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ALCOHOL SYNTHESIS FROM CO_2/H_2 ON SILICA-SUPPORTED MOLYBDENUM CATALYSTS

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In the hydrogenation of CO_2 over alkali-promoted Mo/SiO_2 catalysts, C_1-C_5 alcohols were selectively obtained at 16 kg/cm^2 and 250 °C.

The study of CO_2 hydrogenation has been far less extensive than that of CO hydrogenation. Although more hydrogen is necessary to reduce CO_2, CO_2 hydrogenation can be of practical interest if it presents some advantages such as activity and selectivity over CO hydrogenation. We recently reported alcohol synthesis from CO/H_2 catalyzed by alkali-promoted Mo/SiO_2.$^{1)}$ Here we report CO_2 hydrogenation over Mo/SiO_2 catalysts, producing C_1-C_5 alcohols selectively. A few catalysts have been known to give MeOH in CO_2 hydrogenation.$^{2-6)}$

The catalysts (10 wt% Mo) were prepared by impregnating SiO_2 (Fuji Davison ID) with $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ and alkali metal salts (alkali metal/Mo atomic ratio = 0.4). The reactions were carried out in a flow reactor at 16 kg/cm^2 (CO_2 or $CO/H_2 = 1$). In Table 1, are shown the activity and selectivity changes of CO_2/H_2 and CO/H_2 reactions with time over the $Mo\text{-}KCl/SiO_2$ catalyst pre-reduced in H_2 at 400 °C. Alcohols up to pentanol were formed from CO_2/H_2 in good selectivity defined as alcohols/(alcohols + hydrocarbons). The rate of formation of alcohols and hydrocarbons decreased sharply with time and reached a steady state in ca. 2 h. The C_2+ alcohols/MeOH ratio also decreased, while the selectivity for alcohols remained high. On the other hand, the products were mainly hydrocarbons in initial stage of the CO/H_2 reaction; CO was less active and less selective for alcohol production than CO_2.

In the CO/H_2 reaction over the $Mo\text{-}KCl/SiO_2$ catalyst, the alcohol production gradually increased with time, as has already been reported.$^{1)}$ Table 1 also lists the time dependence of products obtained from CO_2/H_2 over $Mo\text{-}KCl/SiO_2$ activated in CO/H_2 at 250 °C for 24 h. This indicates that CO/H_2 treatment brought about remarkable increase in the rate of alcohol formation from CO_2/H_2, compared to that resulting from H_2 reduction alone. The important point to note is that the selectivity for alcohols, especially for C_2+ alcohols, was much higher than that obtained from the CO/H_2 reaction. This transiently increased rate cannot be ascribed to desorption of surface species impelled by CO_2/H_2 introduction; switch from CO/H_2 to CO_2, H_2 or N_2 resulted in no increase in alcohol production.

The effect of alkali salts on the activity of the CO/H_2-treated Mo/SiO_2 catalysts was also investigated. It is particularly noteworthy that significant amount of alcohols has been formed over the catalyst without alkali addition,

Table 1. Hydrogenation of CO_2 or CO over silica-supported molybdenum catalysts a)

Additive	Feed	Time	Rate of	Selectivity/C-mol%					C_2+alc.	Rate of
		h	alc.+HC b)	CH_4	C_2+	MeOH	EtOH	C_3+alc.	MeOH	CO form. b)
KCl	CO_2/H_2 c)	0.25	29.0	21.8	19.7	30.0	19.4	9.1	0.95	213
		0.90	5.4	17.4	23.9	36.0	11.2	11.4	0.63	143
		2.0	3.4	24.6	20.0	41.1	12.4	1.9	0.35	139
	CO/H_2 c)	0.55	7.7	31.7	66.3	1.0	1.0	trace	1.0	
		1.8	6.3	33.4	61.4	3.6	1.4	0.2	0.7	
		24.0	14.0	13.2	24.2	25.2	26.2	11.3	1.5	
	CO_2/H_2 d)	0.6	89.2	2.3	2.7	27.9	34.9	32.2	2.4	237
		1.0	76.3	2.1	2.4	23.4	30.7	41.4	3.1	213
		2.1	34.1	5.3	4.9	24.8	30.9	34.0	2.6	200
		4.1	13.9	8.0	6.2	28.0	24.3	33.4	2.1	189
None	CO_2/H_2 d)	2.0	26.4	46.6	28.6	22.1	1.6	1.2	0.1	194
K_2CO_3	CO_2/H_2 d)	2.1	19.5	17.6	8.8	31.3	26.2	16.1	1.4	268
KF	CO_2/H_2 d)	2.0	12.5	4.6	3.6	22.4	39.8	29.5	2.7	113
LiCl	CO_2/H_2 d)	2.0	1.6	22.9	17.9	34.5	20.4	4.4	0.7	49
NaCl	CO_2/H_2 d)	2.0	3.4	26.8	21.4	30.2	16.6	5.0	0.7	61

a) 250 °C, 16 kg/cm^2, $CO_2(CO)/H_2 = 1$, CO_2(CO) 50 mmol/g-cat·h, Mo 10 wt%, alkali metal/Mo = 0.4. b) x 10^{-2} C-mmol/g-cat·h. c) After reduction with H_2 at 500 °C for 12 h. d) After activation with CO/H_2 at 250 °C and 16 kg/cm^2 for 24 h.

which showed negligible activity for alcohol synthesis from CO/H_2.1) KCl proved to be the best promoter. The LiCl- and NaCl-promoted catalysts gave only small amount of alcohols, where the C_2+ alcohols/MeOH ratio was rather small.

In the CO_2/H_2 reaction over these catalysts, the reverse shift reaction proceeded faster than synthesis of alcohols and hydrocarbons. This result and especially the particular selectivity for formation of C_2+ products suggest that CO_2 was first converted to CO, followed by reduction with hydrogen to give the products. Enhanced formation of alcohols from CO_2/H_2, relative to that from CO/H_2, might be due to the ability of CO_2 to oxidize Mo into its intermediate oxidation state, bringing about the increased active sites. The gradual decrease in the rate with time in the case of CO_2/H_2 reaction seems to be ascribed to the presence of excess of CO_2. Therefore studies are now being undertaken to pursue the optimum composition using $CO_2/CO/H_2$ mixed gas.

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