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EFFECTS OF ALKALI METAL HALIDES IN THE FORMATION OF ALCOHOLS FROM CO AND H_2 OVER SILICA-SUPPORTED MOLYBDENUM CATALYSTS

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Silica-supported molybdenum catalysts, promoted by alkali metal halides, give C_1-C_5 alcohols with good selectivity (up to 72% by weight of the total product, exclusive of CO_2) from a CO-H_2 mixture at 16 kg/cm^2 and 260-300 °C.

It has been revealed by Anderson et al. that molybdenum has the highest catalytic activity in methanation of CO except for iron group metals and ruthenium.$^{1)}$ However, the catalysis of molybdenum has not been extensively investigated with respect to selective production of oxygenates from synthesis gas which remains as one of the main goals of C_1 chemistry. Here we report molybdenum catalysts which exhibit high selectivity for C_1-C_5 alcohols. Recently Inui et al. reported the effect of molybdenum added to ruthenium catalysts to enhance the activity in alcohol synthesis.$^{2)}$ To our best knowledge, however, no catalysts solely based on molybdenum for alcohol synthesis has been reported.

The catalysts (10 wt% Mo) were prepared by impregnating SiO_2 (Fuji Davison ID) with aqueous solutions of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ and alkali metal salts. The supported salts were decomposed in helium at 400 °C for 1 h and the catalysts were then reduced by H_2 at 400 °C for 1 h and 500 °C for 12 h. The synthesis reaction was carried out at 16 kg/cm^2 (H_2/CO molar ratio = 1) in a flow reactor at 300 °C and W/F (contact time) = 9-12 g-cat h mol^{-1} (W = weight of the catalyst, F = molar flow of CO and H_2), unless otherwise noted.

The addition of K_2CO_3 to the Mo-SiO_2 catalyst lowered the selectivity for CH_4.$^{3)}$ Furthermore, considerable amounts of alcohols were formed over the Mo-K_2CO_3-SiO_2 (K/Mo atomic ratio = 0.4) catalyst. The alcohol formation activity, however, was gradually deteriorated, while hydrocarbon formation was growing (Fig. 1). With the unpromoted Mo-SiO_2 catalyst, methanol and ethanol were scarcely obtained, and methane and C_2-C_5 hydrocarbons rich in paraffins were the chief products.

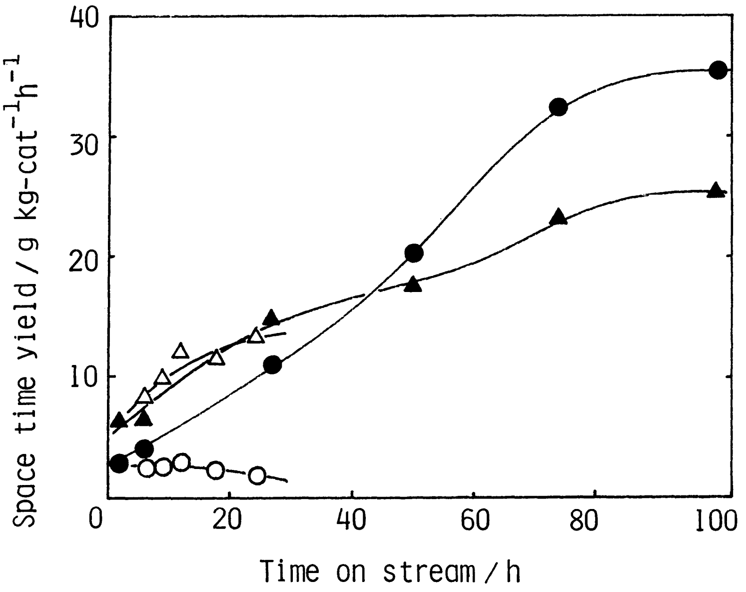

Fig. 1. Change in activity with time on stream under standard conditions: yields of alcohols (○) and hydrocarbons (△) over Mo-K_2CO_3-SiO_2 (K/Mo = 0.4); yields of alcohols (●) and hydrocarbons (▲) over Mo-KCl-SiO_2(K/Mo = 0.4).

As potassium halides (K/Mo = 0.4) were used in place of K_2CO_3, the activity and selectivity for alcohols were markedly improved. Both of them increased with time on stream. In the case of the Mo-KCl-SiO_2 catalyst, the space-time yield of C_1-C_5 alcohols increased significantly to surpass the hydrocarbon yield after ca. 50 h and continued to increase to reach a nearly steady-state (Fig. 1). This suggests a gradual change of the molybdenum surface to favor the formation of alcohols. The increase in activity and selectivity for alcohols with time was also observed for the catalysts doped with chlorides of other alkali metals. Nearly-steady state activities were reached within 24-100 h on stream, depending on the catalyst, and are summarized in Table 1. The selectivity for alcohol formation depended strongly on the anion of the potassium salts in the following order: $F > Cl > Br > I > CO_3$. Alcohols comprised of 72% by weight of the total product obtained over Mo-KF-SiO_2, exclusive of CO_2. The alcohol selectivity increased with decreasing temperature. For example, over Mo-KBr-SiO_2, carbon atom selectivity for alcohols was 16% at 300 °C, 27% at 280 °C, and 36% at 260 °C. The order of the activity for alcohols was $Cl > F - Br - I > CO_3$. The addition of an excess of KCl (K/Mo = 0.8) resulted in a decrease in alcohol formation. The enhancement of alcohol formation among the alkali metal chlorides decreased in the order K > Rb > Na > Li. Although acetaldehyde and acetone were

Table 1. CO-H_2 reaction over silica-supported molybdenum (10 wt%) catalysts[a)]

Alkali salts (MX)	CO conv. (%)	Carbon atom selectivity (%)							STY[b)]	
		CH_4	Other hydrocarbons	MeOH	EtOH	PrOH[c)]	Other oxygenates[d)]	CO_2	Hydrocarbons	Alcohols
None	9.7	18	33	0.4	0.1			48	37	0.7
K_2CO_3[e)]	4.7	11	33	2.6	2.6	1.2	1.0	49	12	3.0
KF	1.6	9.7	16	12	13	5.1	4.3	40	3.0	8.6
KCl	12.9	14	17	10	13	3.9	4.4	38	25	36
KBr	5.5	16	22	7.0	6.7	2.2	1.8	44	12	8.3
KI	5.8	14	24	5.7	6.2	2.0	2.0	46	11	7.5
LiCl	1.7	16	27	5.8	4.9	1.8	2.3	42	5.9	3.8
NaCl	2.0	15	22	6.4	5.3	1.5	1.3	49	5.9	3.7
RbCl	5.7	11	26	5.0	8.8	2.6	2.3	44	13	10
KCl[f)]	4.0	13	20	7.6	6.8	2.3	3.3	47	7.6	6.5

a) Conditions: 300 °C; 16 kg/cm^2; H_2/CO = 1; W/F = 9-12 g-cat h mol^{-1}; M/Mo = 0.4; Nearly steady-state activities obtained after 24-100 h on stream. b) Space-time yield, g-product kg-$cat.^{-1}$ h^{-1}. c) Essentially pure 1-propanol. d) Contain 1-butanol, 2-methyl-1-propanol, 1-pentanol, acetaldehyde, and acetone. e) After 12 h on stream, when the maximum activity for alcohols was achieved. f) K/Mo = 0.8.

also formed, alcohols comprised $>$ 90% of the organic oxygen compounds.

The carbon number distribution of the products obeyed a Schulz-Flory-type distribution,[4)] with α = 0.48-0.32 for hydrocarbons[5)] and α = 0.32-0.14 for alcohols with the exception of methanol. It should be noted that methanol yields are much smaller than the equilibrium conversion, except for the case of the Mo-KCl-SiO_2 catalyst. The little change in selectivity for alcohols effected by the contact time W/F, together with appreciable differences in α value between alcohols and hydrocarbons, suggests the formation of each type of product by independent reaction paths.

As is expected from the CO shift activity of the molybdenum catalysts,[1,3)] these catalysts yielded CO_2 almost exclusively instead of water, as the coproduct. This makes it feasible to use synthesis gas with a low H_2/CO ratio directly thus eliminating a separate shift convertor. The H_2/CO ratio of the synthesis gas is largely determined by the composition of the feedstocks and gasification condition. Coal gasifiers recently under developing produce synthesis gas with a low H_2/CO ratio.6) Moreover, for C_2^+ alcohols synthesis, product purification is simpler with CO_2 coproduction, since there are no water azeotropes.7)

The nature of the active molybdenum sites for alcohol formation and the mechanism of the alkali halide promotion are under investigation.

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5) With the alkali promoted catalysts, the olefin contents of the hydrocabons were much higher than those with the unpromoted catalysts. For example, propylene comprised 60-90% of C_3 hydrocarbon with the promoted catalysts. The details of the behavior of the catalysts promoted with alkali carbonates, which showed a high activity and selectivity for olefins, will be reported elsewhere.

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