

Cu-Cr/ γ -ALUMINA CATALYSTS FOR DIMETHYL ETHER SYNTHESIS

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ABSTRACT

The investigation relates to catalysts, comprising copper-chromium spinel, coated on γ -Al₂O₃ carrier. The effect of catalyst composition on the activity behavior toward dimethyl ether synthesis was discussed. It was found that the mixed CuO – Cr₂O₃ catalysts are very active with regard to the methanol dehydration. A synergetic effect of both copper and chromium species is clearly observed.

Keywords: copper-chromium catalysts, dimethyl ether, synthesis

INTRODUCTION

Dimethyl ether (DME) is a multipurpose clean fuel and chemical feedstock that can be produced from a wide variety of sources and has a number of important applications. It is a useful chemical intermediate for the preparation of many important products, such as dimethyl sulfate and high-value oxygenated compounds (1-3). In addition, it has been used as an aerosol propellant to replace chlorofluoro carbons which can destroy the ozone layer of the atmosphere (4). Recently, it has received much attention as an alternative diesel fuel by virtue of its low NO emission, near-zero smoke and less engine noise compared with those of traditional diesel fuels (5, 6).

Commercially, DME is produced by the catalytic dehydration of methanol at around 300°C at 10 atm pressure over solid acid catalysts such as γ -Al₂O₃ or zeolites, combined with different additives (7, 8). The main problems with the catalysts is coke formation and coating of the surface with carbon, which requires their replacing more frequently than is desirable. This necessitates search for new catalysts with high activity and long period of exploitation.

In this paper we have studied the role of the catalyst composition of the alumina supported CuO - Cr₂O₃ in the methanol dehydration process.

MATERIALS AND METHODS

Commercial $\gamma\text{-Al}_2\text{O}_3$ F-2000 with particle size of 4,8 mm and total pore volume of $0,5 \text{ sm}^3/\text{g}$ was used as a carrier. The catalysts were prepared by impregnation of the support with an aqueous solution of copper and chromium nitrates.

All experiments were carried out on a flow apparatus for estimation of oxide catalysts for methanol oxidation and dehydration, using stainless steel pseudo-isothermal reactor (Fig. 1).

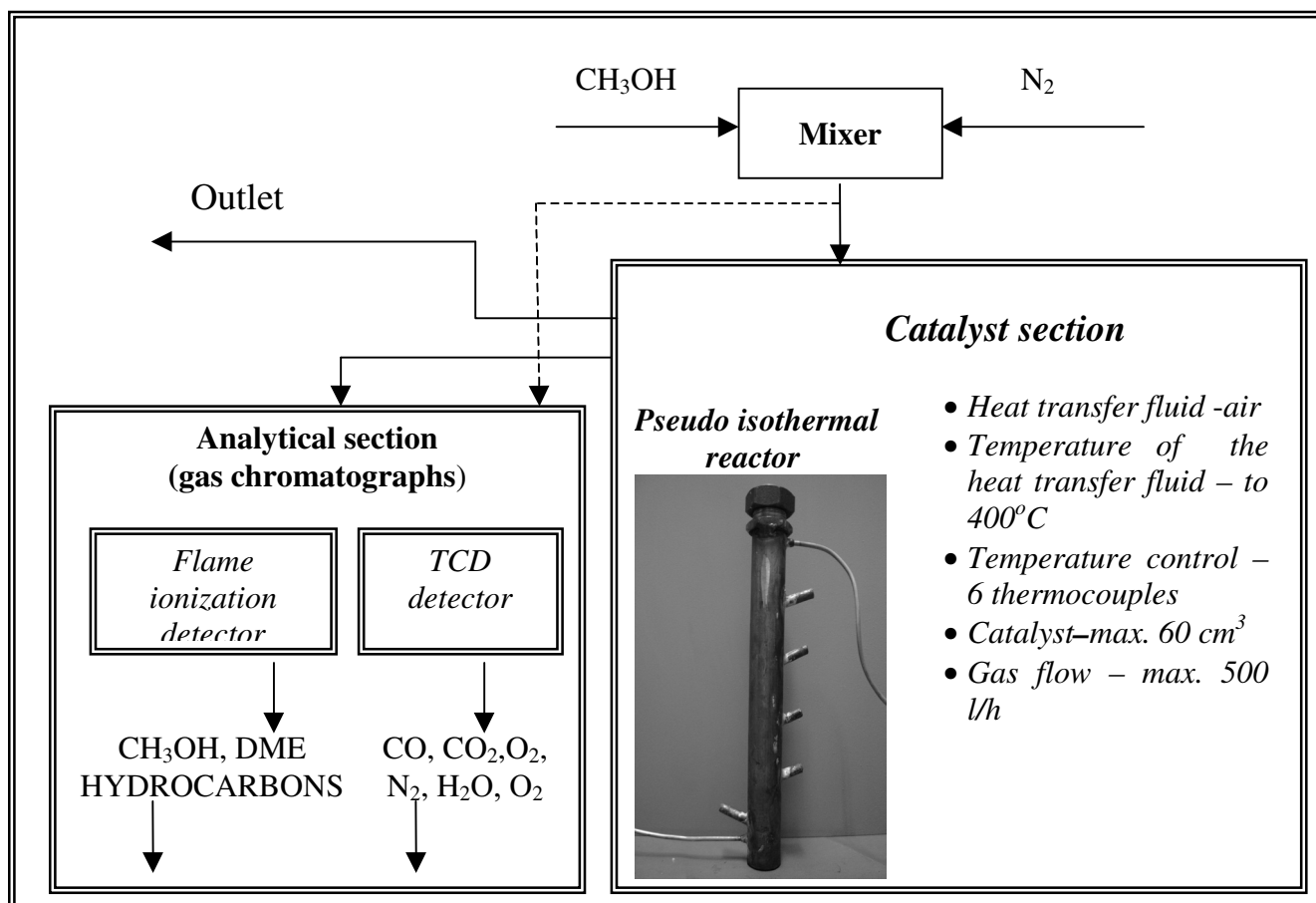


Figure 1. Apparatus for estimation of oxide catalysts for methanol oxidation and dehydration.

The outlet gas mixture was analyzed for dimethyl ether (DME), methanol, CO, dimethoximetan (DMM) and hydrocarbons content in the analytical section by on-line gas chromatograph, equipped with flame-ionization detector and Porapak Q column. A second gas chromatograph, equipped with a thermal conductivity detector and MS-13X column was employed for CO determination.

RESULTS AND DISCUSSION

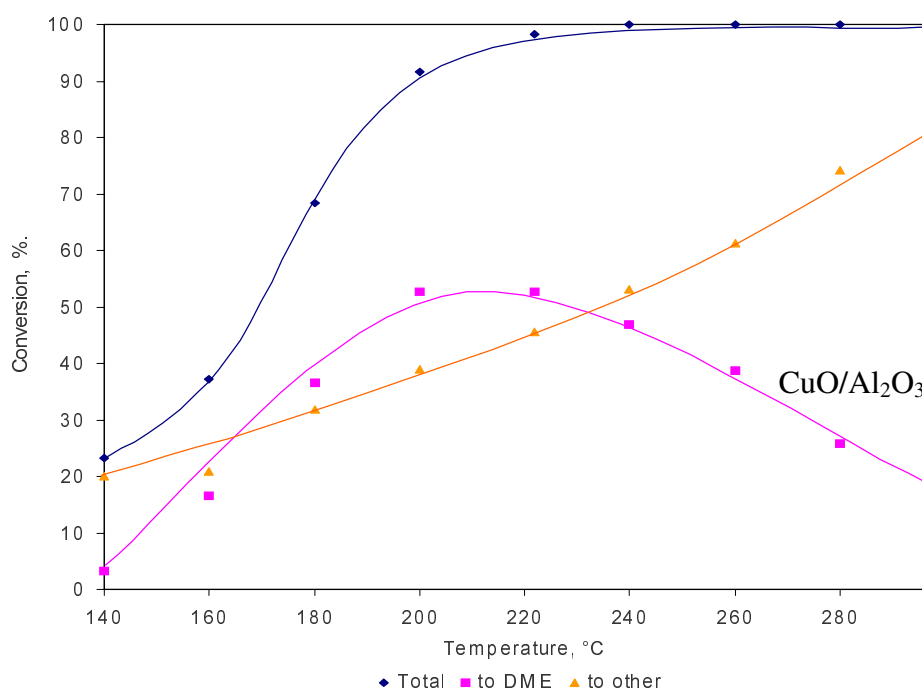


Figure 2. Product distribution versus temperature. Feed gas composition: methanol 4,0 %, nitrogen to 100 %.

Table 1. Product distribution versus temperature. Feed gas composition: methanol 4,0 %, nitrogen to 100 %.

Temperature, °C	Conversion, %		
	Total	To DME	To other products
300	100,0	16,7	83,3
280	100,0	25,9	74,1
260	100,0	38,6	61,4
240	100,0	46,8	53,2
220	98,3	52,7	45,6
200	91,7	52,7	39,0
180	68,3	36,6	31,8
160	37,3	16,5	20,8
140	23,3	3,2	20,1

Fig. 2 and Table 1 reflect the temperature dependence of methanol conversion on alumina supported copper oxide. As it is seen from the results presented, the activity of the catalysts with regard to the total methanol conversion is significant even at temperatures lower than 200°C. The conversion to DME passes through maximum at 200 – 240°C and rapidly decreases along with the temperature, while

conversion to other products (mainly hydrocarbons) increases in the whole temperature interval.

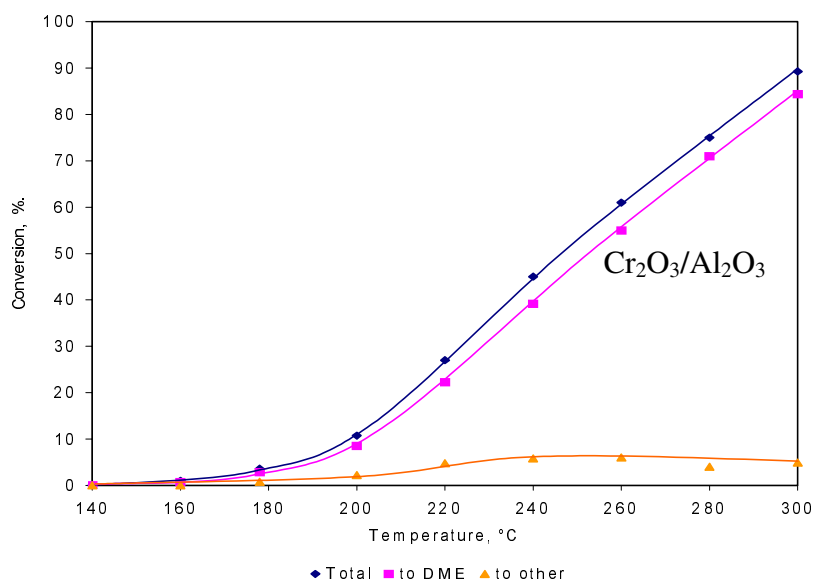


Figure 3. Product distribution versus temperature. Feed gas composition: methanol 4,0 %, nitrogen to 100 %.

Table 2. Product distribution versus temperature. Feed gas composition: methanol 4,0 %, nitrogen to 100 %.

Temperature, °C	Conversion, %		
	Total	To DME	To other products
300	89,3	84,4	4,9
280	75,0	72,0	3,0
260	61,0	55,0	6,0
240	45,0	39,2	5,8
220	27,0	22,2	4,8
200	10,7	8,5	2,2
180	3,6	2,8	0,7
160	0,0	0,0	0,0
140	0,0	0,0	0,0

Fig. 3 and Table 2 reflect the temperature dependence of methanol conversion on alumina supported chromium oxide. The activity of the alumina supported chromium oxide is vastly lower than that of copper oxide. The reaction starts at only about 180°C, but the selectivity towards DME synthesis is very high even at 300°C.

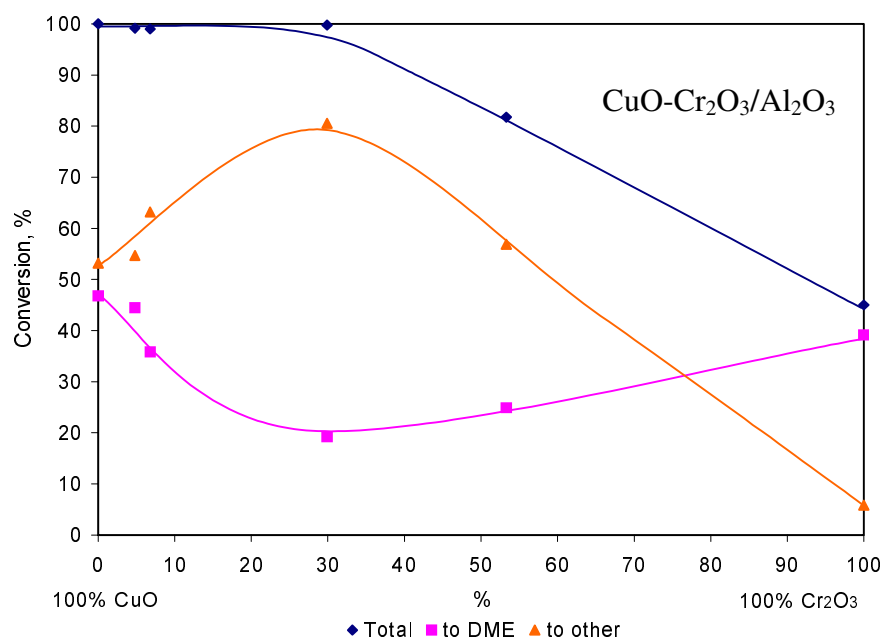


Figure 4. Product distribution versus catalyst composition at 240°C. Feed gas composition: methanol 4,0 %, nitrogen to 100 %.

Table 3. Product distribution versus catalyst composition at 240°C. Feed gas composition: methanol 4,0 %, nitrogen to 100 %.

Catalyst composition		Conversion, %		
Cr ₂ O ₃ , %	CuO, %	Total	To DME	To other products
0,0	100	100,0	46,8	53,2
4,8	95,2	99,1	44,5	54,7
6,8	93,2	99,0	35,8	63,2
29,9	70,1	99,8	19,2	80,5
53,3	46,7	81,8	24,9	56,8
100,0	0,0	45,0	39,2	5,8

Fig. 4 and 5 and Tables 3 and 4 present the influence of catalyst composition on methanol conversion and product distribution at 240 and 300°C. The tendencies at both temperatures are identical. The total conversion of methanol decreases as Cr₂O₃ content increases and the latter proves to be an inert diluent. Completely different is the situation with dimethyl ether and hydrocarbons formation. While the dehydration of the methanol to DME passes through minimum at about 30 wt.% Cr₂O₃, the formation of hydrocarbons reaches a maximum at the same catalyst composition. Summarizing the result presented in Tables 3 and 4 and Figs. 4 and 5 we can conclude that the active component of the mixed catalysts consists of both copper and chromium species. Obviously the association of CuO with Cr₂O₃ leads to a higher methanol conversion to hydrocarbons and lower conversion to dimethyl ether than the sum of conversions on both oxides, i.e., it can be concluded that the synergistic effect occurs over the Cu-Cr/alumina catalysts for methanol dehydration. The same phenomenon was observed by Chang et al. (9) during the investigation of Co oxidation on supported copper-chromium catalysts.

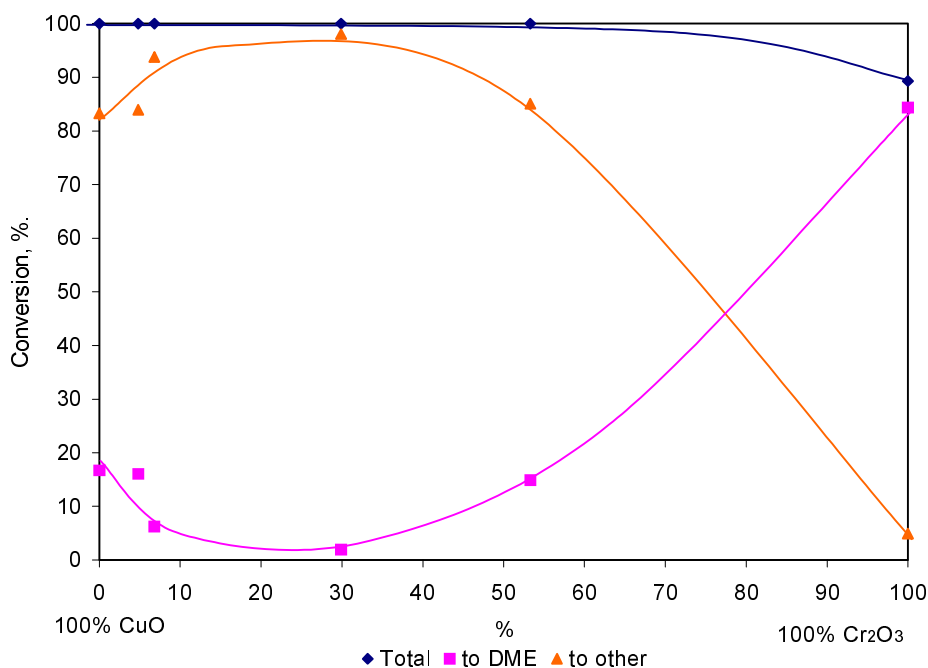


Figure 5. Product distribution versus catalyst composition at 300°C. Feed gas composition: methanol 4,0 %, nitrogen to 100 %.

Table 4. Product distribution versus catalyst composition at 300°C. Feed gas composition: methanol 4,0 %, nitrogen to 100 %.

Catalyst composition		Conversion, %		
Cr ₂ O ₃ , %	CuO, %	Total	To DME	To other products
0,0	100	100,0	16,7	83,3
4,8	95,2	100,0	16,1	83,9
6,8	93,2	100,0	6,2	93,8
29,9	70,1	100,0	1,9	98,1
53,3	46,7	100,0	14,9	85,1
100,0	0,0	89,3	84,4	4,9

CONCLUSIONS

The catalytic activity of γ -alumina supported CuO – Cr₂O₃ catalysts was researched with regard to methanol dehydration. It was found that these catalysts have enhanced activity toward methanol dehydration. The activity toward dehydration to dimethyl ether strongly depends on the catalyst's composition as follows:

- Alumina supported CuO is a very active catalyst with regard to methanol dehydration, but the selectivity toward DME synthesis is not sufficient. It passes through maximum at 200 – 220°C and rapidly decreases along with the temperature at the expense of increasing the formation of other hydrocarbons.
- Alumina supported Cr₂O₃ is less active, but the selectivity toward DME synthesis is remarkable. The most important feature is that the temperature influence on the selectivity toward DME formation is negligible.

- The mixed CuO – Cr₂O₃ catalysts are very active with regard to methanol dehydration. Full degradation of methanol can be reached even at temperatures lower than 240°C. The increase of Cr₂O₃ leads to a slight decrease of activity. Minimum in selectivity toward DME synthesis and maximum in selectivity toward other hydrocarbons are clearly expressed at 30 wt.% Cr₂O₃ content. A synergetic effect of both copper and chromium species is clearly observed.

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