

Kinetic laws of dimethyl ether synthesis reaction

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Abstract. The work consists of a detailed study of the influence of pressure, temperature, volume velocity and the molar ratio of H₂/CO on CO conversion and DME output. CO conversion and DME synthesis in the presence of a CuO·ZnO·Al₂O₃·ZrO₂·CaO/bentonite: γ-Al₂O₃ catalyst was studied in terms of their layer-by-layer loading. It was shown that the method of loading catalysts in the ratio of 2:1:2 is the best option. Further studies of the catalytic activity of the samples were carried out using a 2:1:2 loading method. Operating conditions T=290 °C, P=2 MPa, H₂/CO=2.5, volume velocity 1000 h⁻¹, conversion of CO in a single pass through the catalyst bed DME output "Crystal 5000" gas chromatograph, TriStar II (3020) was determined using an automatic gas adsorption analyzer model BJH (Barett-Joyner-Halenda). The phase composition of the catalyst samples was studied by X-ray phase analysis (X-ray diffraction - XRD) using a Shimadzu XRD-6000 diffractometer. The surface morphology of the samples was studied by scanning electron microscope based on VEGA IILMU electron microscope and INCA ENERGY 350 energy dispersive microanalysis. **Keywords.** synthesis gas, methanol, dimethyl ether, catalyst, conversion, pressure, temperature, volume velocity.

1 Introduction

One of the most beneficial and adaptable compounds that can be created is dimethyl ether [1,2]. About 5 million tons of dimethyl ether is produced globally each year, and this number is anticipated to rise gradually in the near future. 85% of the global market for dimethyl ether is centred in Asia, where it is presently used as a clean fuel for residential purposes [3].

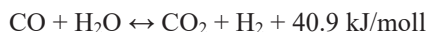
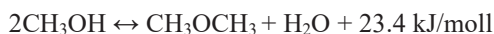
Dimethyl ether is also used as a refrigerant gas and is used in alkyl aromatics, aerosol propellants, abrasives [4], dimethyl sulphate [5], methyl acetate [5], methylating agents used to produce light olefins [6,7], aromatics, is an important raw material in the production of ethanol [8] and other important chemicals [8,9]. Another feature of DME is that it can be used as a "hydrogen carrier" [9].

Dimethyl ether is also a reliable alternative fuel for diesel engines. Among the advantages of dimethyl ether compared to conventional diesel fuels is the formation of low amounts of NO_x, hydrocarbons and carbon monoxide emissions during combustion [10].

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The production process of dimethyl ether from synthesis gas includes three main steps: water-gas exchange reaction, methanol synthesis reaction and intermolecular dehydration of methanol. Traditionally, DME is produced by indirect synthesis. This is a two-step catalytic process. First, synthesis gas turns into methanol in the following reactions: $2\text{CO} + 4\text{H}_2 \leftrightarrow 2\text{CH}_3\text{OH}$; $\Delta H_{298} = -43,4$ kcal/mol; $\text{CO}_2 + 3\text{H}_2 \leftrightarrow \text{CH}_3\text{OH} + \text{H}_2\text{O}$; $\Delta H_{298} = -11,9$ kcal/mol and dehydration of methanol gives DME: $2\text{CH}_3\text{OH} \leftrightarrow \text{CH}_3\text{OCH}_3 + \text{H}_2\text{O}$; $\Delta H_{298} = -5,6$ kcal/mol. In the last 10-15 years, there has been an increased interest in the synthesis of methanol and dimethyl ether (DME), which is obtained from the processing of various carbonaceous feedstocks [11-14] to produce valuable chemical products such as methanol and hydrogen [15, 16] [12, 13, 17, 18] related to production.

Reactions occurring in the synthesis of dimethyl ether from syngas:



Today, world scientists are interested in the reaction of obtaining methanol and dimethyl ether from synthesis gas, the reactions of obtaining lower alkenes from methanol and dimethyl ether, as well as the reactions of obtaining liquid fuel and aromatic hydrocarbons by catalytic aromatization of propane-butane fraction and petroleum-associated gases by oxycondensation of methane to ethylene, aromatization of aromatic hydrocarbons [19-41].

2 Experimental part

Thus, the work consists of a detailed study of the effects of pressure, temperature, volume velocity, and the molar ratio of H_2/CO on CO conversion and DME output. CO conversion and DME synthesis in the presence of a $\text{CuO} \cdot \text{ZnO} \cdot \text{Al}_2\text{O}_3 \cdot \text{ZrO}_2 \cdot \text{CaO}$ /bentonite: $\gamma\text{-Al}_2\text{O}_3$ catalyst were studied in terms of their layer-by-layer loading. The 2:1:2 ratio catalyst loading method showed to be the best option. Further studies of the catalytic activity of the samples were carried out using a 2:1:2 loading method. Operating conditions $T=290$ °C, $P=2$ MPa, $\text{H}_2/\text{CO}=2.5$, volumetric rate 1000 h^{-1} , conversion of CO in a single pass through the catalyst bed DME output Crystal 5000 gas chromatograph, TriStar II (3020) was determined using an automatic gas adsorption analyser model BJH (Barett-Joyner-Halenda). The phase composition of the catalyst samples was studied by X-ray phase analysis (XRD) using a Shimadzu XRD-6000 diffractometer. The surface morphology of the samples was studied by scanning electron microscope based on VEGA IILMU electron microscope and INCA ENERGY 350 energy dispersive microanalysis.

3 Results and discussion

3.1 Effect of temperature

In catalytic reactions, the temperature is the main factor that determines the reaction rate, direction, activity and service life of catalysts. The temperature dependence of DME yield, DME selectivity and CO conversion is shown in Figure 1.

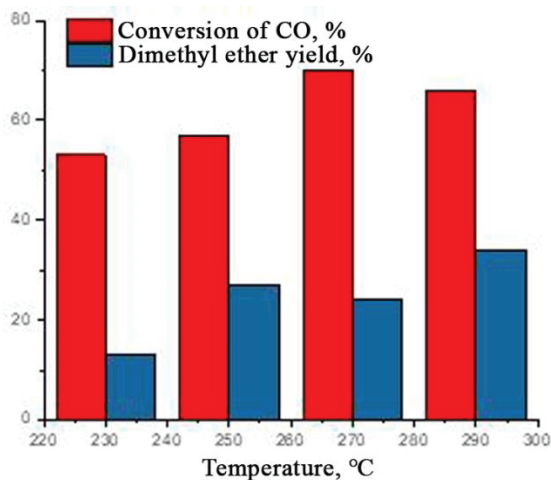


Fig. 1. Effect of temperature on CO conversion and DME yield at 2:1:2 catalyst loading. Operating conditions: P=2 MPa, H₂/CO=2.5, volumetric rate 1000 h⁻¹.

The operating temperature range was chosen based on the fact that at temperatures below 230 °C, methyl format is mainly formed on the copper-zinc catalyst. At temperatures above 270 °C, the yield of DME increases, while CO₂ and CH₄ are formed according to the decomposition reaction of DME (Table 1):

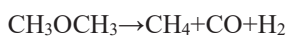


Table 1. Effect of temperature on CO conversion and DME yield at 2:1:2 catalysts loading. Operating conditions: P=2 MPa, H₂/CO = 2.5, volumetric rate 1000 h⁻¹.

Temperature, °C	230	250	270	290
CO conversion, %	53	57	69	65
DME yield, %	14	29	24	34
Gas phase products, % by volume.				
CO ₂	5	11	11	11
CH ₄	<0.01	<0.03	0.06	0.2
Liquid phase products, %				
Methanol	26	45	30	12
Water	74	59	64	86
Ethanol	0.44	0.62	0.28	1.28
Propanol-1	0.07	0.1	0.02	0.01
Butanol-1	0.003	0.02	0.004	0.001

Table 1 shows that the carbon dioxide concentration is the same for all temperatures, while the methane concentration increases with increasing temperature. Analysis of the liquid phase showed that with increasing temperature, the amount of methanol decreases, while the number of water increases. Primary alcohols such as ethanol, propanol, and butanol are also formed in small amounts. The competitive adsorption of CO and CO₂ on the metal centres of the catalyst is to blame for the poor conversion at temperatures up to 270 °C. The thermodynamic constraints of exothermic reactions, which cause this system's equilibrium to move toward reverse endothermic reactions, can be used to explain why CO conversion decreases at temperatures above 270 °C. At 290 °C, the greatest yield of DME (34%) is seen Figure 1.

The study of the effect of temperature on CO conversion and DME yield showed that the optimum temperature at 0.5 MPa pressure is 290 °C because the DME yield reaches the highest 34% when CO is 65% converted. In the condensate, the minimum amount of methanol (12%) is compared to other temperatures and the maximum amount of water (86%), so the reaction proceeds in the direction: of $2\text{CO} + 4\text{H}_2 \leftrightarrow \text{CH}_3\text{OCH}_3 + \text{H}_2\text{O}$.

3.2 The effect of external pressure

To determine the pressure dependence of CO conversion and DME yield, the experiment was carried out according to the following procedure: catalysts were loaded into the reactor according to the 2:1:2 method. The required pressure was created in the reactor, and heating of the reactor furnace with programmable temperature heating was established. The experiment was repeated for the reliability of the results. As can be seen from Figure 2 and Table 2, the CO conversion increases with increasing pressure and the DME yield is parabolic, with a maximum pressure of 2.5 MPa. Chromatographic analysis of the formed condensate at different pressures showed that the higher the amount of methanol, the lower the amount of water formed. Pressure has a significant effect on the course of reactions.

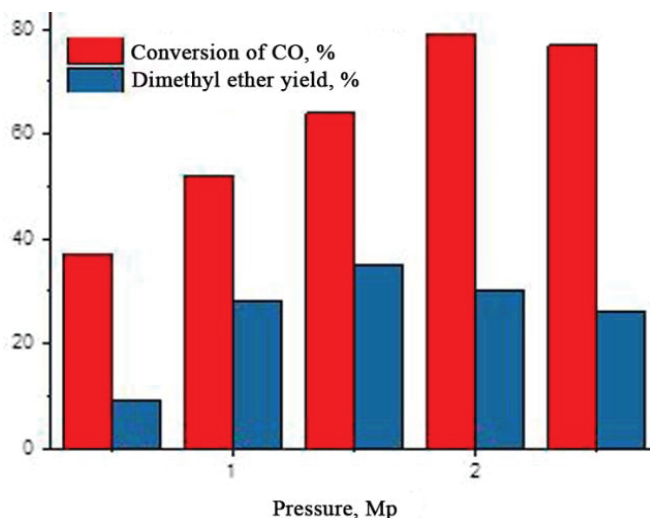


Fig. 2. Effect of pressure on CO conversion and DME yield with 2:1:2 catalyst loading. Operating conditions: T= 290 °C, H₂/CO=2.5, volumetric rate 1000h⁻¹.

The concentration of water is estimated to be between 12 and 15% at 1.5 and 2 MPa pressure, while methanol exhibits indicators between 82 and 86%. DME has a selectivity of 51–52% which is nearly identical, but its conversion value at 2 MPa is 13% greater. Although the conversion value of CO at 2.5 MPa is considerable (79%), the yield and

selectivity of DME are both 31%. The combined amounts of the simultaneous formation of the simple alcohols propanol-1 and butanol-1 are less than 1%.

Table 2. Effect of external pressure on CO conversion, DME yield, DME selectivity. Operating conditions: T= 290 °C, H₂/CO=2.5, volumetric rate 1000 h⁻¹.

Pressure, MPa	1	1.5	2	2.5
CO conversion, %	37	52	65	79
DME yield, %	10	27	34	31
Selectivity by DME, %	28	51	52	41
Gas phase products, % by volume				
CO ₂	5	9	11	11
CH ₄	0.09	0.15	0.2	0.19
Liquid phase product, %				
Methanol	44	15	12	41
Water	55	82	86	58
Ethanol	0.79	2.41	1.28	0.71
Propanol-1	0.18	0.005	0.01	0.12
Butanol-1	0.09	-	0.001	0.007

General indicators of the direction of change in the equilibrium of the system with a change in pressure are given by Le Chatelier's principle: an increase in pressure promotes processes associated with a decrease in volume and vice versa. Therefore, high pressure is a favourable factor for the process of methanol synthesis. In competitive reactions involving a decrease in volume, the pressure is most favourable for a reaction that proceeds with a decrease in maximum volume. In our case, the competing reactions that proceed with volume reduction are methanol synthesis and direct DME production from syngas, among which the maximum volume reduction and CO and H₂ in DME and water or carbon dioxide as intermediates are typical for interaction reactions with formation. This is inconvenient, because in our work, layer-by-layer loading of the catalyst is used to obtain DME, as a result of which methanol is first CuO·ZnO·Al₂O₃·ZrO₂·CaO/bentonite is formed at, then the resulting methanol-Al₂O₃DME is formed as a result of dehydration. The amount of DME obtained depends on the amount of methanol. The study of the effect of external pressure showed that the yield of DME is a parabolic relationship, the maximum of which corresponds to 2 MPa. CO conversion increases with increasing pressure. In further studies, 2 MPa pressure was selected as the working pressure, so at this value, the CO conversion and the working efficiency of DME reach the maximum values of 65 and 34%, respectively.

3.3 The influence of the volumetric rate of raw materials

The reaction's progression relies on how the reactants interact with the catalyst's surface, which necessitates prolonged collisions between the gases or vapours. As a result, it is important to consider how long it will take the reaction mixture to combine with the catalysts' surfaces. To do this, we can use a parameter like a volume velocity. Figure 3 illustrates how the volumetric rate affects CO conversion and DME output.

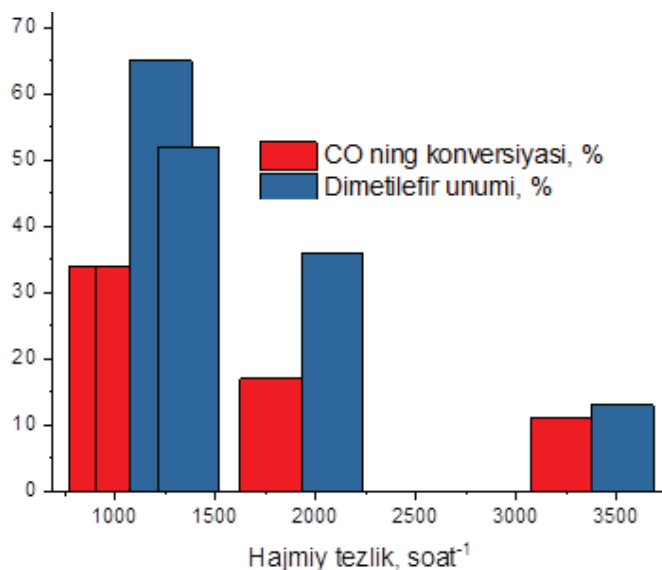


Fig. 3. Effect of volume velocity on catalytic activity.

Working conditions: loading method 2: 1: 2, P=2 MPa, H₂/CO=2.5, T = 290 °C.

It went from 1000 to 3380 h⁻¹ as the measure. 1000 h⁻¹ of CO + H₂ mixing results in a 65% CO conversion and a 34% DME efficacy. As volume rate increases, CO conversion declines. The yield of DME has slightly risen. At a CO conversion of 13%, a further rise in the volumetric rate results in a minimum DME yield of 11%. The occurrence of molecular diffusion and the brief exposure period are likely to blame for this.

3.4 The molar ratio of raw material H₂/CO

The molar ratio of hydrogen to carbon (II) oxide affects the yield of target and intermediate products. Figure 4 shows the effect of the feedstock mole ratio on DME yield, DME selectivity, and CO conversion. A CO conversion value of 13% and a DME yield of 2% were observed on CuO·ZnO·Al₂O₃·ZrO₂·CaO/bentonite and γ-Al₂O₃ catalysts at H₂/CO=1.

At H₂/CO=1.5, the reaction proceeds in the direction of the formation of an intermediate product. A low H₂/CO molar ratio leads to rapid coking of carbon in the catalyst and its deactivation. As the hydrogen content of the mixture increases, the DME yield increases to 34% at 65% conversion and reaches a maximum at H₂/CO=2.5, as the methanol synthesis reaction dominates. Increasing the H₂/CO ratio suppresses the water gas shift and causes water retention.

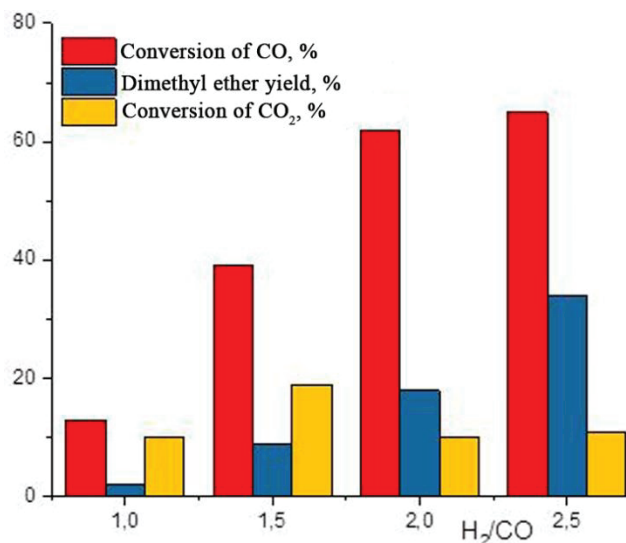


Fig. 4. Effect of H₂/CO molar ratio on feedstock conversion and DME yield. Operating conditions: T = 290 °C, P = 2 MPa, volume speed 1000 h⁻¹.

The diameter of hydrogen molecules (molecular diameter 0.35 nm), carbon monoxide molecules (molecular diameter 0.32 nm), or carbon dioxide molecules (molecular diameter of 0.33 nm) is adequate to diffuse into the internal pores of CuO·ZnO·Al₂O₃·ZrO₂·CaO/bentonite and γ-Al₂O₃ catalysts.

4 Summary

The study of the effect of temperature on CO conversion and DME yield showed that the optimum temperature at 2 MPa pressure is 290 °C because the DME yield reaches the highest 34% when CO is 65% converted. The study of the effect of external pressure showed that the yield of DME is a parabolic relationship, the maximum of which corresponds to 2 MPa. CO conversion increases with increasing pressure. In further studies, a pressure of 2 MPa was chosen as the operating pressure, so at this value, the CO conversion and the efficiency of DME reach the maximum values of 65 and 34%, respectively. At a feedstock H₂/CO molar ratio of 2.5, the DME yield increases to 34% at 65% conversion and reaches a maximum. The influence of the volume rate of raw materials parameter changed from 1000 to 3380 h⁻¹. Working conditions T=290 °C, P=2MPa, H₂/CO=2.5, volumetric rate of 1000 h⁻¹ was chosen as the optimal condition, and then we will use this condition in the works.

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