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Mechanistic Study on the Alcohol Synthesis over Molybdenum Catalysts

Addition of Probe Molecules to $CO-H_2$

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The addition of probe molecules, such as ethylene, propylene, methanol, ethanol, and acetaldehyde, to $CO-H_2$ feed was studied over the KCl-promoted and the unpromoted Mo/SiO_2 catalyst under synthetic conditions, in order to clarify the reaction paths for the formation of hydrocarbons and alcohols. The results of olefin addition study suggest that the alcohol formation from $CO-H_2$ proceeds by a mechanism including steps identical with those in the hydrocarbonylation of olefins and that KCl suppresses the simple hydrogenation of olefins. Both of the Mo catalysts demonstrate a poor catalytic activity for the homologation of methanol to ethanol. Alcohol homologation seems to be only a minor process in the formation of C_2^+ alcohols. No significant activity of Mo catalysts for incorporation of acetaldehyde into C_3 oxygenated compounds may exclude the intermediacy of aldehydes for the chain growth of alcohols. Hydrogenation of acetaldehyde to ethanol is the fast and predominant reaction, in agreement with the fact that alcohols compose more than 90% of the organic oxygenates produced from $CO-H_2$. Aldol condensation is apparently unimportant for the chain growth. The contribution of alcohol dehydration to hydrocarbon formation may be insignificant over the KCl-promoted catalyst with K/Mo = 0.4. Consequently, a mechanism including CO insertion into the alkyl–metal bond is proposed for the main reaction path for the higher alcohol formation from $CO-H_2$. The role of K is supposed to slow the hydrogenation of surface alkyl species to form alkanes as well as to increase the active sites for alcohol formation by retarding the reduction of Mo. © 1989 Academic Press, Inc.

INTRODUCTION

The catalytic conversion of synthesis gas to oxygenated compounds, especially alcohols, is generally recognized as an interesting route for providing clean fuels and petrochemical feedstocks (*1*). The most promising application of the C_2^+ alcohols is as a blending stock for automotive fuel to meet the octane requirement resulting from legislative regulation of lead. Since blending of methanol into gasoline raises problems of phase separation, high volatility, and lowering of calorific value, higher alcohols are better additives. A number of papers have been published on catalysts for the synthesis of mixed higher alcohols. It has been proved that proper modifications of the composition of the methanol synthesis catalysts and of the reaction conditions result in the coproduction of higher alcohols together with methanol (*2, 3*). The alcohol formation over conventional Fischer–Tropsch catalysts has been increased by addition of promoters or nitridation (Fe). Institut Francais du Petrole claimed a series of catalysts useful for the synthesis of mixtures of light alcohols, consisting of methanol synthesis catalysts (Cu) and Fischer–Tropsch catalysts (Co) (*4*).

In our previous studies, supported Mo catalysts have been developed as excellent catalysts for higher mixed alcohol synthesis (*5–7*). The activity and selectivity for alcohol formation over the Mo catalysts were significantly affected by the supports, the

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additives such as alkali metal salts, and the reaction conditions. The space-time yield of mixed alcohols over Mo (20 wt%)–KCl (K = 1.63 wt%)/SiO_2 catalyst amounted to 0.42 kg kg-cat.$^{-1}$ h^{-1} at 573 K and 5.0 MPa (*8*). In addition, Dow and Union Carbide have recently claimed a number of patents of the catalysts based on MoS_2, promoted by CoS and alkali metal salts for higher alcohol synthesis (*9–11*). Somorjai *et al.* reported the effect of pressure on the alcohol synthesis over MoS_2 catalysts (*12*).

The mechanism for higher alcohol synthesis from CO–H_2 is not fully understood. CO hydrogenation reaction should involve various elementary reaction steps, e.g., dissociative and/or nondissociative adsorption of CO on metal, dissociation of H_2, C–H bond formation, C–C bond formation, CO insertion into surface alkyls, elimination from surface intermediates to form hydrocarbon or alcohol, and secondary reactions of the primary products. A reaction scheme based on CO insertion to form oxygenated compounds has been proposed by various investigators for Rh (*13–17*) and Fe (*18*) catalysts. Hackelbruch *et al.* have suggested the consecutive insertion of CH_2 units to surface formyl or methoxycarbonyl species (*19*). Several reaction mechanisms involving a surface aldehyde species have also been proposed to explain the alcohol formation during CO hydrogenation over Cu–Zn-based catalysts in particular. In the 1930s, Graves suggested that the formation of higher alcohols occur via aldol condensation reactions (*20*). Vedage *et al.* found that formation of 2-methyl-branched 1-alcohols over Cu/ZnO was enhanced by alkali promoters and proposed a mechanism for branching involving aldol synthesis of aldehyde precursors (*21*). More recently, Mazanec proposed the insertion of CO into a surface-bound aldehyde as the primary carbon–carbon bond-forming step (*22*).

One informative way of studying the role of the elementary reaction step in complex reaction pathways is by the addition of probe molecules to the reactant stream during reaction (*23*). In order to obtain a better understanding of the reaction mechanism of CO hydrogenation, we have attempted the addition of probe molecules to CO–H_2 over the unpromoted and the KCl-promoted Mo catalyst under synthesis conditions. Ethylene, propylene, methanol, ethanol, and acetaldehyde were utilized as probe molecules in this study. The addition of these probe molecules can produce various intermediates, which may exist in the course of CO hydrogenation to form mixed higher alcohols over Mo catalysts, and thus could bring about a significant change in the overall product distribution. By analysis of their effect on the promotion of a specific reaction, the principal method of formation of hydrocarbons and oxygenates on the Mo catalysts may be identified. A preliminary paper on the mechanism of CO hydrogenation on K-promoted Mo catalyst has been published elsewhere (*24*).

EXPERIMENTAL

Catalysts were prepared by impregnating silica gel (Fuji Davison, ID) with an aqueous solution of $(NH_4)_6Mo_7O_{24}$ (Mo = 20 wt%). The Ca, Na, K, and Fe impurities were present in the ID silica at levels of 0.21, 0.07, 0.002, and 0.015 wt%, respectively. For the promoted catalysts, the silica was impregnated with KCl (K = 1.63 wt%) from the aqueous solution and calcined in air at 673 K for 1 h in advance of the impregnation with the molybdenum salt. The impregnates were dried at 393 K overnight, treated in flowing He at 673 K for 1 h, and then reduced in flowing H_2 at 773 K for 12 h.

The CO hydrogenation and probe molecule studies were carried out by use of a flow reactor made of stainless steel, of which the heated section was 50 cm long and 0.6 cm in inside diameter, containing 1.0 g of catalyst. The reactor was equipped with a microfeeder for introducing the liquid of probe molecules (methanol, ethanol, and acetaldehyde) and gas flow controllers (He, H_2, ethylene, propylene, and CO–H_2).

The synthesis gas ($H_2/CO = 1$, 1.6 MPa, W/F = 10 g-catalyst h/mol) was supplied to the reactor through the stainless-steel tube heated to 473 K to decompose metal carbonyls for elimination. The hydrogen was purified of oxygen by passage through a Deoxo unit (Engelhard), followed by a molecular sieve adsorbent. The $CO-H_2$ reaction was carried out for more than 100 h until steady-state conversion was attained. Then a small amount (1–2 mol%) of the probe molecule was added to the $CO-H_2$ feed. The reaction was continued to reach the steady-state activities under various reaction conditions. After the study on the addition of a certain probe molecule was accomplished, the $CO-H_2$ reaction was performed for more than 50 h under a given set of conditions, followed by the addition of another molecule.

The products were analyzed by gas chromatography. Concentrations of CO, CO_2, and CH_4 in the off-gas were determined by a TCD chromatograph on an active carbon separation column at 323 K using H_2 as a carrier gas. The distribution of organic compounds was determined by an FID gas chromatograph on the following separation columns using N_2 as a carrier gas: 2-m Porapak Q for the analysis of 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.

RESULTS AND DISCUSSION

Co Hydrogenation over Mo Catalysts

Table 1 lists the influence of temperature on the product distribution from CO hydrogenation over the unpromoted and the KCl-promoted Mo catalyst. It is noteworthy that at lower temperatures the unpromoted catalyst gave much more alcohol than the KCl-promoted catalyst. Over the unpromoted catalyst the rise in the temperature resulted in a sharp increase in the hydrocarbon yield at the expense of the selectivity for alcohols. The maximum space-time yield of al-

TABLE 1

CO Hydrogenation over Mo(20 wt%)–KCl/SiO_2 Catalysts[a]

K cont. (wt%)	Temp. (K)	CO conv. (%)	CO_2 yield (%)	Product distribution (C at.%)								STY[b]		C_2^+/C_1 ratio	
				CH_4	C_2H_4	C_2H_6	C_3^+	MeOH	EtOH	C_3 + OH		HC	Alcohol	HC	Alcohol
0	473	0.4	0.1	21.5	2.1	9.4	12.8	30.8	15.7	7.1		1.2	2.6	1.1	0.74
	503	2.4	0.9	30.2	1.6	16.5	18.1	20.9	8.0	4.2		7.7	6.9	1.2	0.58
	523	6.3	2.8	37.3	1.2	21.8	23.5	11.3	2.7	1.8		23.4	8.2	1.2	0.40
	573	52.8	25.1	48.0	0.0	28.6	23.2	0.1	0.0	0.0		220	0.7	1.1	0.52
1.63	473	0.2	0.1	11.4	4.6	2.4	9.1	32.1	20.7	17.9		0.2	1.0	1.4	1.2
	503	0.6	0.3	13.2	4.6	3.8	11.9	26.4	21.9	16.4		0.9	3.2	1.5	1.5
	523	1.8	0.7	14.3	3.2	5.9	10.7	24.5	21.1	18.8		2.9	9.3	1.4	1.6
	573	10.7	4.8	31.4	1.3	19.3	20.9	12.3	9.1	4.8		33.7	21.6	1.3	1.1

[a] Reaction conditions: 1.6 MPa, W/F = 10 g-catalyst h mol^{-1}.
[b] Space-time yield/g kg-catalyst^{-1} h^{-1}.

cohols was obtained at 523 K. At 573 K, the unpromoted catalyst produced mainly C_1 to C_5 hydrocarbons with a small amount of alcohols. In the presence of K, the yield of alcohols increased with increasing temperature up to 573 K, although their selectivity gradually decreased. The addition of KCl proved to be effective in suppressing hydrocarbon production but promoted alcohol yield at higher temperatures. The addition of KCl also caused an increase in C–C bond formation, or the C_2^+/C_1 ratio, especially for alcohols. Over the Mo catalysts, alcohols accounted for more than 90% of the total organic oxygen compounds, while other oxygenates mostly consisted of acetaldehyde and acetone.

Isomer Distribution in Alcohols and Hydrocarbons

Table 2 shows the isomer distribution in alcohols and alkanes in the C_4–C_6 range obtained with Mo (20 wt%)–KCl/SiO_2 at 573 K. 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 alcohol (or aldehyde) formation by hydroformylation or oxo reaction of olefins. Therefore it seems of special interest to examine the activity of Mo catalysts for oxo reactions of olefins.

TABLE 2

Isomer Distribution in Product Alcohols and Alkanes over Mo (20 wt%)–K (1.63 wt%)/SiO_2[a]

Carbon number	Isomer selectivity (mol%)			
	Alcohols		Alkanes	
4	$CH_3(CH_2)_3OH$	68	$CH_3(CH_2)_2CH_3$	93
	$CH_3CH(CH_3)CH_2OH$	32	$(CH_3)_3CH$	7
5	$CH_3(CH_2)_4OH$	54	$CH_3(CH_2)_3CH_3$	92
	$C_2H_5CH(CH_3)CH_2OH$	46	$C_2H_5CH(CH_3)_2$	8
6	$CH_3(CH_2)_5OH$	49		
	n-$C_3H_7CH(CH_3)CH_2OH$	33		
	$(C_2H_5)_2CHCH_2OH$	18		

[a] 573 K, 1.6 MPa, $H_2/CO = 1$, $W/F = 10$ g-catalyst h mol^{-1}.

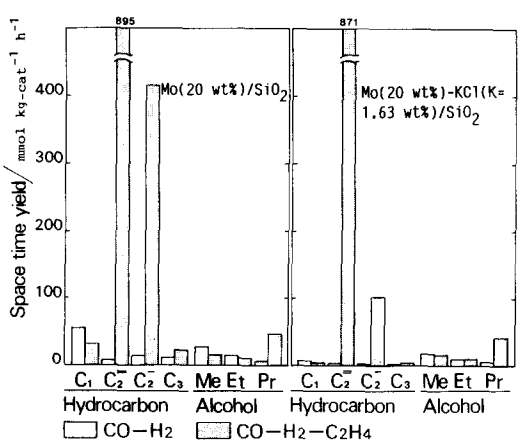

FIG. 1. Effect of the addition of ethylene (1.0–1.3 mol%) to CO–H_2 on product yields over the unpromoted and the KCl-promoted Mo catalysts at 473 K.

Addition of Olefins to CO–H_2

Figure 1 shows the effects of ethylene added to the CO–H_2 feed upon the space-time yields of products at 473 K. The addition of ethylene (1.0–1.3%) resulted in a significant variation in the rate of the formation of hydrocarbons and alcohols over both the promoted and the unpromoted catalyst. When ethylene addition was stopped, the rates of products formation returned closely to the former rates in the absence of ethylene.

Clearly, the unpromoted catalyst exhibited a much higher activity for the hydrogenation of ethylene to ethane than the KCl-promoted catalyst. It is also evident that the addition of ethylene resulted in a marked increase in the yield of n-propanol. Although the high activity of Mo catalysts to dissociate CO has been well established in the literature (*25, 26*), to our best knowledge molybdenum has never been recognized as being active for the insertion of molecular CO (*27*). The increase in the yield of n-propanol as a result of the addition of ethylene suggests the capability of Mo to catalyze CO insertion into surface ethyl–metal bond. As the formation of propionaldehyde was not observed during the addition of ethylene, it is likely that pro-

pionaldehyde initially formed by the oxo reaction was rapidly converted to *n*-propanol.

The decrease in the yield of methane and methanol during the addition of ethylene over the unpromoted catalyst would appear to be due to blockage of sites for formation of methane and methanol by the strongly adsorbed ethylene. As shown in Fig. 1, over the unpromoted Mo catalyst, an increase in the yields of C_3 hydrocarbons during the addition of ethylene to $CO-H_2$ may suggest the incorporation of ethylene 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 C_3 oxygenated compounds, followed by dehydration to C_3 hydrocarbons. The fairly high activity of the unpromoted catalyst for the dehydration of ethanol (vide infra) suggests that the latter reaction pathway may be operative over the unpromoted catalyst. Selectivities for the ethylene conversion to C_3 compounds were rather low, owing to the high activity of the unpromoted catalyst for the simple hydrogenation of ethylene. The Mo catalysts were found inactive for hydrogenolysis of ethylene to methane.

The addition of KCl to Mo/SiO_2 significantly suppressed the rate of hydrogenation of ethylene to ethane. This is reasonable since suppression of hydrogenation ability has been identified as a major effect of alkali promoters on CO hydrogenation reaction over transition metal catalysts (*28, 29*). In contrast, the rate of ethylene hydrocarbonylation to *n*-propanol was practically unchanged. Consequently, the selectivity toward hydrocarbonylation expressed by the rate of *n*-propanol to ethane was improved by a factor of 3 by the addition of KCl.

The relative rate of hydrocarbonylation of ethylene to that of simple hydrogenation increased with decreasing temperature and increasing concentration of added ethylene over the KCl-promoted Mo catalyst. This was accompanied by the emergence of propionaldehyde. The yields of ethane, *n*-propanol, and propionaldehyde were 117, 56, and 57 mmol/kg-cat. h, respectively, under the following reaction conditions: $CO/H_2/C_2H_4$ = 35/35/30 and 453 K. The hydrocarbonylation/hydrogenation ratio was increased to almost unity.

Hydrocarbonylation of higher olefins also took place over the Mo catalysts. In these cases isomers branching in the 2-position were obtained together with straight-chain ones. Table 3 shows the effect of the addition of propylene (1.0 mol%) to $CO-H_2$ 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 propylene, indicating that the butanols from propylene hydrocarbonylation were very similar, in the isomer distribution, to those from $CO-H_2$. This similarity was found to hold in the temperature range 423–573 K. Over both

TABLE 3

Effect of Propylene (1.0 mol%) Addition on Isomer Distribution in Product Butanols (2-Methyl-1-propanol/1-Butanol) over SiO_2-Supported Mo (20 wt%) Catalysts[a]

Feed	Catalyst, K (wt%)			
	0		1.63	
	$CO-H_2$	$CO-H_2-C_3H_6$	$CO-H_2$	$CO-H_2-C_3H_6$
Space-time 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

[a] 523 K, 1.6 MPa, H_2/CO = 1, W/F = 10 g-catalyst h mol^{-1}.

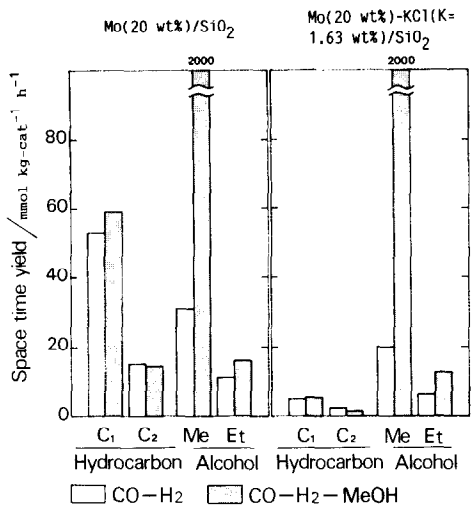

FIG. 2. Effect of the addition of methanol (2.0 mol%) to $CO-H_2$ on product yields over the unpromoted and the KCl-promoted Mo catalysts at 473 K.

the catalysts the selectivity for 2-methyl-1-propanol similarly decreased with decreasing temperature. These findings imply that the alcohol formation from $CO-H_2$ proceeded via the same intermediate as the olefin carbonylation; carbon monoxide was inserted into an alkyl–metal bond to form an acyl species which was subsequently hydrogenated to the alcohol product.

Addition of Alcohols to $CO-H_2$

The product distributions obtained with the addition of methanol (2.0 mol%) are compared with those resulting from simple CO hydrogenation. As shown in Fig. 2, over both of the Mo catalysts at 473 K the yield of ethanol slightly increased during the addition of methanol to $CO-H_2$. In contrast to the addition of ethylene, the addition of MeOH resulted in no significant change in the formation of CH_4. The apparent conversion of feed methanol to ethanol was determined from the increase in the formation of ethanol as a result of methanol addition. At 473 K over the unpromoted and the KCl-promoted catalyst the methanol conversions were estimated to be 0.1 and 0.3%, respectively. The amount of feed methanol was two orders of magnitude larger than the yield of methanol from CO hydrogenation at 473 K. Apparent conversion of ethylene to *n*-propanol was also calculated from the increase in the yield of *n*-propanol caused by the addition of ethylene. The ethylene conversions were 3.5 and 3.4% for the unpromoted and the KCl-promoted catalyst at 473 K, respectively. Hence it is unlikely that the homologation reaction of alcohols to higher alcohols contributes significantly to the production of C_2^+ higher alcohols from $CO-H_2$. This result is indeed consistent with the findings that the C_2^+ alcohol/methanol ratio was independent of contact time (*8*).

Figure 3 shows the change (increase or decrease) in the space-time yields of the products resulting from the addition of ethanol to $CO-H_2$ at 523 K. The large increase in the yield of ethylene and ethane over the unpromoted catalyst may be due to the dehydration of added ethanol and the subsequent hydrogenation of ethylene. This alcohol dehydration activity of Mo catalysts indicates that Mo/SiO_2 has significant acid-

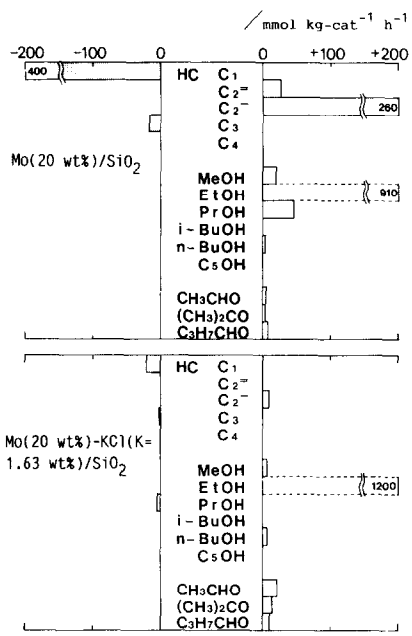

FIG. 3. Differences in product yields due to the addition of ethanol (1.2 mol%) to $CO-H_2$ at 523 K.

ity, in agreement with the observation by Maruyama *et al.* (*30*). The significant increase in the yield of *n*-propanol as a result of the addition of ethanol over the unpromoted catalyst may be explained by dehydration of ethanol to ethylene followed by hydrocarbonylation. Considering the results of the addition of methanol to CO–H_2, the direct homologation of ethanol to propanol could hardly occur on the Mo catalysts; the rate of homologation of ethanol was reported to be much lower than that of methanol (*31*). At 523 K over the unpromoted and the KCl-promoted catalyst apparent conversions of added ethanol to C_2 drocarbons were estimated to be 24 and 0.8%, respectively. Apparently KCl suppresses the ethanol dehydration activity of Mo/SiO_2. This should be due to a K-induced decrease in acidic sites.

The promoted catalyst exhibited a high selectivity for the conversion of ethanol to C_4 oxygenates (butyraldehyde and butanols) as well as the dehydrogenation of ethanol into acetaldehyde, compared to the unpromoted catalyst. Taking into account the C_4 oxygenates formation on addition of acetaldehyde (vide infra), the formation of C_4 oxygenates could be due to the aldol condensation of the acetaldehyde. The ratios of the yield of C_4 oxygenates to that of acetaldehyde were 3.0 and 0.8 over the unpromoted and the K-promoted catalyst, respectively. Hence it is obvious that the activity for aldol condensation was reduced by KCl addition. The addition of KCl reduced the yield of propanol during the addition of ethanol, which might be ascribed to the K-induced decrease in ethylene yield.

It is noteworthy that the addition of ethanol to CO–H_2 resulted in a marked decrease in the yield of CH_4, concomitant with a significant increase in the yield of methanol over the unpromoted catalyst, in particular. This decrease is supposed to be due to the decrease in active sites for hydrocarbon production; the formation of H_2O could increase owing to ethanol dehydration or aldol condensation, leading to

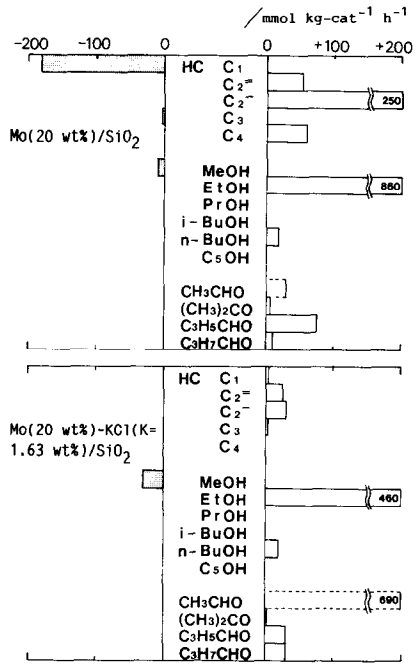

FIG. 4. Differences in product yields due to the addition of acetaldehyde (1.2 mol%) to CO–H_2 at 503 K.

oxidation of metallic Mo species active for hydrocarbon production (*32*). The increase in the yield of methanol may also be related with the increase in the H_2O formation. In fact, the externally added H_2O has been found to impede the hydrocarbon formation but promote the formation of alcohols (*33*).

Addition of Acetaldehyde to CO–H_2

The differences in the yields of the products at 503 K, due to the addition of acetaldehyde, are illustrated in Fig. 4. The unpromoted catalyst showed a higher activity for the hydrogenation of acetaldehyde to ethanol than the promoted catalyst. The conversion of acetaldehyde over the unpromoted catalyst exceeded 97%. The decrease in the activity for the hydrogenation of acetaldehyde upon alkali addition parallels the suppression of ethylene hydrogenation. The unpromoted catalyst also showed a fairly high activity for the conversion of acetaldehyde to C_2 hydrocarbons. This could be ascribed to the high activity of the

unpromoted catalyst for dehydration of ethanol.

Both of the catalysts exhibited a significant activity for the acetaldehyde conversion to C_4 oxygenated compounds, i.e., crotonaldehyde, butyraldehyde, and butanol. Since the rates of formation of C_3 oxygenates remained unchanged on addition of acetaldehyde, the formation of C_4 oxygenates suggests the occurrence of aldol condensation of acetaldehyde. The incorporation of acetaldehyde into C_4 hydrocarbons over the unpromoted catalyst is supposed to occur by way of butanol. Apparent conversions of added acetaldehyde to C_4 compounds including oxygenates and hydrocarbons over the unpromoted and the KCl-promoted catalyst were estimated at 18 and 13%, respectively. Since the addition of KCl caused a sharp decrease in the ratio of C_4 oxygenates and hydrocarbons derived from acetaldehyde to remaining acetaldehyde (4.0 to 0.15), the aldol condensation reaction appears to be catalyzed by acid sites on the surface. Hence the moderately low selectivity for incorporation of acetaldehyde into C_4 compounds could be due to the high activity of the unpromoted catalyst for acetaldehyde hydrogenation.

A slight increase in the yield of acetone was observed during the addition of acetaldehyde. This could proceed through dehydrogenation of the acetaldehyde to acyl intermediates followed by their association with CH_3 species to produce acetone. However, neither catalyst showed activity for the decarbonylation of acetaldehyde to CH_4. On the contrary, a significant decrease in the yield of CH_4 was observed for the unpromoted catalyst. As has been described above, this suppression of CH_4 formation should be related with the increase in the H_2O formation resulting from ethanol dehydration and/or aldol condensation.

Reaction Mechanism of CO Hydrogenation

The unpromoted and the KCl-promoted catalyst exhibited differences not only in product selectivity for CO hydrogenation but also in their catalytic capabilities for hydrogenation, dehydrogenation, CO insertion, dehydration, aldol condensation, and the incorporation of olefins, alcohols, and acetaldehyde during CO hydrogenation. The results of the olefin addition study suggest that the alcohol formation from CO–H_2 proceeds by a mechanism including steps identical with those in the hydrocarbonylation of olefins and that KCl suppresses the simple hydrogenation of olefins. Dissociation of adsorbed CO to form CH_3/CH_2 eventually followed by CH_2 insertion or addition of one hydrogen atom to adsorbed olefins would provide surface alkyl species. The CO insertion into the alkyl–metal bond appears to be a major route to higher alcohols.

Both the Mo catalysts demonstrated a poor catalytic activity for the homologation (carbonylation followed by hydrogenation) of methanol to ethanol. Thus it is clear that alcohol homologation is only a minor process in the formation of the C_2^+ alcohols on the Mo catalysts. The moderate activity for the incorporation of ethanol into propanol displayed by the unpromoted catalyst appears to be due to the hydrocarbonylation of ethylene as a dehydration product of ethanol. However, it is reasonable to assume that this indirect homologation through dehydration followed by hydrocarbonylation may not be operative in the production of higher alcohols, since the addition of KCl led to the improvement of the yield of C_2^+ alcohols from CO–H_2 at higher temperatures. In contrast, incorporation of ethanol into propanol was not observed for the KCl-promoted catalyst principally because of the suppression of ethanol dehydration by KCl.

Neither of the Mo catalysts showed any significant activity for the incorporation of acetaldehyde into C_3 oxygenated compounds. This finding may exclude the intermediacy of aldehydes for the chain growth of alcohols (*22*). Hydrogenation of acetaldehyde to ethanol was the fast and predom-

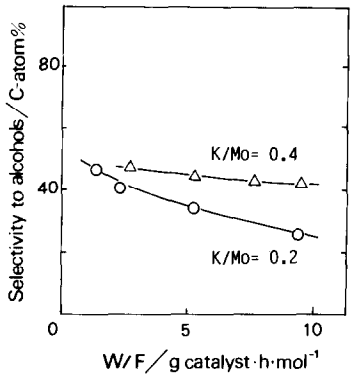

FIG. 5. Effect of the time factor (W/F) on the selectivity to alcohols over Mo (20 wt%)–KCl (K = 1.63 wt%)/SiO_2 (○) and Mo (5 wt%)–KCl (K = 0.83 wt%)/SiO_2 (△) at 573 K and 1.6 MPa.

inant reaction, in agreement with the fact that alcohols composed more than 90% of the organic oxygenates produced from CO–H_2. Vedage *et al.* found that formation of 2-methyl-1-propanol over Cu/ZnO was enhanced by Cs addition and proposed a mechanism for branching involving aldol condensation of aldehydic intermediates with C_1 intermediates (*21*). The activity for aldol condensation of acetaldehyde seems to be catalyzed by acid sites of Mo/SiO_2, which could be poisoned by KCl. As shown in Table 1, however, alcohol chain growth in the CO–H_2 reaction was promoted by adding KCl. Therefore 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 2) cannot be explained by aldol condensation of C_5 aldehyde with C_1 intermediates. In contrast, the oxo reaction mechanism can account for its formation, by assuming CO insertion into the $(C_2H_5)_2CH$–M bond.

The Mo/SiO_2 catalysts exhibited a fairly high activity for dehydration of ethanol. Figure 5 shows the influence of time factor (W/F, g-cat. h mol^{-1}) on the selectivity to alcohols. At short contact time, the selectivity to alcohols was improved, suggesting a significant activity for the dehydration of alcohols to hydrocarbons under synthesis conditions. However, the alcohol selectivity was less dependent on the contact time for the catalyst with the higher K/Mo ratio. This indicates that the contribution of the alcohol dehydration route to hydrocarbon formation decreases with increasing K/Mo ratio.

Let us now consider the reason for the negligible formation of alcohols from CO–H_2 over the unpromoted catalyst at high temperatures. Since this catalyst exhibited a considerable activity for alcohol formation at low temperatures, one would expect that dehydration of alcohols once formed may dominate at high temperatures. Figure 6 shows the temperature dependence of the ratio of ethylene hydrocarbonylation (n-C_3H_7OH) to its simple hydrogenation (C_2H_6) over the promoted and the unpromoted catalyst. Although at lower temperatures the selectivity to n-propanol over the unpromoted catalyst was comparable to that observed for the KCl-promoted Mo catalyst, it declined steeply because of a large increase in the ethane formation as the temperature was raised. Figure 6 also

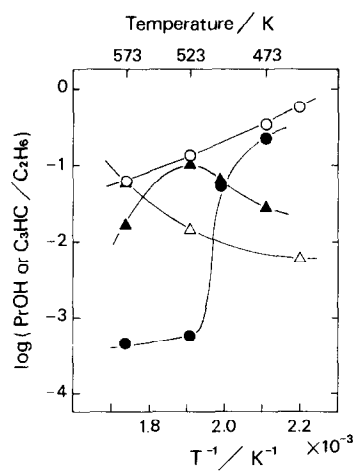

FIG. 6. Temperature dependence of n-propanol/C_2H_6 (○, ●) and C_3 hydrocarbons/C_2H_6 (△, ▲) during the addition of ethylene to CO–H_2: solid symbols, over Mo (20 wt%)/SiO_2; open symbols, over Mo (20 wt%)–KCl (K = 1.63 wt%)/SiO_2.

exhibits the influence of temperature on the ratio of C_3 hydrocarbons to C_2H_6. The ratio was depressed at 573 K, excluding the predominance of the pathway consisting of hydrocarbonylation of ethylene followed by dehydration at high temperatures. Hence negligible alcohol formation from $CO-H_2$ over the unpromoted catalyst at high temperatures (Table 1) would be accounted for by excessive promotion of hydrogenation of surface alkyl species. The difference in isomer distributions in alcohols and hydrocarbons (Table 2) also suggests that the conversion of alcohols to hydrocarbons should be insignificant.

As has been described elsewhere (*6, 8*), the K added retards the reduction of Mo, leading to the increase in the selectivity for alcohols. It is conceivable that the K not only increases the portion of the active sites for alcohol formation but also affects the hydrocarbon-forming sites. Otherwise, two plots of $\log(n\text{-}C_3H_7OH/C_2H_6)$ against $1/T$ (Fig. 6) should be parallel. A marked difference of the temperature dependence of carbonylation/hydrogenation selectivity between the K-promoted and the unpromoted catalyst suggests that the additional role of K is to slow competitive hydrogenation to form alkanes effectively, at high temperatures in particular. Part of K is presumed to be present in the vicinity of the hydrocarbon-forming sites.

In CO hydrogenation to give higher hydrocarbons and alcohols, the growing alkyl chain on the catalyst surface should have the following reaction possibilities, namely, (a) CO insertion to give precursors leading to C_2^+ oxygenates; (b) β-H abstraction to give olefin; (c) hydrogenolysis of the alkyl–metal bond to give paraffin; and (d) addition of methylene units giving longer alkyl groups. The former three modes are considered the chain termination steps. The mode (a) is identical with the hydroformylation of olefins, once the adsorbed olefin has added one hydrogen atom. The addition of KCl resulted in much more suppression in the rate of (c) than in that of (a). Over the KCl-promoted Mo catalyst, the route (c) could be suppressed enough at high temperatures to give a high yield of alcohols. No significant promotion of the carbonylation rate inherent in the addition of K was observed. Readsorption of olefins formed by way of route (b) may lead to reconversion to growing alkyl species. The increased C_2^+/C_1 ratio for alcohols for the KCl-promoted catalyst may be accounted for by the increase in the chance of the chain propagation route (d), resulting from suppression of the termination by competitive simple hydrogenation (a). Low activity for alcohol synthesis at low temperatures on the KCl-promoted catalyst could be due to the low content of metallic Mo (*8, 32*), which might also be requisite for the formation of C_2^+ higher alcohols through the promotion of CO dissociation and/or activation of molecular H_2.

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