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Mixed Alcohol Synthesis from CO-H_2 by Use of KCl-Promoted Mo/SiO_2 Catalysts

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Highly active Mo catalysts for mixed alcohol synthesis were prepared using Fuji Davison ID silica gel as a carrier. KCl promoted the selectivity to alcohols but reduced CO conversions in particular to hydrocarbons. Productivity of alcohols was largely affected by the reaction conditions. High pressure and short contact time enhanced space-time yield of alcohols, i.e. 420 g (kg-catalyst)$^{-1}$ h^{-1} at 5.0 MPa, 573 K, and W/F= 1.4 g-catalyst h mol^{-1}. The presence of K effectively prevented the complete reduction of Mo to metal, resulting in the increase in the production of alcohols. The study on addition of ethene and ethanol to synthesis gas revealed that the other roles of K are to retard dehydration of alcohols to alkenes and their hydrogenation to alkanes.

The development of a selective catalyst for co-production of methanol and C_2+ higher alcohols remains as one of the main goals of C_1 chemistry. The principal use of the alcohol mixtures is for blending in automotive fuel to meet the octane requirement raised by the global trend to lead phase-down. Blending methanol with gasoline requires the addition of cosolvent to mitigate the problems due to phase separation and high volatility. The C_2+ higher alcohols have proved effective as cosolvent.

It is well-known that appropriate modifications of the methanol synthesis catalyst and also of the reaction conditions result in the production of higher alcohols together with methanol.[1,2] The conventional Fischer–Tropsch catalysts based on iron, ruthenium, and cobalt have been also reported to give long chain alcohols. Institut Francias du Petrole patented catalysts for the synthesis of mixed alcohols, consisting of methanol synthesis catalysts (Cu) and Fischer–Tropsch catalysts (Co).[3]

Molybdenum catalysts have long been recognized as being effective for the Fischer–Tropsch synthesis of light hydrocarbons.[4,5] In our previous study, however, the supported molybdenum catalysts were found to be active in the synthesis of mixed alcohols, which was significantly influenced by support and additive.[6] Moreover, the successive impregnation method, in which addition of K to silica gel was followed by impregnation with molybdenum solution, was found to give higher activity and selectivity for alcohol formation.[7] Dow and Union Carbide have claimed a number of patents of the catalysts based on MoS_2, promoted by CoS and alkali metal salts for higher alcohol synthesis.[8–10]

Here we report the improved design of catalyst and reaction conditions for the production of mixed alcohols. High activity and selectivity for alcohols were attained on the KCl-promoted, ID silica-gel-supported Mo catalyst at high pressure and short contact time; alcohol yield exceeded 420 g (kg-catalyst)$^{-1}$ h^{-1} with 68 C-atom% selectivity.

Experimental

Catalysts were prepared by impregnating various silica gels (Fuji Davison ID, RD, and B) with an aqueous solution of KCl first, followed by air calcination at 673 K for 1 h and impregnation with $(NH_4)_6Mo_7O_{24}$ solution. The Mo metal loading was 10 and 20 wt% and the K/Mo ratio was varied in the range of 0—0.4. The impregnates were dried overnight at 393 K and treated in the He stream at 673 K for 1 h and then reduced by H_2 773 K for 12 h.

The synthesis reaction was carried out in a flow reactor made of stainless steel tube with 0.6 cm inside diameter, containing 1.0 g catalyst. The synthesis gas (H_2/CO=1) was supplied to the reactor through the stainless-steel tube heated at 473 K for decomposition of carbonyl impurities. Hydrogen was purified to remove oxygen by passage through a DEOXO unit (Engelhard), followed by a molecular sieve trap. Activity and selectivity of the catalyst were observed over a reaction period of 50—130 h until their steady states were attained. Products were analyzed by gas chromatographs. Concentrations of CO, CO_2, and CH_4 in the off-gas were determined by a TCD gas chromatograph with an active carbon separation column at 323 K using H_2 as a carrier gas. The organic compounds were analyzed by an FID gas chromatograph with the following separation column using N_2 as a carrier gas; 2 m Porapak Q for C_1—C_5 hydrocarbons, 2 m polyethylene glycol 1500 for oxygenates, 2 m Silicone SE-30 for C_6+ hydrocarbons, and 8 m VZ-7 for isomers of C_3, C_4, and C_5.

The catalytic surface areas of reduced Mo catalysts were measured by O_2 adsorption at 195 K. X-Ray powder diffraction measurements were performed using a Rigaku Denki diffractometer RU-200A with Cu *Kα* radiation.

Results and Discussion

As previously reported, excellent activity for alcohol synthesis activity was obtained by the use of KCl as a promoter in preparing silica-supported Mo catalysts. Three kinds of silica gel were investigated as a carrier for Mo-KCl catalyst and the results are summarized in Table 1. With all of the catalysts, both alcohol selectivity and CO conversion gradually increased with time on stream and therefore the data were obtained after 50—130 h on stream when the catalytic activity reached the nearly steady state. As is expected from the shift activity of the molybdenum catalysts,[4,5] these catalysts yielded CO_2, instead of water, almost exclusively. Hence the product selectivities (carbon atom%) in this work are given on a CO_2-free basis. Alcohol synthesis activity is represented by space-time yield of alcohols, STY, which stands for the total weight of alcohols produced per unit weight of catalyst per unit time on stream.

The alcohol formation activity over the KCl-promoted silica-supported Mo catalysts increased in the following order; B<RD<ID. Apparent average oxidation number, estimated from O_2 consumption from 195 to 773 K, increased in the order; B<RD<ID. This sequence conforms to the order of alcohol formation activity. This suggests that Mo species with a relatively high oxidation state participates in the key step of alcohol formation.

Alcohols/hydrocarbons ratio in space-time yield increased in the order; RD<B<ID. This order is in accordance with the sequence of pore diameter of support. The silica-supported Mo catalysts have moderate activity for alcohol dehydration as described below. Therefore, if the pores are smaller, product alcohols would have more chance to be readsorbed and dehydrated to hydrocarbons before leaving the catalysts. RD-silica-supported catalyst gave the highest C_2+ alcohol/methanol ratio. The C_2+ hydrocarbons/methane ratio was in the same order but less dependent on the kind of silica gel than C_2+ alcohols/methanol ratio.

Table 1. Effect of Silica Gel on Performance of Mo(10 wt%)+KCl(K=1.63 wt%)/SiO_2 Catalysts[a)]

Silica gel	ID	B	RD
CO conversion/%	5.5	4.6	6.8
CO_2 yield/%	2.3	2.0	3.1
Carbon atom selectivity/%			
CH_4	19.2	27.1	24.4
C_2H_4	3.3	2.3	3.7
C_2H_6	9.9	14.3	12.3
C_3H_6	5.7	5.3	7.0
C_3H_8	2.1	4.4	3.0
C_4+HC	9.2	9.7	11.1
MeOH	17.3	14.6	9.4
EtOH	20.5	15.2	19.2
n-PrOH	7.1	4.4	5.9
C_4+alcohol	4.3	1.4	2.2
Other oxygenate	1.5	1.5	1.8
Space-time yield/g kg-catalyst^{-1} h^{-1}			
Hydrocarbon	12	11	16
Alcohol	21	11	15
Net O_2 uptake following reduction/μmol g^{-1} [b)]			
	122	131	50
Apparent oxidation number of Mo following reduction[c)]			
	2.1	1.4	1.8
Surface area of support/m^2 g^{-1}			
	270	450	720
Average pore diameter of support/Å			
	140	70	22

a) Reaction conditions; 573 K, 1.6 MPa, W/F=10 g-catalyst h mol^{-1}. b) Measured at 195 K. c) Estimated from O_2 consumption from 195 to 773 K.

Total activities increased in the order; B<ID<RD. This order is not consistent with the order of O_2 uptake.[11] Na_2O impurity (0.25 wt%) in B-silica gel might have the effect of poison on CO hydrogenation activity.[1] ID-silica-supported Mo catalysts were employed for further investigation.

Table 2 shows the influence of Mo loading on the activity for alcohol synthesis, with the K/Mo ratio kept constant at 0.4. The selectivity for alcohols increased with increasing Mo loading. The C_2+ alcohols/methanol ratio and the olefin content also increased. Total activities, however, increased in the order: 5% Mo<20% Mo<10% Mo. In view of the effect of K content on catalyst performance as is described below, this change in activity and selectivity could be accounted for by the K content proportional to the Mo content.

The influence of K content on activities of 20 wt% Mo catalysts is shown in Fig. 1. The addition of KCl reduced CO conversion and also hydrocarbon yield in particular. The selectivity for alcohols increased with KCl content and reached 70 C-atom% at K/Mo=0.4. The yield of alcohols, however, reached a maximum at K/Mo=0.2. With the increase in K/Mo ratio the C_2+ alcohols/methanol ratio largely increased. It

Table 2. Effect of Mo Loading on Alcohol Synthesis over Mo+KCl(K/Mo=0.4)/SiO_2(ID)[a)]

Mo loading	5%	10%	20%
CO conversion/%	3.3	5.5	3.4
CO_2 yield/%	1.4	2.3	1.4
Carbon atom selectivity/%			
CH_4	24.7	19.2	14.9
C_2H_4	3.7	3.3	4.2
C_2H_6	12.8	9.9	7.2
C_3H_6	5.8	5.7	5.2
C_3H_8	2.6	2.1	1.6
C_4+HC	9.6	9.2	9.4
MeOH	17.9	17.3	15.5
EtOH	15.5	20.5	24.2
n-PrOH	4.8	7.1	8.3
C_4+alcohol	1.2	4.3	8.2
Other oxygenate	1.4	1.5	1.4
Space-time yield/g kg-catalyst^{-1} h^{-1}			
Hydrocarbon	9.1	12	6.1
Alcohol	11	21	13

a) Reaction conditions; 573 K, 1.6 MPa, W/F=10 g-catalyst h mol^{-1}.

should be noted that C_2+ hydrocarbons/methane ratio remained almost unchanged.

Table 3 represents the O_2 uptakes for the 20 wt% Mo catalysts. Without KCl addition, O_2 uptake for the fresh (reduced) Mo catalyst amounted to 532 μmol g^{-1}. O_2 uptake was significantly reduced by addition of KCl and was at virtually constant level beyond K/Mo $\geqslant 0.2$. The decrease in CO conversion by addition of K should be partly due to the decrease in O_2 uptake. Concha and Bartholomew reported a linear correlation between CO hydrogenation activity and O_2 uptake for unsupported MoS_2.[11)]

Figure 2 shows X-ray diffractograms of reduced Mo (20 wt%) catalysts with K/Mo ratio changed. Lines corresponding to metallic Mo and MoO_2 appeared on all the catalyst. With increase in K/Mo ratio, the intensity of MoO_2 lines increased at the expense of metallic Mo.[12)] The productivity of alcohols is supposed to depend significantly upon the oxidation state of Mo; MoO_2-like species are responsible for alcohol synthesis while metallic Mo is associated with carbon chain growth and hydrocarbon formation.[13)] Thus the presence of K could retard the reduction of Mo, resulting in increase in the production of alcohols.

The influence of the time factor (W/F) on CO conversion, the yields of alcohols and hydrocarbons, the selectivity to alcohols and C_2+ alcohols/methanol ratio over Mo(20 wt%)+KCl(K=1.63 wt%)/SiO_2(ID) at 573 K and 1.6 MPa are illustrated in Figs. 3 and 4.

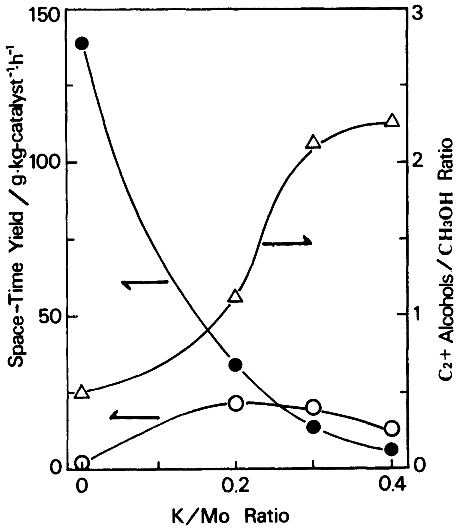

Fig. 1. Effect of K content (K/Mo ratio) on space-time yields of alcohols (○) and hydrocarbons (●), and C_2+OH/CH_3OH ratio (△) over Mo(20 wt%)+KCl/SiO_2(ID) at W/F=10 g-catalyst h mol^{-1}, 573 K, and 1.6 MPa.

Table 3. O_2 Uptake of Mo(20 wt%)+KCl/SiO_2(ID) Catalysts

K/Mo molar ratio	CO conv.	CO_2 yield	Net O_2 uptake before use
	%	%	μmol g^{-1}
0	38.3	18.2	532
0.2	10.7	4.8	144
0.3	5.8	2.5	163
0.4	3.4	1.4	126

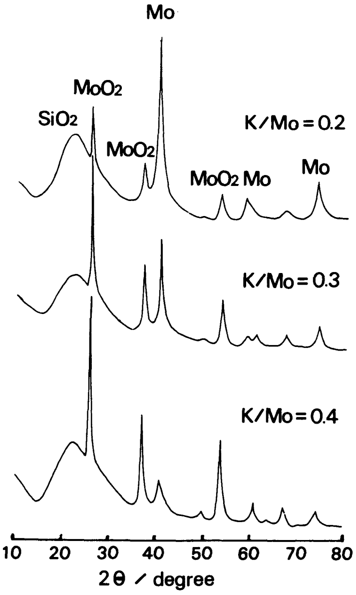

Fig. 2. X-Ray diffractograms of reduced Mo catalysts with K/Mo ratio changed.

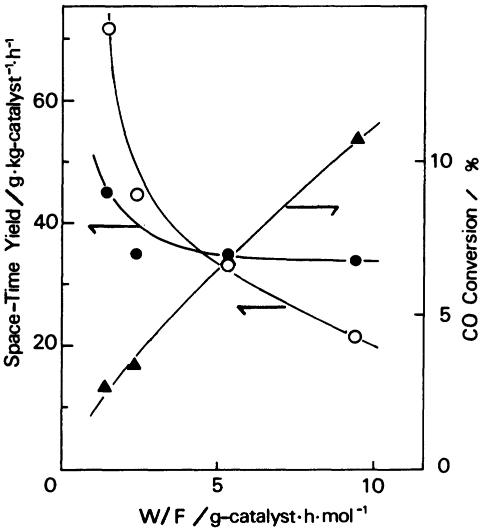

Fig. 3. Effect of time factor on CO conversion (▲) and space-time yields of alcohols (○) and hydrocarbons (●) over Mo(20 wt%)+KCl(K=1.63 wt%)/SiO_2(ID) catalyst at 573 K and 1.6 MPa.

Short contact time enhanced the selectivity for alcohols. The CO conversion vs. W/F plot displayed a convex curvature, which might suggest that the rate of intrinsic surface reaction is not the rate controlling step. At short contact time, the selectivity for alcohols was markedly improved. C_2+ alcohols/methanol ratio was independent of the time factor, ruling out the significant contribution of alcohol homologation, e.g., methanol conversion to ethanol. The alcohol yield tended to be more influenced by W/F with lower K/Mo ratios, indicating that there is a route from alcohols to hydrocarbons promoted by acid sites of the catalysts.

The influence of the addition of ethanol and ethene to $CO-H_2$ feedstock was investigated on unpromoted and KCl-promoted Mo catalysts. Pertinent data are given in Table 4. Over the unpromoted catalyst, added ethanol momentarily converted to ethene and ethane. This alcohol dehydration activity of Mo/SiO_2 indicates that Mo/SiO_2 has significant acidity, in agreement with the observation by Maruyama et al.[14]

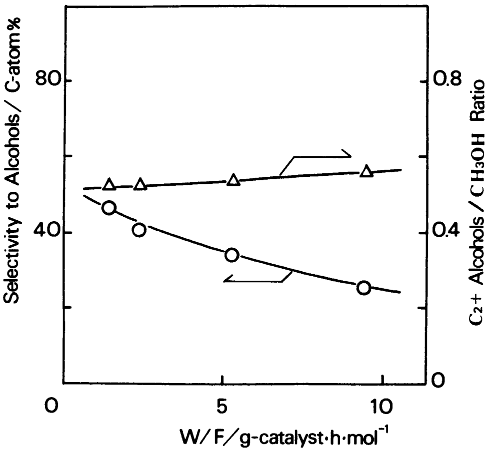

Fig. 4. Effect of time factor on alcohol selectivity (○) and C_2+alcohols/methanol ratio (△) over Mo(20 wt%)+KCl(K=1.63 wt%)/SiO_2(ID) catalyst at 573 K and 1.6 MPa.

Table 4. Addition of Ethanol and Ethene to $CO-H_2$ over Mo(20 wt%)+KCl/SiO_2(ID)[a)]

KCl content	Ethanol conversion rate to ethene and ethane[b)]	Ethene conversion rate to ethane[c)]
wt%	mmol (kg-catalyst)$^{-1}$ h^{-1}	
0	352	410
1.63	12	105

a) Increase in ethene and/or ethane on addition of ethanol and ethene to synthesis gas. b) Reaction conditions; 523 K, 1.6 MPa, W/F = 10 g-catalyst h mol^{-1} C_2H_5OH = 1.0 mol(kg-catalyst)$^{-1}$h^{-1}. c) Reaction conditions; 473 K, 1.6 MPa, W/F = 10 g-catalyst h mol^{-1}, C_2H_4 = 1.3 mol(kg-catalyst)$^{-1}$ h^{-1}.

The addition of KCl led to the considerable decrease in ethene and ethane. This is supposed to be due to the K-induced decrease in acidity. It can be seen in Table 4 that addition of KCl to Mo/SiO_2(ID) remarkably suppressed the ethene conversion rate to ethane. Thus the additional role of K in improving alcohol selectivity is to retard dehydration of alcohol to alkenes and to slow hydrogenation of the alkenes to alkanes.

The yield of alcohols was considerably influenced by raising the total pressure. The effect of total pressure on the product distribution over Mo(20 wt%)+KCl(K=1.63 wt%)/SiO_2(ID) at 573 K and W/F= 1.4 g-catalyst h mol^{-1} was indicated in Fig. 5 and Table 5. Raising the pressure, the yield of alcohols was greatly improved. The C_2+/C_1 ratios of hydrocarbons and alcohols were independent of the pressure. It should be noted that at 5.0 MPa STY of alcohols as large as 420 g (kg-catalyst)$^{-1}$ h^{-1} was obtained in 68 C-atom% selectivity. This STY is comparable with those reported so far with Cu–Co based catalyst[15] and MoS_2–Co–K_2CO_3 catalyst.[11] At 6.5 MPa the selectivity for alcohol formation was deteriorated, while the yield of hydrocarbons was greatly increased. This would also result from the successive reaction of alcohols to hydrocarbons owing to the increase in the contact time under the high pressure. Xie et al. recently claimed that alcohol

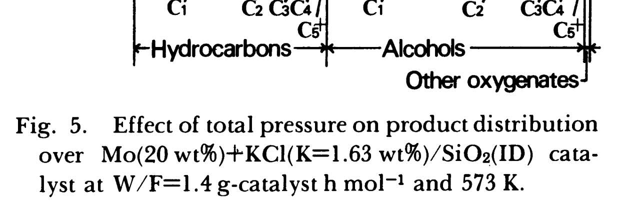

Fig. 5. Effect of total pressure on product distribution over Mo(20 wt%)+KCl(K=1.63 wt%)/SiO_2(ID) catalyst at W/F=1.4 g-catalyst h mol^{-1} and 573 K.

Table 5. Effect of Total Pressure on Activity over Mo(20 wt%) + KCl(K = 1.63 wt%)/SiO_2(ID) Catalyst[a)]

Total pressure	CO conversion	CO_2 yield	Space-time yield Hydrocarbon	Alcohol
MPa	%	%	g(kg-catalyst)$^{-1}$ h^{-1}	
1.6	2.7	1.1	45	72
5.0	10	3.1	124	420
6.5	13	4.5	181	428

a) Reaction conditions; see footnote in Fig. 5.

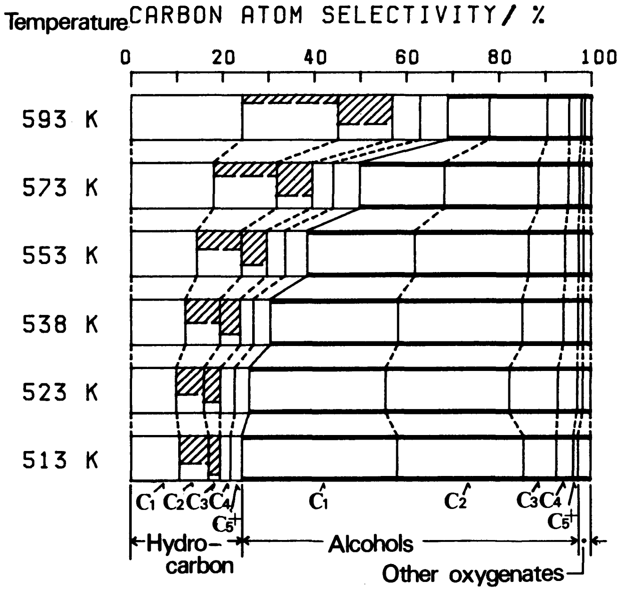

Fig. 6. Effect of temperature on product distribution over Mo(10 wt%)+KCl(K=1.63 wt%)/SiO_2(ID) catalyst at W/F=10 g-catalyst h mol^{-1} and 1.6 MPa.

Table 6. Effect of Temperature on Activity over Mo(10 wt%)+KCl(K=1.63 wt%)/SiO_2(ID) Catalyst[a)]

Temperature	CO conversion	CO_2 yield	Space-time yield Hydrocarbon	Alcohol
K	%	%	g(kg-catalyst)$^{-1}$ h^{-1}	
593	7.3	3.2	22	16
573	5.5	2.3	12	21
553	2.0	0.67	4.0	11
538	1.0	0.33	1.7	6.7
523	0.52	0.15	0.74	3.6
513	0.32	0.10	0.41	2.2

a) Reaction conditions; see footnote in Fig. 6.

yields were very sensitive to total pressure over MoS_2 based catalysts.[16)]

Figure 6 and Table 6 show the effect of reaction temperature on the product distribution over Mo(10 wt%)+KCl(K=1.63 wt%)/SiO_2(ID) at 1.6 MPa and W/F=10 g-catalyst h mol^{-1}. With the decrease in temperature, the selectivity to alcohols was greatly improved. At 513 K, 76 C-atom% of the alcohol selectivity was obtained. A maximum yield of alcohols was attained at 573 K. At temperatures above 573 K, the yield of alcohols was decreased while that of hydrocarbons was strongly promoted. C_2+ alcohols/methanol ratio gradually increased with the increase in temperature.

In the Mo catalyst system, water, the primary product, is rapidly converted to CO_2. This makes the alcohol separation simple and less energy consuming as there is no problem due to azeotrope formation.[17)] Moreover, it is feasible to utilize a synthesis gas with a low H_2/CO ratio produced from coal gasifiers without a separate shift converter.[18)]

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