

CATALYTIC DETOXIFICATION OF METHANOL ON THE Co-Cu-O SYSTEM

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Abstract. A large number of samples of the Co-Cu-O system were synthesised through support of Al_2O_3 with appropriate Co and Cu salts. Their catalytic properties were defined using a flow apparatus. The concentrations of methanol as well as those of its oxidation products were examined using the gas-chromatographic method. The results of the present study show that the proposed method leads to the obtaining of highly active catalysts for complete oxidation of methanol in gaseous phase. A 90% degree of conversion of methanol into CO_2 is achieved at sample with Co/Cu content = 50/50.

Keywords: detoxification, methanol, CO_2 .

AIMS AND BACKGROUND

The use of catalysts and catalytic processes is one of the effective ways of solving ecological problems. The development of ecological catalysts is related to the invention of new catalytic systems. They have to oxidise the organic substances to CO_2 and H_2O . The industrial production of formaldehyde started in 1913 with the use of silver and copper catalysts. Since the middle of the 19th century it has been possible to use another type of catalysts based on the iron and molybdenum oxides¹.

There are numerous attempts to find new solutions using the molybdates of other metals, vanadates and tungstates². Other new possibilities can be found combining metal and oxide catalysts^{3,4}. Christoskova et al.^{5,6} have been studied the oxidation of methanol over Ni oxide system in gaseous phase as well as in aqueous solutions. The results show that due to its high activity the catalyst acts at a lower temperature up to 100°C and under mild conditions and the oxidation yields CO_2 and H_2O (complete oxidation). Gases containing toxic methanol leave the system at the production of formalin. It is necessary to find catalysts which oxidise the methanol to CO_2 . This area is the subject of our present study. The purpose of this study is to assess the possibilities of the catalysts of the Co-Cu-O system for the selective as well as complete methanol oxidation.

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EXPERIMENTAL

The catalysts from the Co-Cu-O system with atomic ratio Co/Cu = 100/0; 10/90; 30/70; 50/50; 70/30; 90/10 and 0/100 have been prepared through support of Al₂O₃ in aqueous solutions of the Co and Cu nitrates in appropriate ratios and calcinations at 300° C for 2 h and at 400°C for 3 h.

Chemical analysis of the samples was performed by atomic absorption and atomic emission. The catalytic activity and selectivity of the samples were determined using a flow apparatus and the conditions of the experiment were changed substantially – from metallic conditions to ones characteristic for the oxide catalysts and temperatures between 200-400°C. In all cases the amount of the catalysts was 3 cm³ and its particle size was 0.3-0.6 mm. The reaction products were analysed for formaldehyde content using the bisulfite method and for CO, CO₂, DME, CH₄ and non-reacted methanol content – using the gas chromatographic method.

RESULTS AND DISCUSSION

Tables 1 and 2 present the distribution of the reaction products depending on the content of the catalytic samples during the process at conditions characteristic for oxide catalysts (excess of oxygen (Table 1)) and at conditions typical for

Table 1. Distribution of the reaction products at the methanol oxidation on mixed Co-Cu catalysts at 6.0% methanol concentration in the methanol – air mixture

Content Co/Cu	T (°C)	Conversion to (%)					S (%)
		CH ₂ O	CO	CO ₂	DME	Total	
100/0	250	39.2	-	1.8	2.0	43.0	91.2
	300	42.2	-	3.6	11.1	56.9	74.2
	350	68.1	3.1	9.3	1.7	82.2	82.8
	400	62.7	6.2	18.3	0.8	88.0	71.2
90/10	250	9.9	-	19.9	0.2	30.0	33.0
	350	2.2	-	70.4	0.8	73.4	3.0
70/30	250	19.7	-	29.1	0.2	49.0	40.2
	350	1.3	-	75.6	0.2	77.1	26.9
50/50	250	24.7	-	74.1	0.2	99.0	24.9
	350	4.8	-	94.6	0.2	99.6	4.8
30/70	250	26.0	-	28.3	0.2	54.5	47.7
	350	41.2	-	56.4	0.1	97.7	42.2
10/90	250	56.5	-	33.4	0.2	90.1	62.7
	350	26.9	-	73.0	0.1	100.0	26.9
0/100	250	58.5	-	40.5	0.1	98.6	58.5
	300	58.5	-	41.5	-	100.0	58.5
	350	58.5	-	41.5	-	100.0	58.5
	400	56.4	-	43.6	-	100.0	56.4

the metal catalysts (excess of methanol (Table 2)). The main products of the first type of oxidation are CO₂ and formaldehyde. The extent of the oxidation to CO and DME is substantial only for the pure Co oxide.

Table 2. Distribution of the reaction products at the methanol oxidation on mixed Co-Cu catalysts at 40.0% methanol concentration in the methanol – air mixture

Content Co/Cu	T (°C)	Conversion to (%)					Total	S (%)
		CH ₂ O	CO	CO ₂	DME	CH ₄		
100/0	250	43.5	-	4.7	0.8	-	49.0	88.8
	300	59.7	-	5.5	0.8	-	66.0	90.5
	350	69.9	1.2	6.2	0.7	-	78.0	89.6
	400	70.8	2.5	6.2	0.5	-	80.0	88.6
90/10	250	27.6	-	5.1	13.3	-	46.0	60.0
	350	59.7	2.5	6.5	4.0	3.3	75.8	78.7
70/30	250	34.4	-	6.0	4.7	-	45.1	76.3
	350	64.5	2.5	7.5	-	4.5	78.0	82.7
50/50	250	36.4	-	6.1	1.2	0.3	44.0	82.7
	350	65.3	2.0	8.1	1.2	1.4	78.0	83.7
30/70	250	54.1	0.2	6.7	0.5	0.4	61.9	87.4
	350	74.4	1.2	9.1	1.0	1.3	87.0	85.5
10/90	250	48.3	-	5.7	1.0	-	55.0	87.8
	350	73.9	0.4	9.8	2.0	-	83.0	89.0
0/100	250	79.4	0.8	11.2	5.4	-	97.0	81.5
	300	81.7	0.9	11.2	4.3	-	98.1	83.3
	350	86.0	1.4	11.5	0.7	-	99.6	86.3
	400	85.4	2.0	11.7	0.2	-	99.3	86.0

The distribution of the reaction products was changed dramatically at a high methanol concentration in the methanol – air mixture. The quantity of the formaldehyde increases substantially compared to the CO₂. Using mixed catalysts we received a new product – methane.

Figures 1 and 2 present the change of the catalytic activity to CO₂ depending on the content of the catalytic samples. The mixed catalysts are more active than the pure Co oxide when there is excess of oxygen in the methanol – air mixture (Fig. 1) and their activity goes over the maximum at ratio Co/Cu=50/50. This means that the increased activity is a result of the presence of the 2 components and, more precisely, of their mutual not separate influence. This result could be explained with the hypothesis that the active centers of the mixed catalysts are found at the border of the two phases. The Cu catalyst has the highest activity and selectivity at the shortage of oxygen. The increase of the Co content leads to a slight increase of the selectivity at the expense of the conversion.

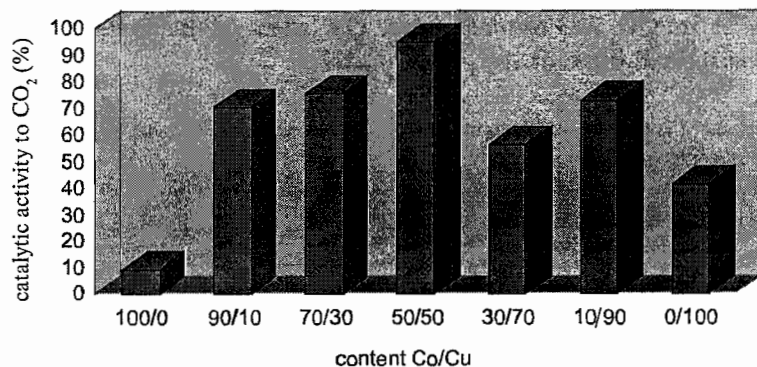


Fig. 1. Change of the catalytic activity to CO₂ depending on the content of the catalytic samples at 6.0% methanol concentration in the methanol – air mixture

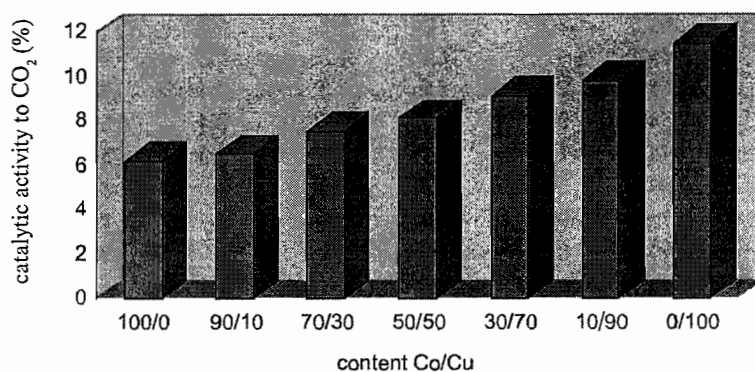


Fig. 2. Change of the catalytic activity to CO₂ depending on the content of the catalytic samples at 40.0% methanol concentration in the methanol – air mixture

CONCLUSIONS

The results of the research lead to the following conclusions:

1. The main products of methanol oxidation on mixed Co-Cu-O catalysts are formaldehyde and CO₂, no matter what the conditions of the process are.
2. The Cu catalyst has the highest activity at the selective methanol oxidation. The mixed Co-Cu-O catalysts have high selectivity but unsatisfactory activity which makes them inappropriate for practical use.
3. The mixed catalysts with atomic ratio Co/Cu=50:50 have the highest activity at the complete methanol oxidation. They might be used for methanol purification from gasses leaving the adsorption lattice at the production of formalin.

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