CHEMISTRY LETTERS, pp. 919-920, 1986.

NICKEL-PROMOTED Mo CATALYSTS FOR ALCOHOL SYNTHESIS FROM CO-H_2

Takashi TATSUMI,* Atsushi MURAMATSU, Tetsuya FUKUNAGA, and Hiro-o TOMINAGA
Department of Synthetic Chemistry, Faculty of Engineering, The University of Tokyo,
Hongo, Bunkyo-ku, Tokyo 113

The Addition of Ni to Mo-KCl/SiO_2 enhanced alcohol production from CO-H_2 reaction, in improving a selectivity for C_2+ alcohols. The production of PrOH increased by adding C_2H_4 to the CO-H_2 mixture, which suggests that CO insersion into a metal-alkyl like bond constitutes the reaction pathway to alcohols.

Alcohols are of great promise as octane improver in motor gasoline. However, the blending of MeOH into gasoline raises the problems of phase separation and lowering in calorific value. Therefore higher alcohols are better additives and their synthesis from CO-H_2 is of special interest.1) We have already reported that silica-supported Mo catalysts give C_1-C_5 alcohols in a good selectivity.2) Here we report that the addition of Ni to Mo-K/SiO_2 enhances the activity for alcohol production in improving a C_2+ alcohol selectivity.

Mo-K/SiO_2 was prepared by the conventional impregnation of KCl onto SiO_2 (Davison #57) first with KCl, followed by air calcination at 673 K for 1 h, and a successive addition of $(NH_4)_6Mo_7O_{24}$ solution. The resulting material was finally dryed at 393 K for 12 h. Nitrates of Fe, Co, and Ni were additionally impregnated onto Mo-K/SiO_2. Catalysts were reduced by H_2 at 773 K for 12 h after treated with a He flow at 673 K for 1 h. The synthesis reaction was carried out in a stainless steel tubular reactor.

As shown in Table 1, in the hydrogenation of CO over the modified Mo/SiO_2 catalysts, almost all of the oxygen in products leaves the reactor as CO_2 rather than H_2O, due to the activity of Mo catalysts for CO shift reaction. Thus the product selectivity is given on a CO_2-free basis. When 5 wt% Ni was added to 5 wt% Mo-0.84 wt% K/SiO_2(abbr. Mo(5)-K(0.84)), CO conversion was greatly enhanced. Yield of alcohols increased by a factor of ca. 6, although selectivity for alcohols was slightly reduced. With increasing the K content, the selectivity for alcohols increased at the expense of CO conversion. The Ni-K/SiO_2 exhibited very little activity for production of alcohol mixture consisting mainly of MeOH. It is noteworthy that coprecipitated Ni-TiO_2 catalysts have been recently reported to be effective for the synthesis of alcohols.3) The addition of Fe or Co provided a moderate increase in a CO conversion, in contrast with the decrease in selectivity for alcohols. This results in no significant change in the yield of alcohols.

Upon addition of Co, Fe, and Ni onto Mo-K/SiO_2 catalyst, the C_2+/C_1 ratio for

Table 1. Performance of Mo-M(Fe, Co, Ni)-K/SiO_2 catalysts[a)]

Catalyst			CO conv.	CO_2 yield	Alcohol		C_2+/C_1 ratio	
					STY[b)]	Sel.		
Mo	M	K	%	%		C-atom%	Alc.	HC
5	-	0.84	0.44	0.14	2.9	66	0.97	1.2
5	5Fe	0.84	0.64	0.13	2.6	33	3.4	1.2
5	5Co	0.84	0.52	0.14	3.1	46	4.2	1.5
5	5Ni	0.84	2.9	1.7	16	48	2.1	1.4
5	5Ni	1.63	1.8	0.74	6.9	56	2.0	1.3
10	-	1.63	0.52	0.15	3.6	71	1.4	1.8
-	10Ni	1.63	0.28	0.14	0.44	21	0.38	0.79

a)Reaction conditions; 523 K, 1.6 MPa(CO/H_2=1), W/F= 10 g-cat·h/mol.

b)Space-time yield (g/kg-cat·h).

Table 2. Influence of C_2H_4 addition on the product yield over Mo(5 wt%)-M(5 wt%)-K(0.84 wt%)/SiO_2[a)]

Additive		Space time yield /mmol/kg-cat·h						
M	Feed	CH_4	C_2H_4	C_2H_6	C_3	MeOH	EtOH	PrOH
Fe	CO-H_2	95	11	9	11	24	26	5
	+C_2H_4[b)]	91	-	239	23	22	21	51
Co	CO-H_2	54	11	3	8	23	25	7
	+C_2H_4[b)]	38	-	178	12	14	27	87[c)]
Ni	CO-H_2	282	31	58	45	209	134	37
	+C_2H_4[b)]	222	-	995	52	106	165	341

a)Reaction conditions; See footnote in Table 1.

b)CO-H_2-C_2H_4; C_2H_4(1.6 mol%) addition.

c)C_2H_5CHO (13 mmol/kg-cat·h) was also formed.

alcohols was remarkably increased, while that for hydrocarbons remained almost unchanged. In order to study on the origin of effect of the metal additives on the activity of Mo catalysts, ethylene was added in small concentrations (1.6 mol%) to the reaction mixture. The formation rates of the major products over Mo(5)-M(5)-K(0.84)(M=Fe, Co, Ni) are listed in Table 2. The increase in the rate of PrOH formation by C_2H_4 addition was essentially the same, or approximately 10 times, for all the catalysts tested. This suggests that in both cases a common precursor may exist, which can be defined as an ethyl surface entity. The insertion of CO into this metal-carbon bond followed by hydrogenation could lead to PrOH. The decrease in the yields of CH_4 and MeOH seems to be due to the coverage of C_2H_4, resulting in the decrease in an amount of absorbed CO.

It is interesting that the catalyst consisting of Mo and Ni provided much higher activity in this oxo reaction than the one containing Co, well-established component of oxo catalysts. The XRD observation for the fresh Mo(5)-Ni(5)-K(0.84) suggested formation of metallic Ni and MoO_2. On the contrary, the formation of a Ni-Mo alloy was confirmed by observation of the corresponding XRD lines over the used catalyst. The Mo content of the alloy was estimated at 30 wt% from its lattice spacing.[4)] The relevance of the alloy to the enhanced alcohol synthesis should be further investigated.

References

1) Chem. & Eng. News, Nov. 2, 29(1984). 2) T. Tatsumi, A. Muramatsu, and H. Tominaga, Chem. Lett., 1984, 685. 3) S. Uchiyama, Y. Obayashi, M. Shibata, T. Uchiyama, N. Kawata, and T. Konishi, J. Chem. Soc., Chem. Commun., 1985, 1071. 4) G. Grude and H. Schlecht, Z. Elektrochem., Bd. 44, 413(1938).

(Received March 12, 1986)