Dimethyl ether transformations over copper chromite/alumina catalysts in the packed bed and microstructured reactors: 1. Deep oxidation

O B Sukhova, E V Matus, I Z Ismagilov and M A Kerzhentsev

1Federal Research Center “Boreskov Institute of Catalysis”, Siberian Branch of the Russian Academy of Sciences, 5 Lavrentiev Ave., Novosibirsk, 630090, Russia

2Novosibirsk State Technical University, 20 Karl Marx Ave., Novosibirsk, 630073, Russia

E-mail: ma_k@catalysis.ru

Abstract. The deep oxidation of DME in a reactor with a supported catalyst and in a microreactor has been studied. Kinetic dependences of DME oxidation were obtained and comparative results are discussed.

1. Introduction

The work of recent years has shown that microreactors open up new opportunities in hydrogen energy when creating autonomous portable power sources that replace traditional electric batteries. Currently, leading Western firms are developing and producing miniature fuel processors for hydrogen production, used in fuel cells for household purposes (for laptops, digital cameras, mobile phones, etc.). Methanol is commonly used as a starting fuel from which hydrogen is obtained for a fuel cell. However, methanol has a number of disadvantages, the main one being its high toxicity. In recent years, dimethyl ether (DME) has been used as a promising new environmentally friendly fuel for many processes. Dimethyl ether has been proposed as an alternative to diesel fuel and liquefied gas (a mixture of propane and butane). In addition, DME can be considered as a promising feedstock for the production of hydrogen for fuel cells. It is important that dimethyl ether has great advantages over methanol due to its inertness and low toxicity. This substance is easily converted into a liquid phase at a pressure of 5 atm, similar to a propane-butane mixture, and can be supplied to the microprocessor directly from a cylinder without using a minipump. Thus, DME is a very promising feedstock for the production of hydrogen-containing gas. Therefore, a great deal of attention is paid to the study of these processes in the world.

The complete oxidation reaction of DME was investigated and described in papers [1-3]. On Rh catalysts, supported on various carriers such as MgO, Al2O3, TiO2, SiO2. The least active catalysts are Rh / MgO [1]. And on catalysts based on platinum group metals, supported on alumina [2], these catalysts can be arranged in a row according to their catalytic activity: Ru > Pt > Ir > Pd > Rh.

2. Experimental

The study of the reactions of complete oxidation of dimethyl ether was carried out in a flow-through automated installation. The reactions were studied in a microreactor and in a quartz reactor. In the microreactor, a 5% CuCr2O4 / Al2O3 catalyst was used, deposited on microchannel plates of an aluminum alloy with a channel diameter of 0.5 mm. In a flow-through reactor, studies were carried out on a granular catalyst 20% CuCr2O4 / Al2O3 (fraction 1.4-2 mm). The flow reactor was a tube with
an internal diameter of 9 mm. All experiments were carried out at atmospheric pressure. The complete oxidation of DME was carried out at an initial DME concentration of 0.5 vol% in the temperature range 200-375°C and three volumetric rates 1600 h⁻¹, 5360 h⁻¹, 10700 h⁻¹.

2. Results and Discussion

\[ \text{CH}_3\text{OCH}_3 + 3\text{O}_2 = 2\text{CO}_2 + 3\text{H}_2\text{O} \]

In a series of experiments on the complete oxidation of DME, the temperature dependences of the conversion of DME were obtained on a granular catalyst IK-12-70 and on a microstructured catalyst.

Figure 1 shows the temperature dependences of the DME conversion for the deep oxidation process carried out on a granular catalyst at an initial DME concentration of 0.5 vol%.

![Dependences of the conversion of DME on temperature during the reaction on a granular catalyst at different values of the volumetric rates: 1. 1600 h⁻¹, 2. 5360 h⁻¹, 3. 10700 h⁻¹.](image)

From Figure 1, it can be seen that the conversion of DME increases with increasing temperature. Complete conversion is observed at a temperature of 300 °C and a space velocity 1600h⁻¹. In the entire temperature range, the activity of the granular catalyst at a rate of 1600 h⁻¹ is noticeably higher than at other studied rates.

Figure 2 shows the temperature dependences of the DME conversion for the process carried out on a microstructured catalyst at an initial DME concentration of 0.5 vol%.
Fig. 2. Dependences of the conversion of DME on temperature during the course of the reaction on a microstructured catalyst at various values of GHSV: 1. 1600 h⁻¹, 2. 5360 h⁻¹, 3. 10700 h⁻¹.

With an increase in temperature, the conversion of DME increases. Almost complete conversion on a microstructured catalyst is achieved at a temperature of 300 °C and a space velocity of 1600 h⁻¹. For clarity, it is necessary to compare the data on the catalytic activity of microstructured and granular catalysts.

Fig. 3. Comparison of the temperature dependence of the DME conversions when carrying out the process on microstructured and granular catalysts. The feed rate of the reaction mixture is 1600 h⁻¹. 1. microstructured catalyst, 2. IK-12-70.
Fig. 4 Comparison of the temperature dependence of the DME conversions when carrying out the process on microstructured and granular catalysts. The feed rate of the reaction mixture is 5360 h⁻¹. 1. microstructured catalyst, 2. IK-12-70.

At a given rate above 200 °C, the catalytic activity of the microstructured catalyst is slightly higher than the granular catalyst. At 250°C 88% conversion on microstructured, 64% on granular. Figure 4 shows the temperature dependences of the conversion when the process is carried out on a microstructured catalyst and on a granular catalyst at a feed rate of the reaction mixture of 5360 h⁻¹.

At temperatures below 250°C, the conversion on a microstructured catalyst is close to the conversion of DME on a granular catalyst. In the investigated temperature range above 250°C, the microstructured catalyst has a slightly higher catalytic activity compared to the granular catalyst. For example, at a temperature of 290 °C, the conversions are 85% on a granular catalyst and about 100% on a microstructured catalyst. Figure 6 shows the temperature dependences of conversion when the process is carried out on a microstructured catalyst and on a granular catalyst at a feed rate of the reaction mixture of 10700 h⁻¹.
Fig. 5 Comparison of the temperature dependence of the DME conversions when carrying out the process on microstructured and granular catalysts. The feed rate of the reaction mixture (GHSV) is 10700 h⁻¹. 1. microstructured catalyst, 2. IK-12-70.

At temperatures above 275°C, a microstructured catalyst exhibits greater catalytic activity than a granular catalyst. At a temperature of 300°C, the conversion on a granular catalyst is 81%, and on a microstructured one 97%. At 380°C 98% for granular and 100% for microstructured catalyst. A series of experiments was carried out on a microstructured catalyst with a change in the concentration of DME in the initial reaction medium at a fixed feed rate of 5360 h⁻¹ and an oxygen content of 20%.
Table 1. Comparison of the activity of a microstructured catalyst at different initial concentrations of DME.

| DME in initial gas mixture – IGM (mmole/l) | Temperature in reactor (°C) | DME concentration (mmole/l) | CO₂ concentration (mmole/l) | Conversion (%) |
|-------------------------------------------|-----------------------------|-----------------------------|-----------------------------|---------------|
| 0.13537                                   | 150                         | 0.12760                     | -                           | 5.7           |
|                                           | 175                         | 0.12506                     | 0.0053184                   | 7.6           |
|                                           | 200                         | 0.11314                     | 0.01697                     | 16.4          |
|                                           | 225                         | 0.08905                     | 0.0506495                   | 34.7          |
|                                           | 250                         | 0.049577                    | 0.122785                    | 64.0          |
|                                           | 275                         | 0.00699185                  | 0.211665                    | 94.8          |
|                                           | 300                         | -                           | 0.23003                     | 100           |
| 0.287295                                  | 150                         | 0.287296                    | -                           | 1.8           |
|                                           | 175                         | 0.2896                      | 0.006852                    | 4.1           |
|                                           | 200                         | 0.2576                      | 0.026834                    | 11.9          |
|                                           | 225                         | 0.20906                     | 0.071483                    | 28.5          |
|                                           | 250                         | 0.1416                      | 0.179245                    | 51.6          |
|                                           | 275                         | 0.047766                    | 0.36988                     | 83.7          |
|                                           | 300                         | 3.94E-4                     | 0.50073                     | 100           |
|                                           | 375                         | 0                           | 0.50576                     | 100           |
| 0.48516                                   | 150                         | 0.48227                     | -                           | 0.6           |
|                                           | 175                         | 0.4727                      | 0.00809685                  | 2.6           |
|                                           | 200                         | 0.4433                      | 0.030188                    | 8.6           |
|                                           | 225                         | 0.3954                      | 0.090570                    | 18.5          |
|                                           | 250                         | 0.31811                     | 0.218075                    | 34.4          |
|                                           | 275                         | 0.1825                      | 0.52896                     | 62.4          |
|                                           | 300                         | 0.028335                    | 0.889475                    | 94.2          |
|                                           | 325                         | -                           | 0.98292                     | 100           |
|                                           | 375                         | -                           | -                           | 100           |

For clarity, the above results are presented in the form of a graph.
**Fig.6** Comparison of the activity of a microstructured catalyst at different initial concentrations of DME. GHSV of the reaction mixture is 5360 h$^{-1}$. The oxygen content is 20%. 1. the concentration of DME in I is 0.30% vol., 2. the concentration of DME in IGM is 0.66% vol., 3. the concentration of DME in IGM is 1.1% vol.

3. **Conclusion**

In paper [1] shown that Rh-catalysts at a concentration of DME in IGM of 1% and a feed rate of the reaction mixture of 4000 h$^{-1}$, 100% conversion of DME is achieved at 600-630K, and in our work, complete conversion is observed at 600 K (the feed rate of the reaction mixture is 5360 h$^{-1}$). In article [2], on catalysts based on platinum group metals supported on alumina at a DME concentration in IGM of 1% and a feed rate of the reaction mixture of 4000 h$^{-1}$, 100% conversion is observed at approximately at 673 K.

Thus microchannel reactor demonstrates comparable and superior activity over conventional catalytic reactors and can be considered as prospective way for creating autonomous portable power sources.

4. **References**

[1] F. Solymosi, J. Cserenyi and L. Ovari, Journal of Catalysis 171,(1997) 476

[2] F. Solymosi, J. Cserenyi and L. Ovari, Cat. Lett. 44 (1997) 89

[3] A. Ishikawa, E. Iglesia, Chem. Commun. (2007), 2992

[4] Arendarskii D A, Ismagilov Z R and Barannik G B 1992 *Catal Lett* **15** 347-51

[5] Simonov A D, Mishenko T I, Yazykov N A and Parmon V N 2003 Chem Sustain Devel **11** 277-83