[Review Paper]

Molybdenum Catalysts for Synthesis of Mixed Alcohols from Synthesis Gas

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Highly active Mo catalysts for synthesis of mixed alcohols from synthesis gas were prepared using SiO_2 as a carrier. KCl promoted the selectivity to alcohols but reduced CO conversions, in particular, to hydrocarbons. High specific activity of $420 \text{ g (kg-catalyst)}^{-1} \cdot \text{h}^{-1}$ was attained at 5.0 MPa, 573 K, and $W/F=1.4 \text{ g-catalyst} \cdot \text{h} \cdot \text{mol}^{-1}$. The alcohol formation was found to require two kinds of Mo species, metallic Mo and MoO_2 , after reduction with flowing H_2 . The presence of K prevented the complete reduction of Mo to metal, resulting in increased production of alcohols. Marked increase in alcohol yield with time on stream indicated that active species for alcohol synthesis were formed during the CO hydrogenation. From the study of the effect of pretreatment of Mo catalysts with CO, CO-H_2 , and butane- H_2 , and Mo 3d XPS, it has been concluded that the formation of CO-reduction induced defects on MoO_2 , MoO_{2-x} , during the CO hydrogenation reaction, is the cause of the increase in the alcohol synthesis rate. On the other hand, the hydrocarbon synthesis appeared to be solely based on metallic Mo. From the study of addition of probe molecules to CO-H_2 , it has been clarified that the higher alcohol formation from CO-H_2 proceeded by way of the same intermediate as the alkene hydrocarbonylation. A dual-site mechanism for the alcohol formation over SiO_2 -supported Mo has been proposed: CO dissociates on metallic Mo to form surface carbide, followed by hydrogenation of carbene and/or methyl species. While addition of methylene unit to surface alkyl species and following hydrogenolysis and/or dehydrogenation of alkyls to give hydrocarbons also occur on metallic Mo, CO insertion leading to alcohols is catalyzed by MoO_{2-x} species. It has been found that K is effective in retarding hydrogenolysis of alkyls, improving the selectivity to alcohols. The mechanism can account for the difference in selectivities to branched products between hydrocarbons and alcohols.

1. Introduction

The catalytic conversion of synthesis gas to oxygenated compounds, alcohols, in particular, is generally recognized as an interesting route for providing clean fuels and chemical feedstocks. The most promising application of the $\text{C}_1\text{—C}_5$ mixed alcohols is a blending stock for automotive fuel to meet the octane number requirement^{1,2)}. Problems caused by the use of methanol (phase separation, vapor lock, *etc.*) can be alleviated by incorporating C_2+ higher alcohols as a cosolvent into the methanol-gasoline mixture. Several investigators reported that an appropriate modification of the methanol synthesis catalyst resulted in the formation of higher alcohols together with methanol^{1)–3)}. Institut Francais de Petrole and Idemitsu patented catalysts for mixed alcohol synthesis, composed of methanol synthesis catalysts (Cu) and Fischer-Tropsch⁴⁾ or methanation⁵⁾

catalysts.

Molybdenum catalysts have long been recognized as being effective for the methanation and/or Fischer-Tropsch synthesis of light hydrocarbons^{6)–9)}. Our previous study, however, revealed that silica-supported molybdenum catalysts were active in the production of $\text{C}_1\text{—C}_5$ mixed alcohols^{10)–14)}. The addition of KCl to Mo/ SiO_2 resulted in a significant increase in the selectivity to alcohol formation. It was also found that the sequence of impregnation profoundly affected the activity and selectivity to alcohols¹²⁾. In this regard it should be noted that Dow and Union Carbide have published a number of patents of the catalysts based on MoS_2 , promoted by CoS and alkali metal salts, for higher alcohol synthesis¹⁵⁾.

The objectives of this study are (1) to investigate improved design of catalysts and the effects of reaction conditions for the mixed alcohol synthesis and (2) to pursue the mechanism for the formation of alcohols and the active species for alcohol production.

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2. Preparation and Pretreatment of Mo/SiO₂ Catalysts

2.1 Mo Species on Freshly Reduced Catalysts

Catalysts were prepared by impregnating silica-gel (Fuji Davison ID) with an aqueous solution of (NH₄)₆Mo₇O₂₄·4H₂O. For promoted catalysts, KCl or Rb₂CO₃ was added to the silica first, followed by air calcination at 673 K for 1 h and impregnation with the molybdenum salt. Unless otherwise noted, the impregnates were dried at 393 K overnight and treated in flowing He at 673 K for 1 h and then reduced in flowing H₂ for 12 h.

The oxidation state of molybdenum naturally lowers on raising the reduction temperature. Saito and Anderson reported that small peaks of Mo metal were found in an X-ray diffraction pattern following reduction of unsupported MoO₃ with H₂ at 673 K and that Mo metal was obtained by the reduction at 873 K⁷⁾.

The effect of temperature for H₂ reduction on the characteristics of SiO₂-supported molybdenum catalysts has been investigated. **Table 1** lists O₂ adsorption uptakes, phases observed by X-ray diffractograms (XRD), and average oxidation numbers of Mo after H₂ reduction (before exposure to synthesis gas). Strong X-ray lines corresponding to metallic Mo and weak lines characteristic of MoO₂ appeared on the catalyst reduced at 873 K. On decreasing the reduction temperature, the intensity of the MoO₂ lines increased at the expense

of metallic Mo lines. On the catalyst reduced at 673 K, metallic Mo lines could be hardly observed. Average oxidation number estimated by O₂ titration was in agreement with the XRD observation. The influence of K content on the surface characteristics of the fresh catalyst are also shown in **Table 1**. The presence of K effectively prevented the complete reduction of molybdenum to metal. O₂ adsorption uptakes for the catalysts at 195 K¹⁶⁾ suggest that the Mo dispersion decreases sharply on addition of K but is insignificantly affected by the reduction temperature.

The influence of the reduction temperature and K content on activity in CO hydrogenation is shown in **Table 2**. The CO hydrogenation was carried out in a flow reactor made of stainless steel tube. As expected from the water-gas shift activity of Mo catalysts⁷⁾, these catalysts yielded CO₂ almost exclusively instead of water as the co-product (*vide infra*). In **Table 2**, specific activities in g (kg-catalyst)⁻¹·k⁻¹ were used to compare alcohol synthesis activities. Clearly there are marked differences between these catalysts, the low conversion of CO on the catalyst reduced at 673 K being the most noticeable. CO conversion increased as the reduction temperature increased. The activity for hydrocarbon formation and the ratio of alkene to alkane also increased. The catalyst reduced at 873 K exhibited the highest activity and selectivity for C₂+ hydrocarbons. Best results in terms of the activity and selectivity for alcohol synthesis were obtained for the catalyst

Table 1 Influence of Reduction Temperature and K Content on Surface Characteristics of Mo/SiO₂ Catalysts

Mo loading [wt%]	K/Mo ratio	Reduction temperature [K]	XRD phases after reduction		O ₂ adsorption uptake ^{a)} [μmol·(g-cat.) ⁻¹]	Apparent oxidation number ^{b)}
			MoO ₂	Metallic Mo		
5	0.4	673	strong	not detected	90	3.4
5	0.4	773	medium	medium	80	2.0
5	0.4	873	weak	strong	70	1.3
20	0	773	weak	very strong	530	
20	0.2	773	medium	strong	140	
20	0.3	773	medium	medium	160	
20	0.4	773	strong	weak	130	

a): Measured at 195 K.

b): Estimated from O₂ consumption from 195 to 773 K.

Table 2 Influence of Reduction Temperature and K Content on Performance of Mo/SiO₂ Catalysts

Mo loading [wt%]	K/Mo ratio	Reduction temperature [K]	CO conv. [%]	CO ₂ yield [%]	Activity		C ₂ +C ₁ Molar ratio		Olefin content in C ₃ [%]
					Alcohols [g·(kg-cat.) ⁻¹ ·h ⁻¹]	HC ^{a)} [g·(kg-cat.) ⁻¹ ·h ⁻¹]	Alcohols	HC ^{a)}	
5	0.4	673	1.9	0.96	2.6	5.3	1.1	1.2	39
5	0.4	773	8.2	3.8	17	25	2.1	1.3	65
5	0.4	873	12	6.5	14	34	2.9	1.8	87
20	0	773	31	18	1.4	140	0.49	1.4	11
20	0.2	773	11	5.0	22	34	1.1	1.4	51
20	0.3	773	5.8	2.5	20	13	2.2	1.7	72
20	0.4	773	3.4	1.4	14	5	2.3	1.7	78

Reaction conditions; 573 K, 1.6 MPa (H₂/CO=1), W/F=10 g-catalyst·h·mol⁻¹.

a): Hydrocarbons.

reduced at 773 K. The C_2+ alcohols/methanol ratio increased on raising the reduction temperature.

The effect of K content on the catalytic performance of Mo/SiO₂ will be summarized as follows. With increasing the K content, the selectivity to alcohols increased at the expense of CO conversion, reaching 70 C-atom% at K/Mo=0.4. At the same time the C_2+/C_1 ratios for alcohols and hydrocarbons increased and the alkene content increased.

Taking into account the findings of the XRD observation, the higher CO conversion seems to be related to the higher metallic Mo content in the catalysts⁷⁾. There was no clear relationship between O₂ uptake and CO conversion. Reduction of Mo at higher temperature or in the absence of K resulted in the evolution of large amounts of metallic Mo, leading to the catalyst producing hydrocarbons predominantly. This is consistent with our previous findings on the effect of Mo precursors¹¹⁾ and the order of impregnation with molybdenum and potassium salts¹²⁾. The catalyst reduced at 673 K and with high K content, for which XRD patterns of metallic Mo phase could be hardly observed, showed very low activity for CO hydrogenation. Thus it is suspected that the presence of both metallic Mo and MoO₂ species on the catalyst surface before exposure to synthesis gas is required to effect the production of alcohols and that there is an appropriate content of metallic Mo.

2.2 Activity Change with Processing Time

It has been shown that the presence of an adequate amount of metallic Mo and MoO₂ on the freshly reduced catalyst is a prerequisite for the superior performance for alcohol synthesis. However, it is inconceivable that the species over the freshly reduced catalysts are directly responsible for the alcohol synthesis from synthesis gas because we found a rather long induction period for alcohol formation. The change in yields of alcohols, hydrocarbons, and CO₂ over Mo (10 wt%)-K(1.63 wt%)/SiO₂, is illustrated in Fig. 1. In the initial stage of the CO-H₂ reaction the yield of alcohols was surprisingly low. The activity for alcohol formation remarkably increased with time on stream and reached a steady state level after ca. 15 h. This implies that active species for alcohol production are formed during the CO-H₂ reaction. In contrast, the yield of CO₂ was remarkably high at the initial stage of the reaction and decreased to reach a nearly steady state after ca. 15 h on stream. The yield of hydrocarbons gradually decreased and leveled off after 8 h on stream.

As mentioned above, Mo catalysts are active in CO shift reaction (Eq. (5)) to form CO₂; under

Catalyst: Mo(10 wt%)-K(1.63 wt%)/SiO₂; Reaction conditions: 523 K, 1.6 MPa (H₂/CO=1), W/F=10 g-cat·h·mol⁻¹.

Fig. 1 Change in Product Yields with Processing Time

conditions employed in this study, the equilibrium conversion of Eq. (5) was estimated at 97% at 573 K. Almost all of the oxygen which had been included in CO left the reactor as CO₂ (Eqs. (3) and (4)) rather than as H₂O (Eqs. (1) and (2)). As shown in Fig. 1, at the steady state the yield of CO₂ was found to be in good agreement with the combined yield of hydrocarbons and alcohols, assuming the equilibrium in the CO shift reaction (Eq. (5)). In the initial stage of the CO-H₂ reaction, however, the yield of CO₂ noticeably exceeded the yield of alcohols and hydrocarbons. The formation of excess of CO₂ should be ascribed to Boudouard reaction (Eq. (6)) or reduction of MoO₂ by CO (Eq. (7)). It should be noted that there was a coincidence between the times required to reach the steady-state of alcohol synthesis and CO₂ formation.

2.3 CO, CO-H₂ and Carburizing Treatment

A control experiment was carried out in which Mo(5 wt%)-K(0.83 wt%)/SiO₂ catalyst reduced in H₂ at 773 K for 12 h was further treated in flowing CO at 523 K, 0.1 MPa, and $W/F=10$ g-catalyst·h·mol⁻¹ for 20 h, left under H₂ stream at 773 K until CH₄ formation virtually ceased, and subjected to CO-H₂ reaction¹⁷⁾. The change in the yield of alcohols over the untreated catalyst and the catalyst treated by a flow of CO is illustrated in Fig. 2. The initial rate of alcohol formation is markedly higher over the CO-treated catalyst than over the catalyst resulting from H₂ reduction alone. Over the former catalyst, the rate of alcohol synthesis was virtually constant during the processing time up to 26 h, while over the latter the rate after 40 h on stream was 20 times as high as that in the initial stage. Hence sites for alcohol synthesis appear to have been formed on the catalyst during the CO treatment. The amount of CO₂ produced from the CO treatment was 117% based on the loaded Mo. We expect that the carbide formed according to Eq. (6) would react with H₂ to form CH₄. The CH₄ formed by the successive H₂ treatment accounted for only 46%; a significant portion of CO₂ seems to have been formed according to Eq. (7), resulting in the reduction of MoO₂ to form oxygen defects according to Eq. (7).

The amount of O₂ adsorption uptakes on the catalyst treated in CO and the untreated catalyst was 46 and 79 mmol (g-catalyst)⁻¹, respectively.

Catalyst: Mo(5 wt%)-K(0.83 wt%)/SiO₂; Reaction conditions: 573 K, 1.6 MPa (H₂/CO=1), $W/F=10$ g-cat·h·mol⁻¹.

Fig. 2 Effect of CO Pretreatment on Change in Alcohol Yields with Processing Time

These two catalysts seem to have similar oxidation state and surface structures. Thus it is speculated that the lower activity of the CO-treated catalyst at the steady state would be explained by the lower dispersion of molybdenum. A linear correlation between O₂ adsorption uptake and CO hydrogenation activity was established for unsupported MoS₂¹⁸⁾.

Pretreatment of the reduced Mo-K/SiO₂ catalyst with atmospheric CO-H₂ at 673 K resulted in similar enhancement of initial alcohol formation activity.

Mo carbides have been known to be very active in methanation of CO^{19),20)}. Hence one might wonder that the enhancement of alcohol synthesis activity during the CO-H₂ reaction and also by the CO or CO-H₂ treatment is due to the carburization of Mo. We have found that by carburizing the H₂-reduced catalyst with C₄H₁₀/H₂, the initial activity for hydrocarbon formation was increased by a factor of 3, whereas the initial yield of alcohols was only slightly increased. The increase in hydrocarbon production is in agreement with the X-ray powder patterns for the catalyst, which contained lines characteristic of Mo₂C.

From these findings, we have ruled out the possibility that Mo carbides is directly related to the active site for alcohol synthesis. It may be concluded that the increase in alcohol production rate during the CO-H₂ catalytic run is ascribable to the formation of CO-reduction induced defects on MoO₂ (Eq. (7)). It has been established that CO reduction induces defects in ZnO faces which

Fig. 3 Mo(3d) ESCA Region of Fresh and Used Mo(10 wt%)-K(1.63 wt%)/SiO₂

cannot be reduced with H_2 and that these are specific sites for methanol synthesis²¹. It has been recently proposed that the active site for hydrogenation of CO to methanol over ZrO_2 is an oxygen anion vacancy²².

Figure 3 shows the Mo 3d XPS peaks of fresh and used Mo-K/SiO₂ catalysts. On the used catalyst there appeared a shoulder on the low binding energy side of the Mo 3d_{5/2} peak, supporting that Mo oxides on the catalyst surface was partially reduced during the CO-H₂ reaction.

3. Effects of Reaction Conditions

As shown in **Fig. 4**, time factor (W/F , g-catalyst·h·mol⁻¹) influenced on the selectivity to alcohols. Over the Mo/SiO₂ the selectivity of alcohols was improved at short contact time, suggesting a significant activity for the dehydration of alcohols to hydrocarbons under synthesis conditions. This is in agreement with the observation by Maruyama *et al.*²³, who reported that Mo/SiO₂ had significant acidity. For the catalyst with higher K/Mo ratio, however, the selectivity of alcohols was less dependent on the contact time²⁴. The contribution of the alcohol dehydration route to hydrocarbon formation seems to decrease on increasing the K/Mo ratio.

The effect of total pressure on the product distribution over Mo(20 wt%)-K(1.63 wt%)/SiO₂ at 573 K and $W/F=1.4$ g-catalyst·h·mol⁻¹ is presented in **Table 3**. Raising the pressure, the yield of alcohols was greatly improved. The C₂+C₁ ratios of hydrocarbons and alcohols were independent of the pressure. It should be noted

Catalyst: Mo(20 wt%)-K(1.63 wt%)/SiO₂; Reaction conditions: 573 K, 1.6 MPa ($H_2/CO=1$), $W/F=10$ g-cat·h·mol⁻¹.

Fig. 4 Influence of Time Factor on Alcohol Selectivity and C₂+ Alcohols/Methanol Ratio

that at 5.0 MPa specific activity of alcohols formation as high as 420 g (kg-catalyst)⁻¹·h⁻¹ was obtained in 68 C-atom% selectivity. At 6.5 MPa the selectivity to alcohols was slightly reduced, probably because of the dehydration of alcohols at increased contact time.

Table 4 shows the effect of reaction temperature on the catalytic performance of Mo(10 wt%)-K(1.63 wt%)/SiO₂ at 1.6 MPa and $W/F=10$ g-catalyst·h·mol⁻¹. With lowering the temperature, the selectivity to alcohols was greatly improved. A

Table 3 Influence of Total Pressure on Performance of Mo(20 wt%)-K(1.63 wt%)/SiO₂ Catalyst

Total pressure [MPa]	CO conversion [%]	CO ₂ yield [%]	Activity	
			Alcohols [g·(kg-cat.) ⁻¹ ·h ⁻¹]	Hydrocarbons [g·(kg-cat.) ⁻¹ ·h ⁻¹]
1.6	2.7	1.1	72	45
5.0	10	3.1	420	124
6.5	13	4.5	428	181

Reaction conditions: 1.6 MPa, $H_2/CO=1$, $W/F=1.4$ g-catalyst·h·mol⁻¹.

Table 4 Influence of Reaction Temperature on Performance of Mo(10 wt%)-K(1.63 wt%)/SiO₂ Catalyst

Reaction temperature [K]	CO conversion [%]	CO ₂ yield [%]	Activity	
			Alcohols [g·(kg-cat.) ⁻¹ ·h ⁻¹]	Hydrocarbons [g·(kg-cat.) ⁻¹ ·h ⁻¹]
513	0.32	0.10	2.2	0.41
523	0.52	0.15	3.6	0.74
538	1.0	0.33	6.7	1.7
553	2.0	0.67	11	4.0
573	5.5	2.3	21	12
593	7.3	3.2	16	22

Reaction conditions: 1.6 MPa, $H_2/CO=1$, $W/F=10$ g-catalyst·h·mol⁻¹.

maximum yield of alcohols was obtained at 573 K. C₂+ alcohols/methanol ratio gradually increased with increasing the temperature.

4. Addition of Probe Molecules to CO-H₂

Table 5 shows the isomer distribution in alcohols and alkanes in C₄–C₆ range obtained with Mo(20 wt%)-K(1.63 wt%)/SiO₂ at 573 K²⁵⁾. The alcohols are exclusively primary, with some methyl branching in the 2-position, whereas hydrocarbons consist mainly of straight chain isomers. The former isomer distribution indicates a strong resemblance to that of the formation of alcohols and aldehydes by hydrocarbonylation of alkenes. Hence it is of special interest to examine the activity of Mo catalysts for hydrocarbonylation of alkenes²⁴⁾.

Figure 5 shows the effects of ethene added (1.0–1.3 mol%) to the CO-H₂ reactant gas on the yields of products at 473 K over Mo(20 wt%)/SiO₂ and Mo(20 wt%)-K(1.63 wt%)/SiO₂. It is evident that over both catalysts the addition of ethene resulted in a marked increase in the 1-propanol yield. This suggests the capability of Mo to catalyze CO insertion into surface ethyl-metal bond. Over the catalyst without K the yields of C₃ hydrocarbons increased by the addition of ethene, suggesting incorporation of ethene into these compounds; the

surface ethyl species could react with surface CH_x to form higher hydrocarbons and/or could react with the adsorbed CO to form C₃ oxygenated compounds, followed by dehydration to C₃ hydrocarbons.

Selectivities for the ethene conversion to C₃ compounds were rather low, however, owing to the high activity of the catalyst without K for the simple hydrogenation of ethene. The addition of KCl significantly suppressed the rate of hydrogenation of ethene to ethane, resulting in the improvement of the selectivity toward hydrocarbonylation by a factor of 3. This may be closely related to the promotion of alcohol selectivity from CO-H₂ by the addition of K.

Hydrocarbonylation of higher alkenes also took place over the Mo catalysts. Isomers branching in the 2-position were obtained together with those with straight chain. **Table 6** shows the effect of addition of propene (1.0 mol%) to CO-H₂ on the isomer distribution in butanols. Along with the increase in the yield of butanols, their isomer distribution was hardly changed by the addition of propene, indicating that the butanols from propene hydrocarbonylation were very similar, in the isomer distribution, to those from CO-H₂.

Table 5 Isomer Distribution in Product Alcohols and Alkanes over Mo(20 wt%)-K(1.63 wt%)/SiO₂

Carbon number	Isomer selectivity [mol%]	
	Alcohols	Alkanes
4	CH ₃ (CH ₂) ₃ OH	CH ₃ (CH ₂) ₂ CH ₃
	68	93
	CH ₃ CH(CH ₃)CH ₂ OH	(CH ₃) ₃ CH
	32	7
5	CH ₃ (CH ₂) ₄ OH	CH ₃ (CH ₂) ₃ CH ₃
	54	92
	C ₂ H ₅ CH(CH ₃)CH ₂ OH	C ₂ H ₅ CH(CH ₃) ₂
	46	8
6	CH ₃ (CH ₂) ₅ OH	
	49	
	n-C ₃ H ₇ CH(CH ₃)CH ₂ OH	
	33	
	(C ₂ H ₅) ₂ CHCH ₂ OH	
	18	

Reaction conditions: 573 K, 1.6 MPa, H₂/CO=1, W/F=10 g-catalyst·h·mol⁻¹.

Catalysts: Mo(20 wt%)/SiO₂ and Mo(20 wt%)-K(1.63 wt%)/SiO₂; Reaction conditions: 473 K, 1.6 MPa (H₂/CO=1), W/F=10 g-cat·h·mol⁻¹.

Fig. 5 Influence of Addition of Ethene(1.0–1.3 mol%) to CO-H₂ Reactant Gas on Product Distribution

Table 6 Influence of Propene (1.0 mol%) Addition on Isomer Distribution in Product Butanols (2-methyl-1-propanol/1-butanol)

Feed	Catalyst, K [wt%]			
	0		1.63	
	CO-H ₂	CO-H ₂ -C ₃ H ₆	CO-H ₂	CO-H ₂ -C ₃ H ₆
Yield of butanols [mmol·(kg-catalyst) ⁻¹ ·h ⁻¹]	1.2	3.3	2.5	18
Selectivity to 2-methyl-1-propanol [mol%]	49	52	30	32

Catalyst: Mo (20 wt%)/SiO₂. Reaction conditions: 523 K, 1.6 MPa (H₂/CO=1), W/F=10 g-catalyst·h·mol⁻¹.

This similarity was found to hold in the temperature range of 423–573 K. Over both catalysts the selectivity to 2-methyl-1-propanol similarly decreased on lowering the temperature. These findings imply that the higher alcohol formation from CO-H₂ proceeded by way of the same intermediate as the alkene hydrocarbonylation; carbon monoxide inserted into an alkyl-metal bond to form acyl species which was subsequently hydrogenated to the alcohol product.

In contrast to the addition of alkenes, the addition of methanol (2.0 mol%) resulted in no significant change in the formation of the homologation product ethanol²⁴. At 473 K over the KCl promoted and unpromoted catalyst, the methanol conversion to ethanol was estimated at 0.3% and 0.1%, respectively, and the ethene conversion to propanol was found to be 3.4% and 3.5%, respectively. Hence it is unlikely that the homologation reaction of alcohols to higher alcohols contributes significantly to the production of C₂+ higher alcohols from CO-H₂. This result is consistent with the findings that C₂+ alcohols/methanol ratio was virtually independent of contact time (Fig. 4).

The change in the yields of the products caused by the addition of acetaldehyde was studied. Neither of the Mo catalysts showed any significant activity for the incorporation of aldehydes for the chain growth of alcohols. However, both catalysts exhibited a significant activity for the acetaldehyde conversion to C₄ oxygenated compounds, namely, crotonaldehyde, butyraldehyde, and butanol. This suggests the occurrence of aldol condensation of acetaldehyde. Because the addition of KCl causes a sharp decrease in the ratio of C₄ oxygenates and hydrocarbons derived from acetaldehyde to remaining acetaldehyde (4.0 to 15), the aldol condensation appears to be catalyzed by acid sites on the surface. As shown in Table 2, however, the alcohol chain growth in the CO-H₂ reaction was promoted by adding KCl. Hence it is unlikely that aldol condensation could be important for chain growth to form higher alcohols.

A different type of evidence against aldol condensation is offered by the carbon chain structure of the alcohols. The presence of 2-ethyl-1-butanol (Table 5) cannot be explained by aldol condensation of C₅ aldehyde with C₁ intermediates. In contrast, the hydrocarbonylation mechanism can account for its formation, by assuming CO insertion into (C₂H₅)₂CH-M bond which could be formed through σ - π interconversions of coordinated *n*-pentyl (Eq. (8)). The hypothesis of the insertion of CO into a

growing alkyl-metal bond has been proposed by many authors²⁵ to explain the formation of oxygenated products over group VIII noble metal based metal catalysts.

5. Reaction Mechanism of CO Hydrogenation

5.1 Mechanism for Branchings

As has been described above, isomer distributions in alcohols and alkanes obtained with SiO₂-supported Mo catalysts were different. The formation of alcohols with branching in the 2-position can be accounted for by Eq. (10); the insertion of CO into the secondary alkyl-metal bond leads to branched alcohols. Eqs. (11) and (12) shows the formation of straight chained and branched alkanes, respectively.

The difference in the selectivity to branched products between hydrocarbons and alcohols suggests that alcohols are formed at sites different from those for hydrocarbon formation, that is, the sites, M', in Eqs. (9) and (10) differ from the sites, M, in Eqs. (11) and (12). From the findings which have been described above, there is good reason to suppose that M' is MoO_{2-x} and M metallic Mo. It has been found that the metal electron density determines the secondary/primary ratio of coordinated alkyls²⁶. The MoO_{2-x} site should be less electron-rich than metallic Mo, allowing the formation of secondary alkyl groups (Eq. (9)). In contrast the pathway Eq. (12) is supposed to be infrequent since secondary alkyl groups should be disadvantageous on electron-rich sites of metallic Mo.

Catalysts: Mo(20 wt%)/SiO₂; Reaction conditions: 573 K, 1.6 MPa (H₂/CO=1), W/F=10 g-cat·h·mol⁻¹.

Fig. 6 Effect of K Content on Branched/Linear Ratio C₄ and C₅ Alcohols

Catalyst: Mo(10 wt%)-K(1.63 wt%)/SiO₂; Reaction conditions: 573 K, 1.6 MPa (H₂/CO=1), W/F=10 g-cat·h·mol⁻¹.

Fig. 7 Anderson-Schulz-Flory Plots for Hydrocarbons and Alcohols

In Fig. 6 the branched/linear ratios in C₄ and C₅ alcohols are plotted against the content of K added to Mo(20 wt%)/SiO₂ catalysts. With increasing K content, the selectivity to branched alcohols significantly decreased. The decrease can be accounted for by K-induced increase in electron density of molybdenum in MoO_{2-x}(M') species, which makes the reaction Eq. (9) more favorable than Eq. (10). In contrast with this observation, Vedage *et al.* found that the yield of 2-methyl-1-propanol over Cu/ZnO was enhanced by addition of Cs and explained its formation by assuming aldol condensation of aldehydic intermediates

with C₁ intermediates²⁷.

5.2 Anderson-Schulz-Flory Distributions for Hydrocarbons and Alcohols

Anderson-Schulz-Flory plots for hydrocarbons and alcohols produced over Mo(10 wt%)-K(1.63 wt%)/SiO₂ catalysts are shown in Fig. 7. Over Mo catalysts, the carbon number distribution obeyed an Anderson-Schulz-Flory type distribution for hydrocarbons and alcohols, respectively, except for methanol. Because the yield of methanol was far below the equilibrium value, the deviation cannot be caused by thermodynamic control. This deviation could be due to a pathway for methanol formation different from other products; methanol is the only product that does not involve the cleavage of carbon-oxygen bond of CO. Over our Mo catalysts, the probability of the chain growth, α , was 0.48–0.32 for hydrocarbons and 0.32–0.14 for alcohols; although the α values were dependent on the reaction conditions such as temperature and pressure and K content of the catalysts, the α value for alcohols was always smaller than that for hydrocarbons.

One might wonder that the difference in the α value between hydrocarbons and alcohols is attributed to the difference in the carbon-chain growth step between these products. However, it is thought that this is not the case. The chain propagation of hydrocarbons is represented by the CH₂ insertion steps in Eqs. (11) and (12). These steps are followed by hydrogenolysis to give alkanes (Eqs. (11) and (12) or β -elimination to give 1-alkenes. We consider that the alkyl groups thus formed on the metallic site, M, migrates to the MoO_{2-x} site, M', and is subject to CO insertion to give alcohols (Eqs. (9) and (10)). If the chain propagation of alkyl groups of alcohols occurred on MoO_{2-x}, we should observe alcohols branching in the 3 or further positions according to the following Eq. (13).

Table 7 shows the dependence of the yields of hydrocarbonylation and hydrogenation products on the carbon number of alkenes which were added to the reactant CO-H₂ gas²⁸. The yields from added alkenes were determined from the increase in the yields of corresponding products as a result of

Table 7 Dependence of Alkene Conversion on Carbon Number

Alkene C_n	Catalyst, K [wt%]					
	0			1.63		
	C_{n+1} alcohols yield (A) [%]	C_n alkane yield (P) [%]	Ratio A/P	C_{n+1} alcohols yield (A) [%]	C_n alkane yield (P) [%]	Ratio A/P
Ethene	3.4	30	0.11	3.3	8.8	0.38
Propene	0.53	20	0.027	0.20	6.3	0.032
1-Pentene	0.031	5.8	0.0053			

Catalyst: Mo (20 wt%)/SiO₂. Reaction conditions: 473 K, 1.6 MPa (H₂/CO=1, alkene 1 mol%), W/F=10 g-catalyst·h·mol⁻¹.

addition of each alkene. As the carbon number of the alkene increased, activities for both hydrocarbonylation and hydrogenation decreased. This was associated with the marked decrease in the ratio of hydrocarbonylation to hydrogenation, suggesting that the insertion of molecular CO to alkyl-metal bonds is more retarded for the longer alkyl chain. It is conceivable that this difference in the carbon number dependence between hydrocarbonylation and hydrogenation results in the difference in the α between alcohols and hydrocarbons even if alcohols and hydrocarbons follow a common chain growth step, namely, the insertion of a methylene unit to an alkyl group.

5.3 Dual-site Mechanism for Alcohols and Hydrocarbons Formation

As described above, oxidized Mo species, MoO_{2-x}, should be responsible for the formation of alcohols, whereas metallic Mo species is necessary for the formation of both hydrocarbons and oxygenates. It is known that metallic Mo readily dissociates CO at room temperature and that oxidation of the surface inhibits the dissociative component of adsorption and increases the associative component⁽²⁹⁾. Presumably C₂+ alcohols are formed *via* a dual-site mechanism as follows. First, CO adsorbed dissociatively on metallic Mo to form surface carbide, which is hydrogenated to give carbene and/or methyl species, while carbon monoxide is nondissociatively adsorbed on MoO_{2-x} sites. The alkyl chain growth mechanism must be identical for hydrocarbons and alcohols. The chain growth is likely to occur on the same metallic Mo site, where carbene insertion into an alkyl-metal bond leads to a longer alkyl group.

It appears that the termination steps for alcohols and hydrocarbons occur on different sites. Hydrocarbons should be formed *via* hydrogenolysis of alkyl-metal bond and/or β -C-H abstraction on metallic Mo sites, whereas the insertion of CO giving rise to alcohols occurs on MoO_{2-x}. K is effective in retarding hydrogenolysis of surface alkyls, resulting in the improvement in the

Scheme 1 Reaction Pathway of CO Hydrogenation on SiO₂-supported Molybdenum Catalysts

selectivity to alcohols. Alkyl groups formed on metallic Mo are assumed to migrate to a molecular CO on MoO_{2-x} species. A similar dual-site mechanism has been proposed for Rh catalysts, yielding C₂ oxygenates selectively³⁰. In a mechanistic study on CO hydrogenation over Fe catalysts, Huff and Satterfield found two sites over Fe catalysts with one site producing 1-alkenes, alkanes and oxygenates, and the other not producing oxygenates³¹. Anderson and Ekerdt claimed a similar mechanism for the carbon chain-growth, occurring on one site to produce alcohols and on the other site to produce hydrocarbons³². These sites may differ only in the type of termination step allowed, alkyl hydrogenation/dehydrogenation to hydrocarbon products *vs.* CO insertion leading to oxygenates. They suggested the difference of Fe valence between sites forming hydrocarbons and sites forming alcohols.

Methanol is the only product that does not involve the carbon-oxygen bond of CO and assumed to be formed solely on MoO_{2-x}. The activity change with processing time is consistent with this mechanism. In the initial stage of the CO-H₂ reaction the yield of methanol was noticeably low compared to C₂+ alcohols. As the CO-H₂ catalytic run was continued, the increase in the yield of methanol was more remarkable than that of C₂+ alcohols, resulting in the decrease in the C₂+C₁ ratio for alcohols. This is interpreted in terms of the conditioning of the catalyst surface;

the amount of MoO_{2-x} was increased through reduction of MoO_2 by CO according to Eq. (7).

Thus the reaction scheme for hydrogenation of CO over the Mo catalysts producing hydrocarbons and alcohols would be summarized as shown in Scheme 1.

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要 旨

合成ガスからの混合アルコール合成用モリブデン触媒

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シリカゲルを担体としてモリブデン触媒を調製したところ、合成ガスからの混合アルコール合成に活性の高い触媒系が実現した。KCl の添加は CO 転化率を低下させ、とりわけ炭化水素の生成を抑制し、アルコール選択率向上に効果があった。5.0 MPa, 573 K, $W/F = 1.4$ g-触媒・時間/モルにおいて 420 g/kg-触媒/時間という高いアルコール生成活性が達成された。アルコールの生成には水素還元後、金属モリブデンならびに MoO_2 の両者が存在することが必要であることが分かった。K を添加するとモリブデンの金属への完全還元が抑制され、この際アルコールの生成増加が認められた。アルコール収量は反応時間とともに顕著に増加することから、CO 水素化反応中にアルコール合成の活性種が生成することが示された。触媒を CO, CO-H_2 , ブタン-水素で前処理した時の効果, Mo (3d) の XPS スペクトルを調べることにより、CO 水素化反応中、CO で MoO_2 が還元されて酸素欠陥 MOO_{2-x} が生成し、こ

れがアルコール合成活性の向上をもたらすことが示唆された。一方、炭化水素合成は金属モリブデンのみによるものと思われる。プローブ分子を CO-H_2 ガスに添加することにより、 C_2 以上のアルコールの生成はアルケンのヒドロカルボニル化と同様の中間体を経由していることが明らかになった。シリカゲル担持モリブデン触媒上でのアルコール生成機構としてデュアルサイト機構を提案した。すなわち、金属モリブデン上で CO が解離し、表面カーバイド種を生成し、水素化によりカルペンやメチル種を与える。メチレンの表面アルキル種への挿入と続いての水素化分解や脱水素による炭化水素生成もまた金属モリブデン上で起こるが、CO 挿入によるアルコール生成は MoO_{2-x} により触媒される。K はアルキル種の水素化分解の抑制によりアルコール選択率を向上せしめる効果を持つ。このデュアルサイト機構により、枝分かれ化合物への選択率が炭化水素とアルコールで大きく異なっていることも説明できる。

Keywords

Molybdenum catalyst, Silica gel, Carbon monoxide, Hydrogenation, Alcohol