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CATALYSIS

Carbonylation of Methanol with Carbon Monoxide in the Presence of Sulfur-containing Catalysts

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Abstract—Physicochemical features of methanol carbonylation with carbon monoxide catalyzed with sodium sulfides Na_2S_x (x = 1, 2, 4) were studied. The effect of admixtures of sulfur dioxide in the gas phase on the yield of the target product (methyl formate) was revealed.

Methanol is a versatile intermediate, which can be used in syntheses of various chemical substances by the reaction with carbon monoxide or synthesis gas [1]. Some of such syntheses are performed on the commercial scale, e.g., production of acetic acid by catalytic carbonylation of methanol using complex rhodium homogeneous catalyst. It is well known [2] that base catalysts effect formation of methyl formate by reaction of carbon monoxide with methanol at elevated pressure:

$$CH_3OH + CO \xrightarrow{\text{Cat.}} HCO_2CH_3. \qquad (1)$$

Methyl formate is formed in a high yield with sodium methylate as catalyst. However, metallic sodium is required for the synthesis of this catalyst, which restricts its use.

It was shown previously [3, 4] that sulfur-containing catalysts can be used for the synthesis of urethanes by carbonylation of aromatic nitro compounds with carbon monoxide in methanol.

The goal of this work was to study carbonylation of methanol with carbon monoxide in the presence of sulfur-containing catalysts.

Sodium sulfides Na_2S_x with x = 1, 2, 4, which are relatively available and cheap commercial products, were used as catalysts.

As seen from Table 1, anhydrous sodium monosulfide is the most active catalyst. With increasing its concentration within the 0.3–1.2 M range, the yield of the target product (methyl formate) increases to 95%. As opposed to nitrobenzene carbonylation [5], V(V) compounds, pyridine, or polyethylene glycol added as activators of sulfur-containing catalysts did not increase the methyl formate yield.

The catalytic activity of sodium sulfide in carbonylation of methanol with carbon monoxide depends on the solvent (Table 2). This reaction proceeds most easily in neat methanol or in aromatic hydrocarbons (benzene, toluene). The yield of methyl formate at the constant Na_2S : methanol ratio increases with increasing methanol concentration in benzene from 1.3 to 5.0 M. The further growth of the methanol concentration up to pure methanol does not increase the methyl formate yield. The above results can be explained by variation of the solvent polarity and CO solubility in the solvent.

Water added to methanol even in small amounts (0.2–0.4 M) noticeably inhibits the reaction and practically stops it at concentrations higher than 0.9 M (Table 3). This effect is probably caused by deactivation of the catalyst due to its shielding by the hydrate shell.

Table 1. Activity of sulfur-containing catalysts in carbonylation of methanol with carbon monoxide* (1 h, temperature 80°C, CO pressure 15 MPa)

Catalyst	C_c, M	Y_{mf}, %	P_c, g l^{-1} h^{-1}
Na_2S	0.3	80	1190
	0.6	90	1338
	1.2	95	1396
Na_2S_2	0.6	10	146
Na_2S_4	0.6	8	117
Na_2S : KVO_3	0.6 : 0.06	89	1323
Na_2S : pyridine	0.6 : 0.6	85	1260
Na_2S : polyethylene glycol	0.6 : 0.6	85	1266

* Y_{mf} is the yield of methyl formate; P_c is the catalyst performance.

Table 2. Effect of solvent on carbonylation of methanol with carbon monoxide in the presence of sodium sulfide* (1 h, temperature 80°C, CO pressure 10 MPa)

Solvent	C_{CH_3OH}, M	K_{CH_3OH},** %	S,** %	Y_{mf}, %	P_c, g l^{-1} h^{-1}
–	24.8	94	90	85	1266
CCl_4	5.0	0	0	0	0
Dioxane	5.0	1	80	1	3
Ethyl acetate	5.0	94	29	27	79
Chlorobenzene	5.0	96	80	77	227
THF	5.0	86	90	77	227
Toluene	5.0	97	85	82	241
Benzene	1.3	71	69	49	34
	2.5	80	77	62	91
	5.0	96	89	86	251
	9.9	94	88	84	466

* Molar ratio Na_2S : methanol = 0.024; the same for Tables 4 and 5.

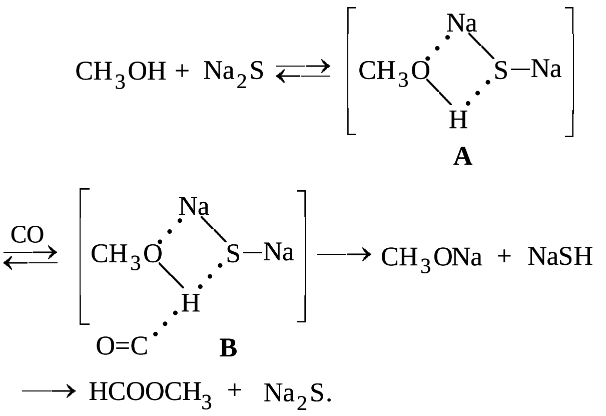
** K_{CH_3OH} is the methanol conversion; S is the selectivity with respect to methyl formate.

The effect of the CO pressure on the methanol carbonylation in benzene in the presence of sodium sulfide was also studied (Table 4). As the CO pressure is increased from 3 to 7 Mpa, the methyl formate yield grows substantially, but it does not appreciable grow further at the pressure of about 15 MPa.

The carbonylation rate noticeably increases with the CO pressure. For instance, at the CO pressure of 10 MPa the methyl formate yield in 10 min is the same as in 60 min at 7 MPa; in 10 min at 7 MPa the yield is lower by half.

The temperature also affects the methanol carbonylation with CO (Table 5). The maximal yield is observed at 80°C. At lower temperatures, the reaction is too slow. At higher temperatures, the methyl formate yield also decreases probably because of low thermal stability of the intermediate participating in the catalytic step; both methanol conversion and reaction selectivity with respect to methanol decrease.

The above results suggest the following scheme of the catalytic carbonylation of methanol with CO:



(2)

Table 3. Effect of water on carbonylation of methanol with carbon monoxide in the presence of sodium sulfide* (1 h, temperature 80°C, CO pressure 10 MPa)

C_{H_2O}, M	Y_{mf}, %	P_c, g l^{-1} h^{-1}
0.2	85	1266
0.4	69	1024
0.9	1	14
1.8	Traces	Not determined
7.4	0	0

* Initial concentration of Na_2S 0.6 M.

Table 4. Catalytic carbonylation of methanol in benzene at various CO pressures and 80°C

P_{CO}, MPa	τ, min	K_{CH_3OH}, %	S, %	Y_{mf}, %	P_c, g l^{-1} h^{-1}
3	60	65	76	49	144
5	60	89	86	77	226
7	60	95	88	84	247
10	60	96	89	86	251
15	60	98	92	90	263
7	10	59	80	42	735
10	10	96	86	82	1442

Table 5. Catalytic carbonylation of methanol with carbon monoxide in benzene (1 h, CO pressure 10 MPa)

T, °C	Y_{mf}, %	P_c, g l^{-1} h^{-1}
60	62	183
80	85	251
100	71	209
180	21	62

Table 6. Effect of SO_2 on methanol carbonylation with carbon monoxide in the presence of sodium sulfide* (0.5 h, 80°C, CO pressure 10 MPa)

C_{SO_2}, vol %	P_{SO_2}, MPa	Y_{mf}, %
0	0	97
0.72	0.06	97
1.05	0.09	50
1.30	0.11	25
5.61	0.49	Traces

* Initial Na_2S concentration 1.2 M.

Methanol forms hydrogen-bonded intermediate **A** with sodium sulfide and then **A** reacts with CO to form intermediate **B**. The latter rearranges through sodium methylate and hydrosulfide and converts into methyl formate with regeneration of sodium sulfide. In addition, **A** can decompose with formation of sodium methylate and sodium hydrosulfide.

Saturation observed with increasing the methanol concentration in the solvent (Table 2) and the effect of the temperature on the target product yield (Table 5) confirm formation of intermediate **B**. Inhibition of the reaction by water is explained by blocking of the active centers of the catalyst by the hydrate shell. It is well known [6] that small admixtures of sulfur compounds in exhaust gases deactivate many catalytic systems. Therefore, we studied the effect of acidic gaseous admixtures, in particular, sulfur dioxide, which are present together with CO in exhaust gases of metallurgic, heat and power, and other plants and can affect carbonylation of methanol with carbon monoxide.

The initial SO_2 concentration in the gas mixture was varied within the 0–5.61 vol % range (Table 6). As seen, at an SO_2 content from 0.72 to 1.30 vol % carbonylation of methanol is inhibited, and at 5.61 vol % it completely stops.

EXPERIMENTAL

Anhydrous Na_2S was prepared by dehydration of $Na_2S \cdot 9H_2O$ [7]. Na_2S_2 and Na_2S_4 were synthesized by fusion of anhydrous Na_2S with stoichiometric amounts of chemically pure grade sulfur [8].

CO and SO_2 were used without additional purification. Methanol, benzene, toluene, dioxane, tetrahydrofuran, chlorobenzene, ethyl acetate, and carbon tetrachloride were purified by common procedures [9].

Carbonylation of methanol was performed in a stainless steel (KhM-18) 50 cm^3 autoclave charged with the calculated amounts of methanol and catalysts. The autoclave was purged with carbon monoxide at continuous agitation of the reaction mixture. After that CO was pumped to a pressure of 6–10 MPa. Then the temperature of the experiment, which was monitored with a thermometer inserted into the body of the autoclave, and the required pressure were set. This instant was taken as the reaction start. The reaction process was monitored by the pressure decrease. After the reaction completion, the autoclave was cooled, and the pressure was relieved. Liquid reaction products were analyzed by GLC on a Tsvet-101 chromatograph with a thermal conductivity detector. Helium was used as a carrier gas (flow rate 30 $cm^3 min^{-1}$); 3000×3 mm glass column was used; stationary phase PEG 1500, temperature 60°C.

CONCLUSION

Anhydrous sodium sulfide is the effective catalyst of carbonylation of methanol with carbon monoxide. Sulfur dioxide as an admixture in CO deactivates the reaction.

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