AMERICAN JOURNALS
Open Access, Peer Reviewed Journals

American Journal of Technology and Applied Sciences
ISSN (E): 2832-1766 Volume 40, September - 2025

KINETICS OF CATALYTIC SYNTHESIS OF DIMETHYL ETHER FROM SYNTHESIS GAS

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ABSTRACT	KEYWORDS
In this work, the effect of various factors on the process of direct synthesis of dimethyl ether from synthesis gas in one stage on the catalyst CuO·ZnO·Al2O3·ZrO2/bentonite was studied. As a result of the studies of the influence of various factors on the yield of target products in the process of obtaining dimethyl ether from synthesis gas, it was found that an increase in the molar ratio, pressure, temperature and molar ratio of hydrogen to greenhouse gas leads to an increase in the conversion of greenhouse gases due to the fact that the reaction of direct synthesis of dimethyl ether from synthesis gas prevails.	

Introduction

Deep processing of natural gas, associated petroleum gas, etc. into valuable petrochemical products is one of the most important processes of the chemical industry [1-3]. The transformation of natural and petroleum associated gas into easily transportable products makes it possible to convert these sources into universal energy resources [4-6].

In recent years, the process of processing synthesis gas into dimethyl ether (DME) in one stage has been of great interest to scientists around the world. The composition and characteristics of synthetic hydrocarbons obtained from DME depend on the properties of the zeolite catalyst used in this process, the conditions of the process and the composition of the synthesis gas. Control of the acidic properties of high-siliceous zeolites and the composition of the initial synthesis gas makes it possible to obtain light sulfur-free synthetic oil from methanol and DME [7-9]. It is known that the acidic properties of zeolites depend on the nature of exchangeable cations and the method of their administration [10-15]. It is known that the synthesis of ethylene and propylene from DME is easier than the synthesis of ethylene and propylene from methanol [16-21], compared to methanol, DME is a stronger methylating agent [22-27], which makes the reaction of ethylene and propylene synthesis from DME even on catalysts with low acidity allowing transfer at a sufficiently high rate [28-31]. In addition, DME is less active than methanol in hydrogen transfer reactions that cause coke formation, as a result of which the rate of catalyst deactivation in the reaction of ethylene and propylene from DME is significantly lower than in the reaction with methanol [32-39].

EXPERIMENTAL PART

In the work, the catalyst CuO·ZnO·Al2O3·ZrO2/bentonite was used to produce DME from synthesis. The catalytic activity of catalysts was studied at a fixed-bed catalyst unit in a flow-through reactor by feeding a mixture of gases into the reactor at a pressure of 1-2 MPa and a temperature of 220-300 °C (Fig. 1).

Qualitative and quantitative analysis of the reaction products was carried out on the Crystal 5000.2 gas chromatograph.

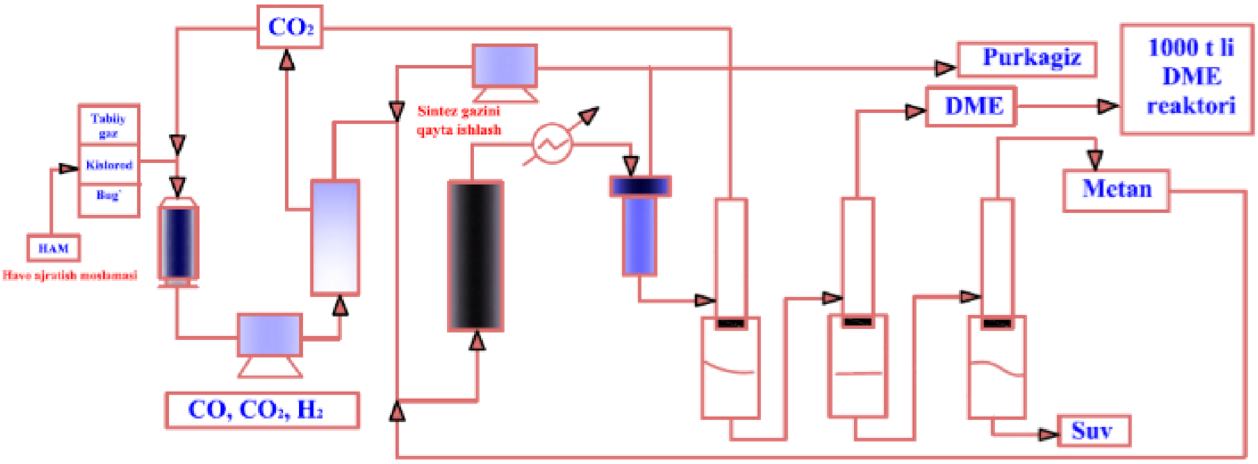
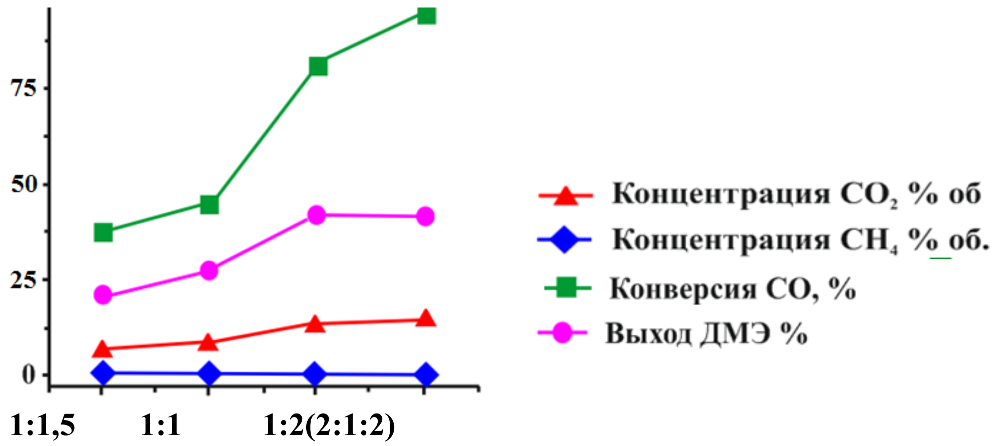


Figure 1. Diagram of a laboratory installation for the production of dimethyl ether from synthesis gas

The phase composition of the CuO·ZnO·Al2O3·ZrO2/bentonite catalysts was determined by X-ray phase analysis using unfiltered CuK α radiation (*l* = 1.5418 Å) before and after catalytic tests on the Shimadzu XRD-6000 refractometer. To determine the textural characteristics of the catalysts, the Brunauer-Emmett-Teller and Barrett-Joyner-Haland methods were used. The relative surface area was calculated from the data of nitrogen adsorption isotherms at 77 K. Pore volume was determined at a relative pressure of R/RO = 0.97. The acidic properties of the catalysts were determined using the Nicolet IR200 IR spectrometer.

EXPERIMENTAL RESULTS AND DISCUSSION

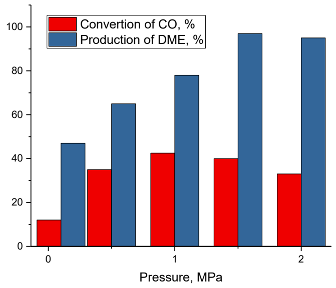
As a result of studying the effect of different ratios of the mixture of source gases, it was found that the highest yield of DME is achieved with a mixture of source gases in a ratio of 1:2 (Fig. 2). As a result of the experiments, it was also proved that the yield of DME increases with an increase in the concentration of CO2. It has been established that the DME yield is maximal at a molar ratio of gases equal to 2:1:2.



P = 1 MPa, T = 300 $^{oC,\ H2}$:CO = 2, volume velocity 1000 $^{h-1}$, catalyst volume 5 cm3

Figure 2. Influence of Gas Mixture Ratios on CO Conversion and DME Yield

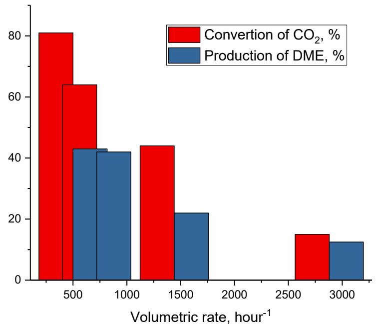
During the synthesis of DME from syngas, the volume decreases, so the process was carried out at high pressure. The effect of pressure on the DME outlet is shown in Figure 3. It can be seen that CO conversion increases with increasing pressure, with DME yield having the highest value at a pressure of 1 MPa. The decrease in the yield of dimethyl ether can be explained by its decomposition: $CH3OCN3 \leftrightarrow CH4 + CO + H2$. As the temperature increases, CO conversion and DME yield increase.



T = 300 $^{\circ C,\ H2}$: CO = 2, volume velocity 1000 $^{h-1}$

Figure 3. Effect of Pressure on CO Gas Conversion and DME Yield

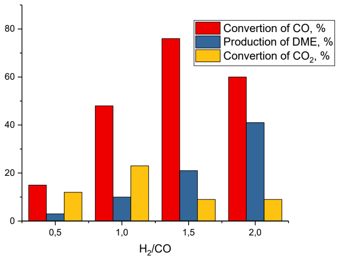
As can be seen from Fig. 4, With increasing volumetric velocity, CO conversion and DME output decrease. The reason for this is that with an increase in the volume velocity, the contact time of the reactants with the catalyst surface decreases, that is, an increase in the volume velocity reduces the gas conversion, since due to the short contact time, the reaction between the reactant and the catalyst surface does not have time to pass into the gas phase.



P = 1 MPa, T = 300 $^{oC,\ H2}$: CO, volumetric velocity 1000 $^{h-1}$

Figure 4. Effect of Volumetric Velocity on CO Conversion and DME Output

At the same time, an increase in the mole ratio of H2 and CO leads to an increase in DME yield and CO conversion (Fig. 5).



T = 300 $^{\circ C,}$ P = 1 MPa, volume velocity 1000 h-1

Figure 5. Effect of the H2:CO molar ratio on CO conversion, DME yield and carbon dioxide concentration

As a result of studies of factors affecting the reaction rate, the efficiency of the process of direct production of DME from synthesis gas, it was proved that an increase in pressure, temperature, and the mole ratio of H2:CO leads to an increase in DME yield and CO conversion.

Thus, the following optimal conditions for obtaining DME from synthesis gas in one stage were determined: P = 1 MPa, T = 300 $^{oC,\ H2}$: CO = 2, *vob* = 1000 $^{p-1}$. At the same time, the exhaust gas conversion does not decrease within 220 hours.

Before and after catalytic tests, the composition of the catalyst for the synthesis of DME from synthesis gas in the current of a mixture of hydrogen and helium was determined by the method of thermocontrolled reduction to a temperature of 400 °C. Fig. 6 shows the reduction peaks of the CuO·ZnO·Al2O3·ZrO2/bentonite catalyst before and after catalytic tests.

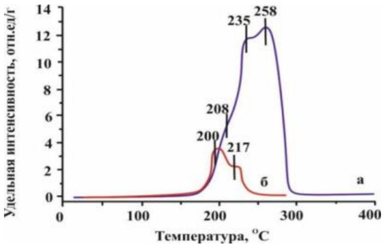


Figure 6. Comparison of the thermally programmed reduction spectra of the CuO·ZnO·Al2O3·ZrO2/bentonite catalyst before (curve a) and after (curve b) catalytic tests for 70 hours. Reduction in a mixture of hydrogen and helium

Fig. 7 shows a diffractogram of the initial catalyst CuO·ZnO·Al2O3·ZrO2/bentonite spent in the synthesis of DME from CO and H2 at a temperature of 320 °C and a pressure of 1 MPa for 4, 10 and 70 hours.

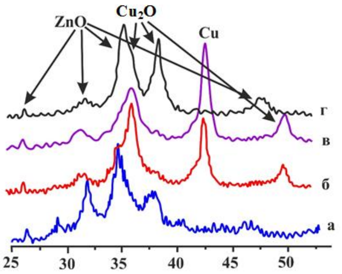


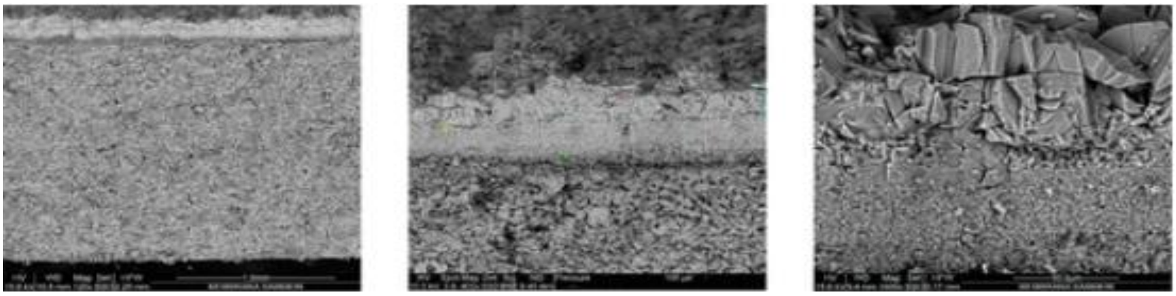
Figure 7. Diffractogram of the catalyst CuO·ZnO·Al2O3·ZrO2/bentonite for the synthesis of DME from CO and H2 at a temperature of 320 °C and a pressure of 1 MPa: a – initial, b – used for 4 hours, c – used for 70 hours, d – used for 10 hours

Table 1 shows the analysis of the results of the textural characteristics of the CuO·ZnO·Al2O3·ZrO2/bentonite catalyst, which shows that after treatment in a hydrogen current, the specific surface area of the catalyst decreases from 138 to 82 m2/g, and the average pore diameter increases from 13 to 21 nm.

Table 1. Textural characteristics of catalysts for the synthesis of DE from CO and H2

Catalyst Treatment Conditions	CuO·ZnO·Al2O3·ZrO2/бентонит		
	Sol, m2/g	Vpor, m2/g	Pores dўr, nm
Initial catalyst	138	0,355	13
In the H2 current for 4 hours at 320 °C	82	0,375	21
After synthesis for 10 hours at 320 °C and 1 MPa	71	0,355	18
After synthesis for 70 hours at 320 °C, 1 MPa.	68	0,355	15

Fig. 8 shows micrographs of the CuO·ZnO·Al2O3·ZrO2/bentonite catalyst used for the synthesis of DME under various processing conditions. The surface of the initial catalyst is heterogeneous (a), rough (b), and covered with individual particles (c).



and **B** **in**

Figure 8. Micrographs of CuO·ZnO·Al2O3·ZrO2/Bentonite Catalyst

a – initial, b – after 3 hours at 300 $^{\circ}$C, c – after 70 hours at 200-300 °C, P = 1-5 MPa

Reduction with hydrogen leads to a large porosity of the surface and the formation of individual particles. After testing the catalyst in the synthesis of DME, at a temperature change of 200 to 300 $^{\circ}$C and a change in pressure within 1-2 MPa, the textural characteristics of the catalyst changed significantly (Fig. 8c), that is, the surface became smoother, the average pore size changed from 1 to 40 µm.

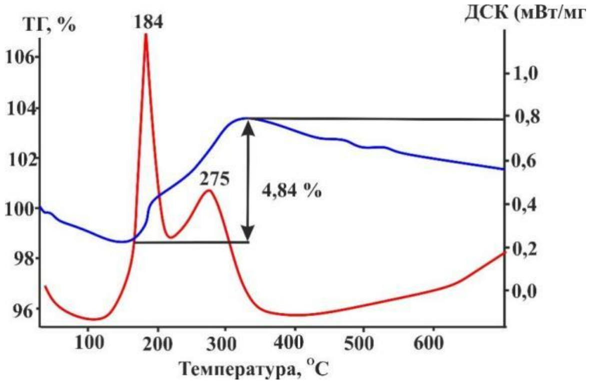
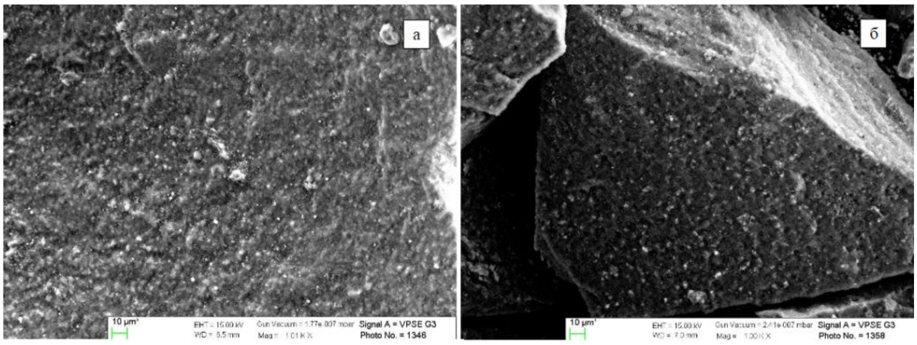


Figure 9. Differential thermal analysis of the treated catalyst after 70 hours of use. Heating rate with an air flow of 10 $^{oC/min.}$

Despite the fact that the catalyst worked for more than 120 hours, no change in its surface was expected, that is, a carbon layer was practically not formed on the surface.

Fig. 9 shows that two effects are observed in the derived diagrams. The first effect with a temperature of 192 °C also consists of two effects. The first is the release of carbon dioxide from the surface of the catalyst as a result of carbon combustion, which is confirmed by the data of differential thermal analysis and the temperature-controlled oxidation method. The second peak is observed at 275 °C, which indicates a total mass gain of 4.84%.

Fig. 10 shows micrographs of the CuO·ZnO·Al2O3·ZrO2/bentonite catalyst under various processing conditions. The surface of the catalyst (Fig. 10a) is homogeneous, slightly rough and almost identical to the surface of the catalyst treated in the hydrogen and nitrogen stream in Fig. 10b shows a micrograph of a catalyst treated only with hydrogen. The results obtained show that the surface of the catalyst CuO·ZnO·Al2O3·ZrO2/bentonite, treated only with hydrogen, is uniformly coated with particles with an average diameter of 2 µm.



a – initial, b – worked out in current H2 at 300 $^{\circ}$C for 3 hours

Figure 10. Micrographs of the YCC catalyst

The acidity of the surface of the CuO·ZnO·Al2O3·ZrO2/bentonite catalyst was determined by temperature-controlled ammonia desorption. The acidity was 0.165 mmol NH3/gcat. The calculated acidity value in the pure catalyst was 0.26 mmol NH3/gkat. The concentration of Lewis acid centers in the initial catalyst was determined by IR spectroscopy, which was 49 μmol/g. The sum of Brønsted acid centers is 56 μmol/g of the total concentration of the centers Acidity. Therefore, catalytic studies were carried out after the initial reduction of the catalyst, the IR spectra of CO2 adsorbed on the catalyst showed that after treatment in a hydrogen current at 350 °C for 2 hours, the concentration of Lewis acidity centers decreased by more than ten times.

CONCLUSION

1. An increase in the volumetric rate of syngas and hydrogen supply decreases, and an increase in the molar ratio increases the yield of dimethyl ether and the conversion of synthesis gas at the CuO·ZnO·Al2O3·ZrO2/bentonite catalyst.
2. As a result of the research, it has been established that an increase in pressure, temperature and molar ratio of hydrogen to synthesis gas leads to an increase in the conversion of synthesis gas and the yield of dimethyl ether.
3. As a result of the studies carried out, the following optimal conditions for obtaining dimethyl ether from synthesis gas in one stage were determined: P = 1 MPa, T = 300 $^{oC, H2}$: CO = 2, volume velocity 1000 $^{h-1}$.
4. Physicochemical and textural characteristics of the CuO·ZnO·Al2O3·ZrO2/bentonite catalyst were investigated.

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