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A Single-Stage Catalytic Process for Obtaining Dimethyl Ether from Synthesis Gas

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Abstract

Obtaining dimethyl ether from synthesis gas with the use of a two-layer catalyst was studied. An optimum level-by-level loading was determined for two catalytic systems such as methanol production catalyst Katalco-58 and methanol dehydration catalyst γ -Al₂O₃. It was demonstrated that increasing the temperature and contact time results in increasing the CO conversion level and the yield of dimethyl ether, whereas their maximum values are attained at a pressure of 3 MPa. The optimum process conditions are: $T = 280$ °C, $P = 3$ MPa, $H_2/CO = 2$, the contact time 6 s.

Key words: synthesis gas, CuO/ZnO/Al₂O₃ catalyst, dimethyl ether

INTRODUCTION

The exhaustion of oil resources and the discovery of new gas fields determine growing interest in the chemical processing of gas whose proven resources in Russia in 2007 amounted to 58 trillion m³ [1]. Natural gas is considered a source of energy and raw material for the chemical industry. Most developed is natural gas processing into methanol widely used in industry. Since recently, they began using to process methanol into dimethyl ether (DME).

The use of DME as an additive to petrol allows improving the exhaust quality of diesel engines and reducing the emission of hazardous components. Owing to a high cetane number (55–60), higher than the mentioned parameter for diesel fuel, and a lower boiling point (–25 °C) of DME [2], using the DME promotes accelerating the mixture formation and combustion, provides reducing the ignition delay period, as well as a good start of diesel engines at low ambient temperature values. High oxygen content in DME (35 %) provides smokeless combustion with no formation of solid particles. In addition, DME is used as an intermediate product which is easily converted into

gasoline with improved environmental characteristics and minimum content of undesirable impurities [3].

At the present time, DME in Russia is produced via dehydration of methanol, although industrial systems for single-stage DME production from synthesis are already realized in Japan, China and Denmark. In this connection, the development of the mentioned technology in Russia for single-stage DME production and for obtaining appropriate catalysts is of urgency.

In this study, we investigated a single-stage process of DME synthesis from synthesis gas using a mixture of a methanol synthesis catalyst and methanol dehydration catalyst in a flow-through catalytic reactor.

EXPERIMENTAL

In this work we used commercial catalyst Katalco-58 (Johnson Matthey Catalysts) with the composition CuO/ZnO/Al₂O₃ (hereinafter designated as R-1) for the synthesis of methanol, as well as γ -Al₂O₃ (the Boreskov Institute of Catalysis, SB RAS, Novosibirsk, Russia) as a catalyst for methanol dehydration.

TABLE 1

Parameters of initial catalyst R-1 and γ -Al₂O₃

Catalysts	Specific surface, m ² /g	Pore volume, cm ³ /g	Pore radius, Å	Acidity, mol ammonia/g _{cat}
R-1	110	0.3	81	0.064
γ -Al ₂ O ₃	250	0.7	77	0.254

The pore structure and specific surface area of the samples were determined by BET technique using TriStar II (3020) automatic gas adsorption analyzer. The distribution of acidic sites was obtained *via* desorption of ammonia (Table 1).

Before testing, we grinded the samples and took a 1–0.5 mm fraction for loading into the reactor. The total load volume was equal to 5 cm³. Before the experiment, the catalyst was reduced by a mixture of hydrogen and nitrogen (10 vol. % H₂ + N₂) at 300 °C during 3 h. The reduction procedure was chosen basing on the results of the temperature-programmed reduction (TPR), obtained using ChemiSorb 2750 chemisorption analyzer. According to the TPR, the peaks correspond to the temperature range of 150–300 °C (Fig. 1).

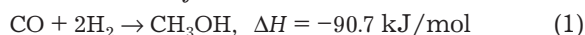
Catalytic studies were conducted using a catalytic set-up that allows one to realize the process at elevated pressure values. Hydrogen and carbon monoxide, whose purity was tested by chromatographic method was supplied from gas cylinders. The mixture of products formed leaving from the reactor after the catalysis was passed through the cooling system. The products were analyzed using a Crystal 5000.2 gas chromatograph. The identification of CO, CH₄,

CO₂ was carried out using a column filled with sorbent activated charcoal; the identification of water, dimethyl ether and methanol was performed using a column with Porapak N (thermal conductivity detector) and a capillary column (flame ionization detector). Argon and helium were used as carrier gases.

RESULTS AND DISCUSSION

The synthesis of DME from the mixture of CO + H₂ includes the following basic exothermic reactions:

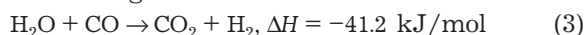
methanol synthesis:



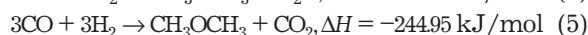
methanol dehydration:



water gas shift reaction:



direct DME synthesis from synthesis gas:



As a rule, DME is produced from synthesis gas with the composition of H₂/CO = 1 : 1 (see eq. (5)). Nevertheless, under the conditions of the process, of H₂O enters into the reaction with CO, and the steam conversion of carbon monoxide results in the formation of hydrogen and carbon dioxide (see eq. (3)). Consequently, taking into account the steam conversion of CO, the H₂/CO molar ratio should be equal to 2 in order to achieve the maximum conversion level of CO [4].

The experiment was carried out at the mentioned ratio between hydrogen and carbon oxide (II). The mixture was fed sequentially through the copper-containing catalyst R-1 for the obtaining methanol and then through γ -Al₂O₃ for the methanol dehydration. Catalytic studies were not performed at the temperature values higher than 300 °C, since Cu–Zn-containing catalyst for the production of methanol represents a low temperature catalyst.

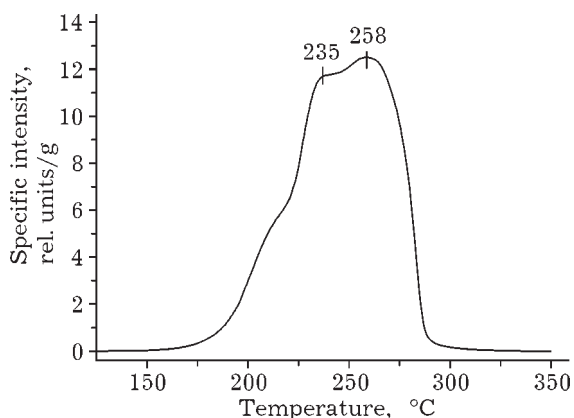


Fig. 1. TPR spectrum of initial catalyst R-1 reduced in a mixture of hydrogen and nitrogen (10 vol. % H₂ + N₂) at 300 °C for 3 h.

TABLE 2

Effect of catalyst loading arrangement on the conversion level of CO and the yield of DME ($P = 3 \text{ MPa}$, $T = 280 \text{ }^\circ\text{C}$, $\text{H}_2/\text{CO} = 2$, $\tau_{\text{cont}} = 6 \text{ s}$)

Parameters	Catalyst loading arrangement*		
	1 : 1	2 : 3	2 : 1 : 2
CO conversion level of, %	33	44	56
DME yield, %	12	10	17
CO ₂ volume fraction, %	7	5	10
CH ₄ volume fraction, %	0.06	0.05	<0.05

* 1 : 1 – the first layer is R-1 (2.5 cm³), the second layer is $\gamma\text{-Al}_2\text{O}_3$ (2.5 cm³); 2 : 3 – the first layer is R-1 (2 cm³), the second layer is $\gamma\text{-Al}_2\text{O}_3$ (3 cm³); 2 : 1 : 2 – the first layer is R-1 (2 cm³), the second layer is R-1 + $\gamma\text{-Al}_2\text{O}_3$ (1 cm³), the third layer is $\gamma\text{-Al}_2\text{O}_3$ (2 cm³).

Effect of a catalyst loading technique

For the completeness of the initial mixture reaction with the catalyst surface we investigated different ways to load the catalyst (Table 2), which resulted in determining the best variant (2 : 1 : 2): the first layer represented a copper-containing catalyst for the production of methanol, whereas the second layer was a mixture of a methanol-producing catalyst and $\gamma\text{-Al}_2\text{O}_3$ for its dehydration and converting unreacted CO and H₂, and the third layer being aluminum oxide for the dehydration of methanol into DME.

With this method of loading the catalyst the conversion level of CO amounts up to 56 %, whereas the yield of DME with singly passing the CO and H₂ mixture through the reactor is equal to 17 %. Further, we used just this method for loading catalysts. The main contribution to the formation of carbon dioxide is drawn by water gas shift reaction (see eq. (3)). The authors of [5] demonstrated the source of CO₂ formation to be linear methoxy groups those convert into formate-like and aldehyde-like surface complexes. This is in a good agreement with the data obtained. In the case of 1 : 1 loading, the concentration of CO₂ amounted to about 7 %, the yield of DME was equal to 12 %. With the increase in the fraction of acidic catalyst $\gamma\text{-Al}_2\text{O}_3$, the CO₂ concentration reaches a minimum value equal to 5 vol. % with the yield of DME amounting to 10 %. This could be explained by the fact that CO₂ as a by-product is directly involved in the synthesis of DME [6], so the yield of DME increases with the increase of CO₂ content in the gas phase.

Methane can be formed in the course of C, CO and CO₂ hydrogenation according to reactions [7]



From the data presented in Table 2 one can see that with increasing the CO₂ content the concentration of methane exhibits a decrease. To all appearance, this could be connected with the fact that the presence of water vapour and CO₂ inhibits the reaction (8), so this reaction can be ignored.

Effect of pressure

The effect of pressure on the catalytic activity of systems at certain temperature and preset mixture flow rate is demonstrated in Fig. 2. It is seen that the values of CO conver-

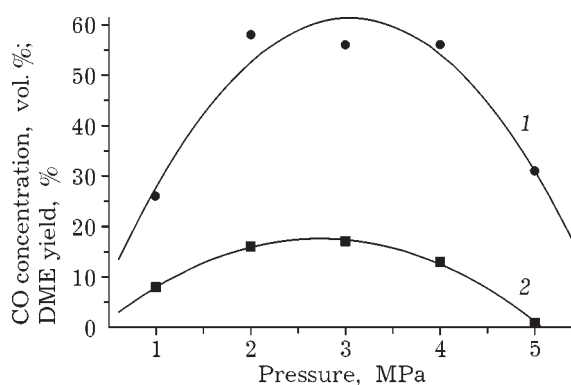


Fig. 2. Effect of pressure on the CO conversion level (1) and the yield of DME (2) with the catalyst loading arrangement 2 : 1 : 2 ($P = 3 \text{ MPa}$, $T = 280 \text{ }^\circ\text{C}$, $\text{H}_2/\text{CO} = 2$, $\tau_{\text{cont}} = 6 \text{ s}$).

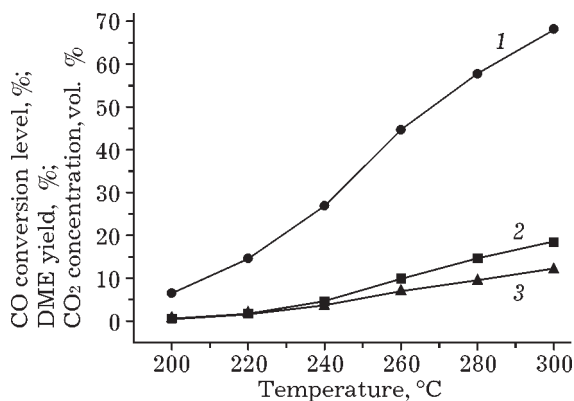


Fig. 3. Effect of temperature on the conversion level of CO and the yield of DME with the catalyst loading arrangement 2 : 1 : 2 (for the process conditions, see Fig. 2): 1 – the conversion level of CO, %; 2 – the yield DME, %; 3 – the concentration of CO₂, vol. %.

sion level and DME yield reach a maximum at 3 MPa. The reaction of obtaining DME from synthesis gas occurs with heat generation and decreasing the number of moles, so the process should be efficient at lower temperature values and higher pressure. Probably for this reason, the conversion level of CO and the DME yield demonstrate a decrease with increasing pressure at the temperature of 280 °C.

Temperature effect

Figure 3 demonstrates the effect of temperature on the yield of DME and on the CO conversion level. One can see that at low temperature values (200–220 °C) the CO conversion level and DME yield are very low. With further increasing the temperature, both values exhibit an increase to reach values of 58 and 18%, respectively. To all appearance, this could be connected with the predominance of hydrocracking reactions at elevated temperature, which is indicated by the increase in the formation of by-product CO₂.

Effect of contact time

Figure 4 demonstrates the effect of contact time on the CO conversion level and on the yield of DME in the case of loading the catalysts R-1 and γ -Al₂O₃ at a ratio of 2 : 1 : 2. As the contact time increases, the yield of DME exhibits an

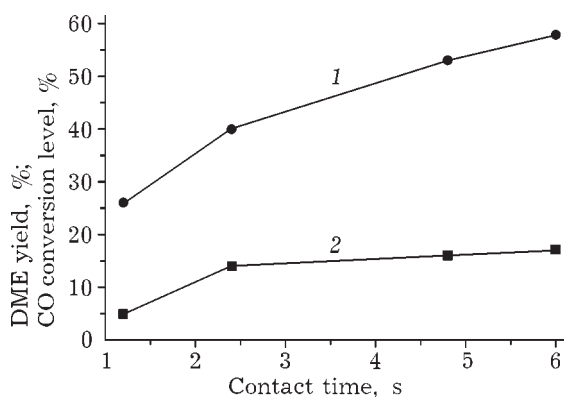


Fig. 4. Effect of contact time on the parameters of the process (for the process conditions see Fig. 2): 1 – the conversion level of CO, %; 2 – the yield of DME, %.

increase to amount to 16% at the CO conversion level equal to 53%. When $\tau_{\text{cont}} = 6$ s, the conversion level of CO is as high as 58%, whereas the yield of DME is equal to 17%.

CONCLUSION

We have studied the process of obtaining DME from CO and H₂ using a two-layer catalyst within one reactor. An optimum layer-by-layer loading is determined for two catalytic systems: the layer of methanol catalyst, the layer of a mechanical mixture of the methanol catalyst and γ -Al₂O₃, the layer of γ -Al₂O₃. Single passing the synthesis gas through the reactor under such loading at 280 °C and a pressure of 3 MPa, H₂/CO = 2, and the contact time equal to 6 s provides the conversion level of CO amounting to 58%, and the yield of DME amounting to 17%. It has been demonstrated that with increasing the temperature and contact time the CO conversion level and DME yield exhibit an increase.

REFERENCES

- 1 Popova N. M., Diosumova K., Katalizatory Selektivnogo Okisleniya i Razlozheniya Metana i Drugikh Alkanov, Ylym, Almaty, 2007.
- 2 Arcoumanis C., Bae C., Crookes R., Kinoshita E., *Fuel*, 87, 7 (2008) 1014.
- 3 Kolesnichenko N. V., Kitaev L. E., Bukina Z. M., Markova N. A., Yushchenko V. V., Yashina O. V., Lin G. I., Rozovskiy A. Ya., *Kinetika i Kataliz*, 48, 6 (2007) 846.
- 4 Erena J., Garona R., Arandes J. M., Aguayo A. T., Bilbao J., *Int. J. Chem. Reactor Eng.*, 3 (2005) 1.

- 5 Rozovskiy A. Ya., Lin G. I., *Teoreticheskiye Osnovy Sinteza Metanola*, Khimiya, Moscow, 1990.
- 6 Kuznetsov V. D., Shub F. S., Temkin M. I., *Kinetika i Kataliz*, 23, 4 (1982) 932.

- 7 Zhorov Yu. M., *Termodinamika Khimicheskikh Protsessov. Neftekhimicheskiy Sintez, Pererabotka Nefti, Uglya i Prirodnogo Gaza*, Khimiya, Moscow, 1985.