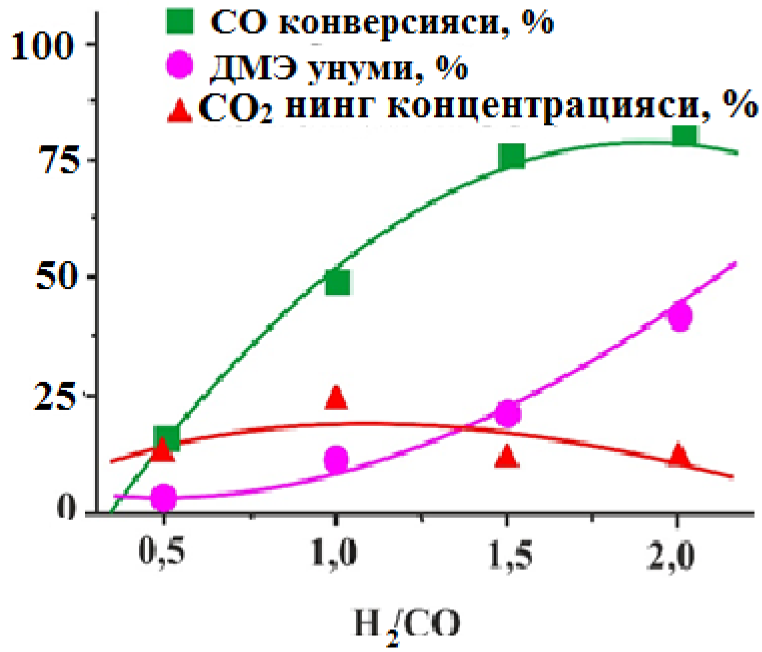
Figure 2. Effect of temperature on carbon dioxide conversion and dimethyl ether yield

As can be seen from Fig. 3, with the increase in volume velocity, the conversion of SO gas and the yield of dimethyl ether decrease (Fig. 3). The reason for this is that the contact time of the reagents with the catalyst surface decreases with the increase in the volumetric velocity, that is, the increase in the volumetric velocity reduces the gas conversion, because due to the low contact time, the reaction between the reagents and the catalyst surface does not have time to occur in the gas phase. At the same time, an increase in the mole ratio of carbon dioxide and hydrogen leads to an increase in the yield of dimethyl ether and conversion of carbon dioxide (Fig. 4).



P=1 MPa, T=300°C, hydrogen: carbon dioxide, volumetric rate 1000 h^{-1}.

Figure 3. Effect of Volumetric Velocity on Gas Conversion and Dimethyl Ether Yield



T=300℃, P=1 MPa, volumetric rate 1000 h^{-1}.

Figure 4. Effect of hydrogen:gas mole ratio on gas conversion and dimethyl ether yield and carbon dioxide concentration

Studies on the influence of the main parameters on the efficiency of the process of dimethyl ether extraction from synthesis gas have shown that the increase in pressure, temperature, and hydrogen:hydrogen gas mole ratio leads to an increase in the yield of dimethyl ether and conversion of hydrogen gas. Thus, the following optimal conditions for obtaining dimethyl ether from hydrogen gas in one step were determined: R=1 MPa, T=300℃, hydrogen:gas gas=2, volume velocity 1000 h^{-1}. In this case, the conversion of exhaust gas does not decrease for 220 hours. Figure 5 shows the diffractogram of $Cu_2O\cdot ZnO\cdot ZrO_2$/YuKTs catalyst, which was initially used at 300℃ for 3 hours in hydrogen, used in catalysis for 70 hours, and used in N_2 for 10 hours at 300℃ and 1 MPa.

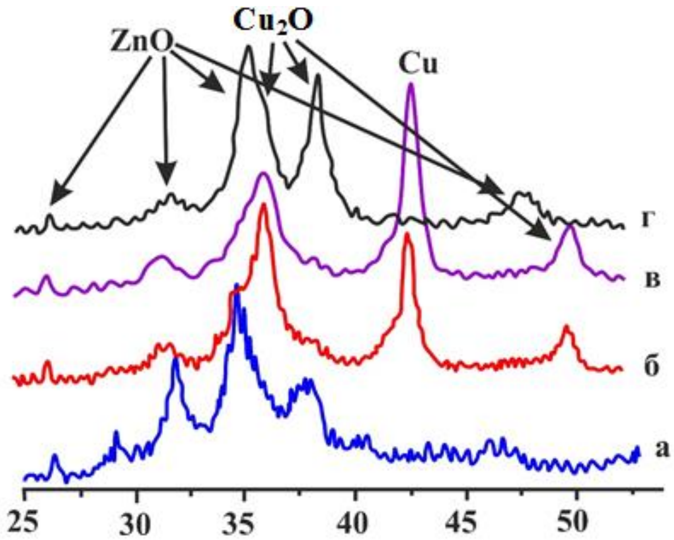


Figure 5. a – initial, b – diffractogram of $Cu_2O\cdot ZnO\cdot ZrO_2$/YuKTs catalyst used in hydrogen at 300℃ for 3 hours, v – used in catalysis for 70 hours, g – N_2 at 300℃, 10 hours at 1 MPa.

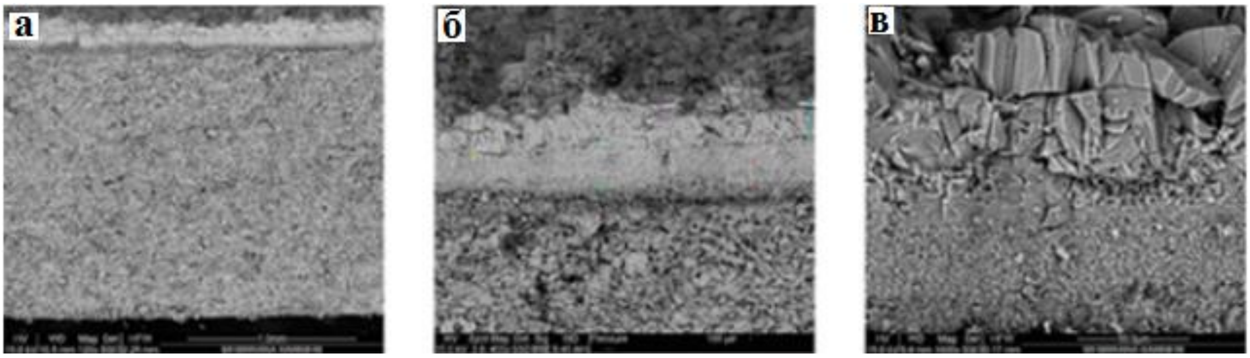
The analysis of the results of the textural characteristics of the catalysts shows that the specific surface area of the $Cu_2O\cdot ZnO\cdot ZrO_2$/YuKTs catalyst decreases from 138 to 82 m^2/g and the average diameter of the pores increases from 13 to 21 nm as a result of treatment in hydrogen or helium flow.

Table 1

Textural characteristics of catalysts for the production of dimethyl ether from gas and hydrogen

Catalyst treatment conditions	$Cu_2O{\cdot}ZnO{\cdot}ZrO_2$/YuKTs		
	S_{com}, m^2/g	V_{por}, m^2/g	Pores d_{av}, nm
Дастлабки	138	0,355	13
Treated with hydrogen at 320°C for 4 hours	82	0,375	21
Used in synthesis for 70 hours	71	0,355	18
Used in N_2 at 320°C, 1 MPa for 10 hours	68	0,355	15

Figure 6 shows the micrographs of $Cu_2O{\cdot}ZnO{\cdot}ZrO_2$/YuKTs catalyst used for methanol synthesis under different processing conditions. The surface of the initial $Cu_2O{\cdot}ZnO{\cdot}ZrO_2$/YuKTs catalyst (Fig. 6a) is inhomogeneous, rough, covered with some individual particles.



a - initial, b - treated with hydrogen at 320°C for 4 hours, v - after being used in synthesis in the presence of hydrogen: is gas for 70 hours at T=200-300°C, R=1-5 MPa

Figure 6. Micrographs of $Cu_2O{\cdot}ZnO{\cdot}ZrO_2$/YuKTs sample

Reduction in hydrogen leads to a lot of porosity of the surface and the formation of individual particles. After testing the catalyst in the synthesis of dimethyl ether from carbon dioxide and hydrogen, when the temperature was changed from 200 to 300 °C and the pressure was changed in the range of 1-2 MPa, the textural characteristics of the catalyst changed significantly (Fig. 6v), that is, the surface surface became smoother, the average size of the pores changed from 1 to 40 μm.

CONCLUSION

The effect of various factors on the process of direct synthesis of dimethyl ether from synthesis gas in one step was studied in the $Cu_2O{\cdot}ZnO{\cdot}ZrO_2$/YuKTs catalyst, and the increase in volume velocity decreased the conversion of is gas and the yield of dimethyl ether, the increase in the mole ratio of is gas and hydrogen led to the increase of the yield of dimethyl ether and the conversion of is gas proved to come.

As a result of the studies conducted to study the effect of various factors on the yield of target products in the process of obtaining dimethyl ether from synthesis gas, it was found that increasing the mole ratio of pressure, temperature, and mole ratio of hydrogen to greenhouse gas leads to an increase in greenhouse gas conversion due to the fact that the reaction of synthesis of dimethyl ether directly from synthesis gas prevails.

The decrease in the conversion of is gas with an increase in volume speed is explained by the fact that the reagents in the gas phase do not have time to react on the surface of the catalyst when the contact time is small. As a result of the research, the following optimal conditions for obtaining dimethyl ether from hydrogen gas in one step were determined: R=1 MPa, T=300°C, hydrogen:gas gas=2, volumetric speed 1000 hour^{-1}.

The physico-chemical and textural characteristics of the $Cu_2O·ZnO·ZrO_2$/YuKTs catalyst were studied. The acidity of the $Cu_2O·ZnO·ZrO_2$/YuKTs catalyst surface was determined by the method of thermoprogrammed desorption of ammonia.

REFERENCES

1. 1.Wood D. // Oil & Gas J. 2007. No 12. P. 20.
2. 2.Арутюнов В.С. // Катализ в промышленности.2008. No 1. С. 51.
3. 3.Simonetti D.A., Carr R.T., Iglesia E. // J. of Catalysis.2012. No 285. P. 19.
4. 4.Hazari N., Labinger J.A., Scott V.J. // J. of Catalysis.2009. No 263. P. 266.
5. 5.Ahn J. H., Temel B., Iglesia E. // Angewandte Chemie.2009. No 121. P. 3872.
6. 6.Simonetti D.A., Ahn J.H., Iglesia E. // J. of Catalysis.2011. No. 277. P. 173.
7. 7.Хаджиев С.Н., Магомедова М.В., Пересыпкина Е.Г. //Нефтехимия. 2016. Т. 56. No 3. С. 198.
8. Букина З.М., Ионин Д.А., Колесниченко Н.В.,Куоумбегов Н.В., Маркова Н.А., Хаджиев С.Н. //Патент РФ No 2442650. 2012.
9. Букина З.М., Графова Г.М., Ионин Д.А., Колесниченко Н.В., Лин Г.И., Маркова Н.А.,Хаджиев С.Н. // Патент РФ No 2442767. 2012.
10. Патент РФ No 2616981. 2017.
11. 11 .Conte M. // Catalysis Science and Technology. 2012.No2. P. 105.
12. 12.Lee K.Y., Lee S.W., Ihm S.K. // J. of Industrial and Engineering Chemistry. 2014. No 53. P. 10072.
13. 13.MentzelU.V. // Applied Catalysis A: General. 2012.No 417–418. P. 29 0.
14. 14.Meng F., Wang X., Wang S., Wang Y. // Catalysis Today.2017. No 298. P. 226.
15. 15.Bjørgen M., Joensen F., Holm M.S., Olsbye U. // Applied Catalysis A: General. 2008. No 345. P. 43.
16. 16.Rac V., Rakic V., Miladinovic Z. // Thermochimica Ac-ta. 2013. No 567. P. 73.
17. 17 .Van der Bij H.E., Aramburo L.R., Arstad B. //ChemPhysChem. 2014. No 15. P. 283.
18. 18.Rahmani F., Haghighi M., Estifaee P. // Microporous and Mesoporous Materials. 2014. No 185. P. 213.
19. 19.Zaidi H.A., Pant K.K. // Korean J. of Chemical Engineering. 2005. No 22. P. 353.
20. 20.Zaidi H.A., Pant K.K. // Catalysis Today. 2004. No 96.P. 155.
21. 21.Niu X., Gao J., Miao Q., Dong M. // Microporous and Mesoporous Materials. 2014. No 197. P. 252.
22. Mamadoliev, I.I., Fayzullaev, N.I., Khalikov, K.M. International Journal of Control and Automation, 2020, 13(2), стр. 703–709.

23. Mamadoliev, I.I., Fayzullaev, N.I. International Journal of Advanced Science and Technology, 2020, 29(3), стр. 6807–6813.
24. Fayzullaev, N.I, Bobomurodova, S.Y, Xolmuminova, D.A. Journal of Critical Reviews, 2020, 7(7), стр. 917–920.
25. Bobomurodova, S.Y., Fayzullaev, N.I., Usmanova, K.A. International Journal of Advanced Science and Technology, 2020, 29(5), стр. 3031–3039
26. OnoY.,AdachiH.,SenodaY. // J. of the Chemical Society, Faraday Transactions. 1988. No1. V. 84. P. 109.
27. Ni Y., Sun A., Wu X., Hai G. // Microporous and Mesoporous Materials. 2011. No 143. P. 435.
28. Centi G., Perathoner S., Arrigo R., Giordano G. // Applied Catalysis A: General. 2006. No 307. P. 30.
29. Palin L., Lamberti C., Kvick A., Testa F. // J. of Physical Chemistry B. 2003. No 107. P. 4034.