1. Introduction

Recently, transformation of syngas to a short-chain alcohol with more than two carbons, described as C$_2$ alcohols, higher alcohols or mixed alcohols, has become important because higher alcohols can act as octane number enhancers, alternative liquid fuels, chemical intermediates, and other useful products$^{1,2}$. Noble metals such as rhodium exhibit good catalytic performance with selectivity for C$_2$ alcohols$^{3,4}$, but are sensitive to sulfur poisoning$^5$. Consequently, from a cost perspective as well, new types of non-noble metals catalysts are very desirable for alcohol synthesis applications. Molybdenum-based catalysts were considered to be promising candidates for the synthesis of higher alcohols$^{1,2,6-8}$. Use of bulk MoS$_2$ catalysts resulted in hydrocarbons as the main products$^9$. Addition of potassium to reduced Mo/Al$_2$O$_3$ catalysts enhanced the selectivity for both C$_2$ alcohols and methanol, with yields increasing from 0.0 to 25 %, and from 0.8 to 9.9 %, respectively$^{10}$. Alkali-MoS$_2$-based catalysts were highly selective for the synthesis of alcohols and resistant to sulfur poisoning$^{11}$. K-MoS$_2$ catalysts had selectivity for total alcohols of 55-68 % (excluding CO$_2$), but the main product was methanol (44-63 %)$^{12-14}$. Addition of alkali metals also increased the selectivity for alcohols and space time yield (STY) with oxide or hydroxide as precursors$^{15-17}$. Addition of transition metals, such as cobalt, as a promoter to sulfided Mo/Al$_2$O$_3$ or MoS$_2$ drastically improves hydrodesulfurization (HDS) activity$^{18}$. Therefore, addition of a transition metal to a MoS$_2$ system may also promote the synthesis of higher alcohols, i.e., improve the propagation of carbon chains, based on the fact that transition metals, such as Fe, Co, and Ni, also act as catalysts for Fischer-Tropsch (F-T) synthesis. Addition of Group VIII metals, especially cobalt, to unsupported alkali-MoS$_2$ catalyst shifted the selectivity for alcohols toward C$_2$ alcohols, and decreased the selectivity for hydrocarbons$^{19}$. Thus, an alkali-promoted Co-MoS$_2$ catalyst could be expected to produce more C$_2$ alcohols in mixed alcohol synthesis. Catalysts supported on materials, such as silica and alumina, are highly dispersed in comparison to bulk unsupported catalysts. Our previous study investigated the effects of acidity on the supports or catalysts in mixed alcohol synthesis$^{16}$. In other reports, the selectivities for C$_2$ alcohols with unsupported and activated carbon-supported K-Co-MoS$_2$ were 71-72 %$^{20,21}$ and 84-90 % (CO$_2$ excluded)$^{22-25}$, respectively. CO conversion with either unsupported or supported catalyst was 13-15 %. Higher alcohol synthesis over sulfided alkali Co-MoS$_2$ based catalysts depends on the multiple effects of...
the load of metal on the active sites, which result in cata-
lyst selective for C$_2$ alcohols, and the effects of un-
supported and supported catalysts. Besides, alcohol
synthesis competes with F-T synthesis and the wa-
tergas-shift reaction (WGS) in the CO hydrogenation
reaction. The selectivity for C$_2$ alcohols will also be
influenced by the reaction temperature, pressure, H$_2$/CO
ratio, and other factors. Therefore, the present study
focused on thermodynamic calculation of the equilibrium
compositions during the synthesis of alcohols to esti-
mate the optimum reaction condition for catalytic tests.
To elucidate the effects of the load of metal on the active
sites, which form C$_2$ alcohols on sulfided Co–Mo cata-
lysts, and the relationship between the unsup-
ported and supported catalysts were prepared using precipi-
tation and impregnation procedures. The catalytic activ-
ity for C$_2$ alcohol synthesis was evaluated using a
fixed-bed reaction system.

2. Experimental

2.1. Materials

γ-Al$_2$O$_3$ (Nippon Ketjen Co., Ltd., NK31925) and
SiO$_2$ (JGC Corp.) were used as the catalyst supports as
20-80 mesh. Catalyst preparation used 40-48 wt%
ammonium sulfide ((NH$_4$)$_2$S) in water (Sigma-Aldrich),
and commercial GR grade hexaammonium hepta-
molybdate 4-hydrate ((NH$_4$)$_6$Mo$_7$O$_{24}$·4H$_2$O), cobalt
nitrate hexahydrate (Co(NO$_3$)$_2$·6H$_2$O) and potassium
nitrate (KNO$_3$) (Wako Pure Chem. Ind., Ltd.) as catalyst
preursors. The feed gas was a mixture of carbon
monoxide (purity: 99.9 vol%) and hydrogen (purity:
99.999 vol%) or a standard gas of H$_2$/CO (50/50 vol%).

2.2. Preparation of Catalysts

All unsupported and supported catalysts were pre-
pared using a conventional precipitation method$^{26}$, or a
sequential impregnation method$^{16}$. The loadings of
metal, equivalent to K$_2$O, CoO, MoO$_2$, and MoO$_3$, are
listed in Table 1.

For the preparation of unsupported catalysts, the
MoO$_3$ precursor was prepared as follows. Hexaammonium
heptamolybdate 4-hydrate was dis-
solved in distilled water and concentrated NH$_3$OH.
(NH$_4$)$_2$S (40-48 wt%) was gradually added to the solution
at ambient temperature. A yellow precipitate was
isolated by suction filtration, and dried under vacuum at
room temperature. To remove ammonia, the sample
was dried under a nitrogen atmosphere at 500 °C
for 2 h. The precursor (MoOS$_2$) was impregnated into an
aqueous solution of Co(NO$_3$)$_2$·6H$_2$O and was evaporated
to dryness. The aqueous solution of KNO$_3$ was then
added. The impregnated sample was dried under a
nitrogen atmosphere at 500 °C for 2 h, was shaped
under 60 MPa for 5 min, and then pulverized to 20-80
mesh.

For the preparation of supported catalysts, the silica
support ($S_a$: 339 m$^2$/g, $V_p$: 1.1 mL/g) or alumina support
($S_a$: 201 m$^2$/g, $V_p$: 0.65 mL/g) was impregnated with
aqueous solution of (NH$_4$)$_2$MoO$_4$·4H$_2$O, and then
evaporated to dryness. Next, the aqueous solution of
Co(NO$_3$)$_2$·6H$_2$O was introduced. After calcining in
air at 450 °C for 12 h, the cobalt–molybdenum oxide/ cut-
support was impregnated with a solution of KNO$_3$, and
then similarly calcined.

All catalysts were presulfided with a gaseous mixture
of 5 vol% H$_2$S and 95 vol% H$_2$ in-situ at a flow rate of
30 mL/min/g-cat., at 400 °C using a temperature ramp
rate of 5 °C/min, under atmospheric pressure for 3 h.
The unsupported and supported sulfided catalysts were
named as K$_2$CoMoS and K$_2$CoMo/X, respectively, except
for MoS$_2$ (X: silica or alumina support, abbrevi-
ated as Si or Al; x: molar ratio of K/Mo; and y: molar
ratio of Co/Mo).

2.3. Characterization of Catalysts

The specific surface areas and pore sizes of all samples
were determined by the N$_2$ adsorption technique
with an automatic specific surface area and pore volume
measurement device (SA 3100, Beckman Coulter, Inc.).
X-ray diffraction (XRD) measurements were conducted
using an X-ray diffractometer (RAD-IIIC, Rigaku Corp.)
with Cu K$_{\alpha}$ radiation. A continuous scan mode was
used to collect 2θ data from 5 to 80° at a rate of 1.5°/
min. The voltage and current were 40 kV and 30 mA,
respectively. The reducibility of the sulfided catalysts
was measured using temperature-programmed reduc-

| Catalyst  | K$_2$O [wt%] | CoO [wt%] | MoO$_2$ [wt%] | MoO$_3$ [wt%] | S$_a$ [m$^2$/g] | $V_p$ [mL/g] | $d_a$ [nm] |
|-----------|--------------|-----------|--------------|--------------|----------------|-------------|-----------|
| MoS$_2$   | 0            | 0         | 100          | -            | 3.5            | 0.027       | 31        |
| Co$_{0.2}$MoS | 0          | 15        | 85           | -            | 28             | 0.10        | 15        |
| K$_2$CoMoS | 9.0         | 7.1       | 84           | -            | 3.9            | 0.029       | 30        |
| K$_2$CoMoS | 11.0        | 18        | 71           | -            | 6.4            | 0.039       | 24        |
| K$_2$CoMoS | 13.0        | 4.7       | 83           | -            | 13             | 0.063       | 20        |
| K$_2$CoMoS | 21.0        | 12        | 68           | -            | 12             | 0.048       | 17        |
| K$_2$CoMoS | 4.4         | 14        | 82           | -            | 13             | 0.055       | 16        |
| K$_2$CoMoMo/Al | 1.0     | 4.9       | -            | 20           | 202            | 0.54        | 11        |
| K$_2$CoMoMo/Si | 1.3     | 6.2       | -            | 20           | 99             | 0.82        | 33        |

S$_a$: specific surface area, $V_p$: pore volume, $d_a$: average pore diameter.
tion (H₂-TPR) with a ChemBET Pulsar TPR/TPD instrument (Quantachrome Instruments). Before the H₂-TPR measurements, all samples (0.1 g) were sulfided in-situ at 400 °C for 3 h, with a 5 % H₂S/95 % H₂ gaseous mixture at a flow rate of 20 mL/min. Subsequently, all samples were treated at 450 °C for 2 h in helium at a flow rate of 14 mL/min. After pretreatment, the samples were cooled to room temperature at 30 °C in a helium atmosphere. Then, the flow of helium was switched to 5 % H₂/95 % Ar, and allowed to stabilize for 60 min at a flow rate 14 mL/min. The sample was heated from 30-1000 °C at a heating rate of 5 °C/min, after which the sample was cooled to room temperature. Before the X-ray photoelectron spectroscopy (XPS) analyses, all samples were presulfided in a quartz reactor as the case used for H₂-TPR analysis. The sealed reactor containing the sulfided sample was transported into a glove box under a N₂ atmosphere and the samples were ground to fine powder without exposure to air. XPS measurements of the catalysts were carried out using a Shimadzu ESCA 3200 photoelectron spectrometer equipped with a magnesium source (Mg Kα = 1253.6 eV) and operated at 8 kV and 30 mA under previously published conditions²⁷. The binding energy of various elements on the samples. The envelopes of Mo 3d, Co 2p, S 2p, K 2p, O 1s, Si 2p, Al 2p, Al 2s were analyzed and the peaks were calculated with a curve-fitting Gaussian function.

The quantification of all species was calculated as follows:

\[ N_i = \frac{A_i/S_i}{\sum A_i/S_i} \]  

where \( N_i \) denoted the surface composition of a species \( i \) on a sample, \( A_i \) and \( S_i \) were the measured area of a species \( i \) and the sensitivity factor related to the species \( i \), as specified by the manufacturer.

2.4. CO Hydrogenation

The feed gases were high-pressure carbon monoxide (purity: 99.9 vol%) and hydrogen (purity: 99.999 vol%) or a gaseous mixture of H₂/CO (50/50). The synthesis tests of alcohols from syngas were performed in a fixed-bed pressurized flow reaction system with a conventional design micro-reactor consisting of an 8-mm i.d. stainless-steel tube containing 0.5 g of the packed catalyst. The flow rate of the feed gas was controlled using a high pressure mass flow controllers (EL-FLOW, OVAL Corp.). The volumetric flow rate of the reactor outlet gas was measured using a bubble flow meter and a dry-system gas meter. The detailed experimental procedures and sampling methods were as previously published²⁹. The reaction conditions were as follows: 250-350 °C, 8.0 MPa, gas hourly space velocity (GHSV) of 5000 h⁻¹, and H₂/CO ratio of 1.0. The majority of the activity tests for the synthesis of higher alcohols from syngas were performed during a period of less than 12 h. In all experiments on the various catalysts, no significant deactivation was observed during the reaction. When the reactor temperature increased to the required temperature, the feed gas was introduced into the reactor. After the activity and selectivity had become constant for approximately 2-3 h, the outlet gas, which was heated to approximately 70-80 °C at atmospheric pressure, was sampled every 30 min. The samples were injected into an online gas chromatography instrument equipped with an hydrogen-flame ionization detector (FID, Model GC-9A, Shimadzu; CP-Si1 SCB, 0.25 mm × 60 m length) to analyze the oxygenated compounds produced, such as C₁₋₄ alcohols, and traces of C₆ hydrocarbons. Alcohols with more than 5 carbons and hydrocarbons with more than 7 carbons were not detectable as those products could not be determined quantitatively. Another online GC-TCD (Unibeads C, 1/8 inch × 2.0 m length, GC-323, GL Sciences Inc.) was equipped to analyze CO as a reactant, and CO₂ and C₁₋₄ light hydrocarbons products, which consisted mostly of paraffin and traces of olefins, after being passed through a cooling line by a dumping-type cooler (model: BE200F, Yamato Scientific Co., Ltd.) at -30 to -40 °C. At least three samples were collected under every reaction condition, and the three stabilized data points were averaged. The relative error was ±5 % for stabilized data. For the subsequent reaction conditions, the activity tests were stabilized after ca. 2 h.

The molar flow rates of CO at the inlet and outlet were denoted as \( F_{CO,l} \) and \( F_{CO,o} \), respectively. The activities of the catalysts for the synthesis of alcohols were primarily assessed based on the CO conversion (\( X_{CO} \)), the carbon-based selectivity for product \( i \) with carbon number of \( n \) (\( S_{product,i} \)), and the probability of carbon-chain growth in hydrocarbons and alcohols (\( P \)). These parameters were defined with Eqs. (2)-(4). The selectivity was defined as the molar flow rate of a product based on the moles of carbon for all products (CO₂, methanol, C₂₊ alcohols, and C₁₋₄ hydrocarbons).

\[ X_{CO} = \frac{F_{CO,o} - F_{CO,l}}{F_{CO,l}} \]  

\[ S_{product,i} = \frac{n \cdot F_{product,i}}{\sum n \cdot F_{product,i}} \]  

\[ Y_n = P^{n-1} (1 - P) \]  

The probability of chain growth was determined using the Anderson-Schultz-Flory (ASF) distribution, where \( Y_n \) is the molar composition of an alcohol or a hydrocarbon with a carbon number of \( n \)²⁸.
3. Results

3.1. Thermodynamic Calculation

First, to identify the reaction conditions for C$_2$ alcohols synthesis, the equilibrium compositions during the synthesis of alcohols were calculated thermodynamically using HSC Chemistry® software. Stoichiometric alcohol synthesis and water-gas-shift (WGS) reaction, and formation of C$_1$-$3$ alcohols, CO$_2$, and H$_2$O were assumed to occur according to the following Eqs. (5) and (6).

$$nCO + 2nH_2 \rightarrow C_nH_{2n+1}OH + (n - 1)H_2O$$  \(n \leq 3\)  \(\text{(5)}\)

$$CO + H_2O \rightarrow CO_2 + H_2$$ \(\text{(6)}\)

The effects of temperature on the equilibrium compositions are shown in Fig. 1, indicating formation of C$_2$ alcohols at lower temperatures of approximately 300 $^\circ$C because all of the reactions were exothermic. The amount of CO$_2$ product increased from approximately 300 $^\circ$C and peaked at 450 $^\circ$C because high temperatures promoted the endothermal WGS reaction. Therefore, low temperatures (less than 300 $^\circ$C) were predicted to favor synthesis of C$_2$ alcohols.

The effects of pressure on the equilibrium compositions are shown in Fig. 2 over the range of 1-100 bar (1 bar = 1 $\times$ 10$^5$ Pa). CO conversion and C$_2$+ alcohol selectivity were favorable but selectivity for CO$_2$ was unfavorable under high pressures, as shown in Figs. 2 (I), (II), and (III). High pressure resulted in greater activity and selectivity for C$_2$+ alcohols in the synthesis of alcohols from syngas.

Next, stoichiometric F-T synthesis, alcohol synthesis and WGS reactions were assumed to occur based on Eq. (7), including Eqs. (5) and (6).

$$nCO + (2n + 1)H_2 \rightarrow C_nH_{2n+2} + nH_2O$$  \(n \leq 3\)  \(\text{(7)}\)

The effects of temperature on the equilibrium compositions are shown in Fig. 3. The main products were predicted to be methane, H$_2$O, and CO$_2$, with only trace alcohols such as methanol and ethanol. Alcohol synthesis, including F-T synthesis, was considerably more unfavorable than the synthesis of only alcohols. This result indicates that the thermodynamic properties of competitive CO hydrogenation reactions do not favor high selectivity for C$_2$+ alcohols. Consequently,

Fig. 1 Effects of Temperature on Equilibrium Compositions of C$_1$-$3$ Alcohols in Hydrogenation of CO, Including Water-gas-shift Synthesis, at H$_2$/CO = 2.0 and 50 bar

Fig. 2 Effect of Pressure and Temperature on (I) CO Conversion, (II) Selectivity for Propanol and Ethanol, and (III) Selectivity for CO$_2$ in Hydrogenation of CO, Including Water-gas-shift Synthesis, at H$_2$/CO = 2.0, (a) 1 bar, (b) 25 bar, (c) 50 bar, and (d) 100 bar
kinetic control of the reactions must be considered.

Under all conditions, C2 alcohol synthesis was relatively favorable at low temperatures less than 300 °C, and under higher pressure in the synthesis of alcohols from syngas, although alcohol synthesis, including F-T synthesis, was considerably more unfavorable than the synthesis of only alcohols.

### 3. 2. Characterization of Catalysts

#### 3. 2. 1. N\textsubscript{2} Adsorption

The surface areas ($S_a$) and pore volumes ($V_p$) of the unsupported and supported catalysts are listed in Table 1. The surface area of the unsupported catalysts was 3.5-28 m$^2$/g and in bulk because of the low surface area, and low pore volume and mesopore (<50 nm). The MoS\textsubscript{2} catalyst surface area was increased to 28 m$^2$/g by adding Co. The surface area was the highest with a Co/Mo ratio of 0.4 for the K\textsubscript{02}Co\textsubscript{02}Mo\textsubscript{02} catalyst. The K\textsubscript{02}Co\textsubscript{02}Mo\textsubscript{02} surface area had little effect on the K/Mo ratio, although the Co\textsubscript{04}Mo\textsubscript{02} surface area was decreased after adding the K precursor.

The SiO\textsubscript{2} support had surface area of 339 m$^2$/g; pore volume of 1.1 mL/g; and mean pore diameter of 12.4 nm. The Al\textsubscript{2}O\textsubscript{3} support had surface area of 201 m$^2$/g, pore volume of 0.65 mL/g, and mean pore diameter of 13.0 nm.

#### 3. 2. 2. XRD

XRD patterns of the oxidized and sulfided catalysts are shown in Fig. 4. The MoS\textsubscript{2} catalyst showed several peaks with broad intensities. The peaks at 9.5, 30.2, and 57.1° were attributed to the MoS\textsubscript{2} phase. The peaks at 19.8, 34.0, 46.1, 51.7, 59.0, and 65.7° were attributed to the Co\textsubscript{04}Mo\textsubscript{02} phase based on the pattern of Co\textsubscript{04}Mo\textsubscript{02}, according to the JCPDS database. The MoS\textsubscript{2} and Co\textsubscript{04}Mo\textsubscript{02} phases were clearly detected on KCoMoS for the bulk catalysts. In contrast, the metal oxides were not clearly detected on the supported catalysts, and the crystal characteristics were different for the supported catalysts compared to the bulk catalyst. This finding also indicates a high dispersion of metals on the two supported samples.

#### 3. 2. 3. H\textsubscript{2}-TPR

H\textsubscript{2}-TPR profiles of the unsupported and supported catalysts are shown in Fig. 5. Three main peaks were detected for the sulfided Mo catalyst: the first peak resulted from reduction of the S-H group at 200-400 °C; the second peak resulted from decomposition of the CoMoS phase at 700-900 °C (Co\textsubscript{04}Mo\textsubscript{02} → Co\textsubscript{04}Mo\textsubscript{02} + MoS\textsubscript{2}); and the third peak resulted from reduction of MoS\textsubscript{2} at 900-1000 °C.

The first peak at 269 °C on sulfided K\textsubscript{02}Co\textsubscript{02}Mo/Si (Fig. 5 (a)) was attributed to reduction of the S-H group,
and the peak at 810 °C was attributed to decomposition of the CoMoS phase. Two main peaks appeared at 547 °C and 910 °C for oxidized K02Co06Mo/Si (Fig. 5 (b)). The peak at 547 °C was assigned to partial reduction of Mo6+ to Mo4+ in the amorphous, highly defective, multilayered Mo oxides or heteropolymolybdates, and octahedral Mo species30). The peak at 910 °C was generally related with deep reduction from Mo6+ to Mo and strong binding of all Mo species to the support, including the highly dispersed tetrahedral Mo species30). The reduction peaks for bulk K02Co06MoS (Fig. 5 (c)) appeared at 670, 836, and 946 °C. The second peak was attributed to decomposition of the CoMoS phase. The third peak was attributed to reduction of the remaining MoS2.

Sulfided K02Co06Mo/Si was more reducible than unsupported K02Co06MoS because of the lower reduction temperature for sulfided K02Co06Mo/Si. The higher metal loading on the bulk K02Co06MoS sample resulted in greater consumption of H2 compared to the supported samples.

3.2.4. XPS

The surface compositions of unsupported and supported catalysts were characterized by XPS. The XPS spectra of K02Co06MoS as a representative sample are shown in Fig. 6. The envelope of the Mo 3d spectrum contained various components: Mo4+ 3d5\2, Mo4+ 3d3\2, Mo5+ 3d, Mo6+ 3d5\2, and Mo6+ 3d3\2. As shown in Fig. 6, the Mo 3d envelopes showed two strong peaks of Mo4+ 3d5\2, Mo4+ 3d3\2 at binding energies of 228.8 eV and 231.9 eV, which indicated the formation of MoS2 species37). Small peaks at 232.8 eV and 235.8 eV were assigned to Mo6+ 3d5\2, and Mo6+ 3d3\2, which indicated that the oxidized form was still present after sulfidation. The presence of Mo5+ species was very small, which is characteristic of the oxysulfide MoOxSy phase with a peak at 230.1 eV39,41). The peak at 225.9 eV was assigned to S 2s42). The Co 2p spectrum consisted of peaks at 778.2, 778.9, 781.5, and 785.0 eV, which were assigned to Co9S8, CoMoS, and Co2ʴ(CoO), and one shakeup peak, respectively42,43). The CoO species is usually not fully sulfided, so Co2ʴ was related to that present in the CoAl2O4 phase, which represents the interaction of Co with the support42,44). The shakeup peak of Co 2p was excluded from the composition of Co species.

The binding energies, and the ratios of various species with different valences are summarized in Tables 2 and 3. The binding energies were estimated with an accuracy of ±0.1 eV. Table 3 shows the ratio of CoMoS phase to all Co elements on the three catalysts decreased in the order: K02Co06MoS > K02Co06Mo/Si > K02Co06Mo/Al, whereas the ratio of Co2ʴ /Co showed the inverse order. The ratios of Co2ʴ /Co on the two supported catalysts were higher than on the unsupported catalyst, which indicated strong interactions between cobalt and the support on the two supported catalysts compared to the unsupported catalyst. Furthermore, the component of Co2ʴ on the Al-supported catalyst had stronger interaction with the alumina support than the silica support. The amount of Mo4+, assigned to the MoS2 phase, accounted for 79-86 % of Mo corre-
sponding to the sulfidation degree of various catalysts. The amounts of Mo\(^{5+}\) and Mo\(^{6+}\) on the unsupported catalyst was larger than on the supported catalysts, indicating that sulfidation of the MoO\(_x\)S\(_y\) precursor of the bulk unsupported catalysts was difficult.

3. 3. Alcohol Synthesis

3. 3. 1. Addition of Co to Unsupported MoS\(_2\) Catalyst

To investigate the effects of adding Co to the bulk MoS\(_2\) catalyst on the activity and selectivity for C\(_2\) alcohols synthesis, activity tests were conducted under the following conditions: 250-350 °C, 8.0 MPa, 5000 h\(^{-1}\), and H\(_2\)/CO molar ratio of 1.0. The results of these tests are shown in Fig. 7. The main products using the bulk MoS\(_2\) catalyst were hydrocarbons and CO\(_2\), which accounted for at least 96 % of all products. Paraffins were the majority of the hydrocarbons, whereas olefins were only present as trace amounts. At a higher reaction temperature, the selectivity for CO\(_2\) increased from 23 to 48 % because the water-gas-shift reaction proceeded. Addition of Co to the MoS\(_2\) catalyst enhanced the formation of C\(_2\) alcohols and improved the total alcohol selectivity. Furthermore, the formation of hydrocarbons was inhibited, whereas CO conversion was suppressed except at 250 °C.

The effects of the Co/Mo ratio on the activity and selectivity for the synthesis of alcohols were investigated at a Co/Mo ratio of 0.2-0.6, as shown in Table 4. At a Co/Mo ratio of 0.4, CO conversion and selectivity for C\(_2\) alcohols were the highest, and selectivity for hydrocarbons was the lowest. As the Co/Mo ratio increased, the CO\(_2\) selectivity decreased. With high Co/Mo ratio the distribution of alcohols shifted to higher carbon number. The formation of hydrocarbons was promoted at a Co/Mo ratio of 0.4.

3. 3. 2. Addition of K to Unsupported CoMoS-type Catalysts

The effect of adding K to the CoMoS catalyst was also investigated, as shown in Fig. 7. Although the selectivities for methanol and CO\(_2\), and carbon-chain growth were increased with K added to the CoMoS catalyst, the selectivity for total alcohols remained almost constant, although the formation of hydrocarbons was suppressed compared to CoMoS. The activity and selectivity for alcohol synthesis were investigated at a K/Mo ratio of 0-0.4 as shown in Fig. 8. As the K/Mo ratio increased, the CO conversion slightly decreased, whereas the selectivity for methanol and C\(_2\) alcohols increased. In contrast, hydrocarbon selectivity was markedly decreased even at higher temperatures. Formation of CO\(_2\) peaked at a K/Mo ratio of 0.1, and decreased at ratios over 0.1.

The probabilities of chain growth in alcohols and hydrocarbons were calculated according to Eq. (4). The compositions of the reaction products are shown in Table 5, and the chain-growth probabilities for alcohols and hydrocarbons are listed in Table 6. The chain-growth probability of alcohols was smaller or almost constant with higher K/Mo ratio, and the chain growth of hydrocarbons also decreased except at the low temperature of 250 °C.

If the chain-growth probability is 0.38, theoretically, C\(_{1-6}\) hydrocarbons will be formed at 62, 24, 9.0, 3.4, 1.3, and 0.49 mol%, respectively, based on Eq. (4). In fact, the molar compositions of C\(_{1-5}\) hydrocarbons were smaller than these theoretical values, and that of C\(_3\) hydrocarbon was larger, as shown in Table 6. In this study, the reaction occurred under higher pressure than that of conventional F-T synthesis, and alcohols as well as hydrocarbons were produced in the synthesis of C\(_2\) alcohols. These features probably account for the
slight deviation in chain-growth probabilities for hydrocarbons from the ASF distribution.

3.3.3. Role of Supports

To investigate the involvement of supports in alcohol synthesis, CO hydrogenation over catalysts unsupported and supported by silica and alumina was performed, with Co/Mo and K/Mo ratios of 0.6 and 0.2, respectively, under conditions of 8.0 MPa, 5000 h⁻¹, and H₂/CO = 1.0. The results of the activity tests are listed in Table 7. Although CO conversion with the K₀₂Co₀₆Mo/Al catalyst was higher than with the other two catalysts, the K₀₂Co₀₆Mo/Al catalyst had lower selectivity for C₂⁺ alcohols and methanol, and higher selectivity for by-products than the other catalysts. Therefore, the alumina-supported catalyst was the most favorable for F-T synthesis, and was unfavorable for C₂⁺ alcohol synthesis. CO conversion and methanol selectivity were higher for the K₀₂Co₀₆MoS catalyst compared to the K₀₂Co₀₆Mo/Si catalyst. C₂⁺ alcohol selectivity was nearly twice as high for the K₀₂Co₀₆Mo/Si catalyst compared to the K₀₂Co₀₆MoS catalyst. The selectivity for byproducts, such as hydrocarbons and CO₂, de-

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Table 4 CO Conversion and Selectivity for Various Co/Mo Ratios under the Following Reaction Conditions: 8.0 MPa, 5000 h⁻¹, H₂/CO = 1.0, K₀₂Co₀₆MoS

| Temperature [%] | Co/Mo ratio [mol/mol] | Conversion [%] | Selectivity [%] |
|-----------------|-----------------------|----------------|-----------------|
|                 |                       |                | C₂⁺ alcohols   | Methanol | CO₂ | Hydrocarbons |
| 250             | 0.2                   | 2.2            | 12.0           | 16.4     | 38.0 | 33.6         |
|                 | 0.4                   | 12.8           | 24.6           | 45.1     | 25.9 | 4.8          |
|                 | 0.6                   | 8.4            | 15.0           | 25.5     | 17.3 | 42.9         |
| 300             | 0.2                   | 6.6            | 8.6            | 14.5     | 49.1 | 27.8         |
|                 | 0.4                   | 14.6           | 24.3           | 38.8     | 29.6 | 7.7          |
|                 | 0.6                   | 9.6            | 15.4           | 30.5     | 25.1 | 29.6         |
| 350             | 0.2                   | 14.3           | 4.2            | 7.9      | 59.1 | 28.8         |
|                 | 0.4                   | 23.2           | 14.5           | 23.0     | 42.8 | 20.7         |
|                 | 0.6                   | 17.9           | 8.6            | 18.7     | 42.6 | 30.5         |

Fig. 7 CO Conversion and Selectivity on K- and Co-containing MoS₂ Catalyst under the Following Reaction Conditions: 8.0 MPa, 5000 h⁻¹, H₂/CO = 1.0, K₀₂Co₀₆MoS; (a) 250 °C, (b) 300 °C, (c) 350 °C.
creased for the K02Co06Mo/Si catalyst compared with the K02Co06MoS catalyst.

4. Discussion

The processes involved in the synthesis of higher alcohol from syngas are extremely complex and can be classified into the following reactions: alcohol synthesis, F-T reaction for hydrocarbons, and water-gas shift reaction (WGS). A detailed kinetic network on the basis of the CO insertion mechanism was proposed\(^{47,48}\). In terms of adsorbed CO species types on active sites, the non-dissociation of CO on MoS\(_2\) is the only energetically favorable reaction, and the barrier energy for dissociation of adsorbed CO (2.6 eV) is much higher than the non-dissociative CO adsorption energy (~2.24 eV)\(^{49}\).

In alcohol synthesis from syngas over MoS\(_2\)-based catalysts, the CO molecule is thought to adsorb on active sites, such as the Co-Mo-S phase and CoS\(_8\) species as well as the lamellar structure of the MoS\(_2\) phase in two processes of dissociative and non-dissociative adsorption. The so-called Co-Mo-S(K) phase on alkali-CoMoS catalyst may also be involved in non-dissociative CO adsorption, and the CoS\(_8\) and Co-Mo-S phases in dissociative CO adsorption\(^{6,35,50}\). In addition, the CoS\(_8\) phase has a spillover effect on hydrogen\(^{51,52}\), which promotes dissociative H\(_2\) adsorption.

Based on these various proposals, a hypothetical mechanism for CO hydrogenation on alkali-CoMoS catalysts was proposed as shown in Scheme 1. The mechanism involves both non-dissociatively and dissociatively adsorbed CO species on the catalysts. If the non-dissociative CO\(^*\) species adsorbed on MoS or CoMoS(K) phase react with dissociatively adsorbed H\(^*\) species, methanol is formed via hydrogenation of a formyl intermediate. Then the dehydration of the formyl intermediate occurs on acid sites such as hydroxyl group over an Al support\(^{6,53}\), or the CO species is dissociatively adsorbed on the CoMoS or CoS\(_8\) phase, so that the intermediate can be transformed to an alkyl species. The non-dissociatively adsorbed CO species is then inserted into the alkyl species to form a C\(_2\) alcohol precursor such as an acyl species, and the C\(_2\) alcohol is formed via hydrogenation of the acyl species. The alkyl species is hydrogenated to form hydrocarbons. CO\(_2\) is formed via reaction of the non-dissociatively adsorbed CO\(^*\) species (or CO into feed gas) with O\(^*\) species derived from the dissociatively adsorbed CO species\(^{6,35,50}\).

Addition of Co to the MoS\(_2\) catalyst enhanced the formation of C\(_2\) alcohols and improved the selectivity for total alcohols (Fig. 7). This observation indicates that both MoS phases and CoMoS(K) phases on the catalyst are important, and non-dissociatively adsorbed CO\(^*\) species enhances the formation of alcohols. Furthermore, high cobalt loading up to a Co/Mo ratio of 0.4 results in the highest CO conversion and selectivity for C\(_2\) alcohols, and the distribution of alcohols shifts to higher carbon number. The distribution of hydrocarbons was promoted (Table 4). Such observations show that increases in some CoMoS phases promote non-dissociative CO adsorption, and enhance the formation of alcohols. These trends were reversed at Co/Mo ratios greater than 0.4, indicating that, with the larger
amount of Co, more CoMoS or Co9S8 phases promoted dissociative CO adsorption and the H2 spillover effect on the Co9S8 phase. The active sites on these phases would promote the formation of alkyl groups, as shown in Scheme 1.

Increases in the K/Mo ratio enhanced the selectivity for methanol and C2+ alcohols (Fig. 8). With the addition of K, the non-dissociatively adsorbed CO* species on the CoMoS(K) phase particularly promotes the formation of CO2 and favors alcohols such as C2+ alcohols or methanol (Scheme 1). If the K/Mo ratio was increased to greater than 0.1, the CO2 selectivity decreased and the selectivity of alcohols increased, as shown in Fig. 8. These shifts in selectivities were different. The increase in K loading may be related to the formations of CO2 and alcohols, and increasing the K loading causes the formation of CO2 to shift to the formation of methanol and C2+ alcohols on the non-

Table 5 Compositions of Alcohols and Hydrocarbons for Various K/Mo Ratios at 350 °C

| K/Mo ratio [-] | Composition of alcohols [mol%] | Composition of hydrocarbons [mol%] |
|---------------|---------------------------------|-----------------------------------|
|               | Methanol | Ethanol | Propanol | Butanol | Methane | Ethane | Propane | n-Butane | n-Pentane | n-Hexane |
| 0             | 77.0     | 18.6    | 2.96     | 1.44    | 48.4    | 27.1   | 21.9    | 2.05     | 0.00      | 0.65     |
| 0.1           | 58.7     | 33.3    | 7.15     | 0.89    | 69.7    | 16.4   | 8.95    | 4.95     | 0.01      | 0.02     |
| 0.2           | 78.6     | 16.4    | 4.53     | 0.47    | 74.8    | 12.9   | 9.99    | 2.32     | 0.00      | 0.02     |
| 0.4           | 72.3     | 23.8    | 3.54     | 0.30    | 79.2    | 7.84   | 4.14    | 8.83     | 0.01      | 0.02     |

Table 6 Effects of K/Mo Ratio on Chain Growth over K2Co06MoS at 8.0 MPa, 5000 h⁻¹, H2/CO = 1.0

| K/Mo ratio [-] | Chain-growth probability of products |
|---------------|-------------------------------------|
|               | Alcohols | Hydrocarbons |
|               | 250 | 300 | 350 | 250 | 300 | 350 |
| 0             | 0.16 | 0.14 | 0.24 | 0.40 | 0.41 | 0.38 |
| 0.1           | 0.14 | 0.16 | 0.24 | 0.13 | 0.21 | 0.15 |
| 0.2           | 0.11 | 0.18 | 0.19 | 0.21 | 0.18 | 0.15 |
| 0.4           | 0.15 | 0.09 | 0.16 | 0.39 | 0.20 | 0.16 |

Table 7 Effects of Unsupported or Supported Catalyst on Conversion and Selectivity at 8.0 MPa, 5000 h⁻¹, H2/CO = 1.0, and at Co/Mo and K/Mo Ratios of 0.6 and 0.2, Respectively

| Catalyst | Conversion [%] | Selectivity [%] |
|----------|----------------|-----------------|
| K2Co06MoS | K2Co06Mo/Si | K2Co06Mo/Al |
| 250 | 300 | 350 | 250 | 300 | 350 | 250 | 300 | 350 |
| Methanol | C2+ alcohols | C2+ alcohols |
| 7.9 | 9.1 | 17.4 | 7.0 | 8.1 | 13.9 | 10.7 | 9.2 | 21.5 |
| 20.5 | 19.2 | 9.9 | 59.1 | 42.7 | 16.9 | 4.4 | 1.2 | 0.5 |
| 35.5 | 38.0 | 21.6 | 28.3 | 22.7 | 8.5 | 6.2 | 3.2 | 1.0 |
| 24.1 | 31.2 | 49.2 | 10.8 | 30.3 | 40.5 | 40.1 | 48.6 | 49.5 |
| Hydrocarbons | | | | | | | | |
| 19.8 | 11.6 | 19.4 | 1.8 | 4.4 | 34.1 | 49.3 | 47.0 | 49.0 |

Scheme 1 Mechanism of CO Hydrogenation on K-CoMoS Catalysts
dissociatively adsorbed CO sites derived from the CoMoS(K) phase.

The alumina-supported catalyst had lower selectivity for alcohols and higher selectivity for hydrocarbons than the unsupported and silica-supported catalysts (Table 7). Therefore, the Al-supported catalyst was more favorable for F-T synthesis, because the presence of acid sites derived from the hydroxyl group on the Al support results in the dehydrogenation of the oxygenated intermediate and formation of alkyl species (Scheme 1). From a report by Phung et al.54), in dehydration of ethanol on alumina supported catalysts, ethanol is adsorbed as ethoxy species. The ethoxy species is dehydrated by acid sites on Al2O3 to form hydrocarbons. The acetyl intermediate can be transformed to ethoxy species before dehydration or formation of ethanol over MoS2-based catalysts5).

Our previous study showed that the formation of hydrocarbons was also suppressed at higher calcination temperature of the Al support, i.e., resulting in fewer hydroxyl groups for dehydration6). Therefore, alkyl groups were presumably formed by dehydrogenation of alkoxy groups, and hydrogenated to hydrocarbons, as shown in Scheme 1. On the basis of this hypothesis, the decrease in acid sites on the Al2O3 support inhibited the formation of hydrocarbons. There are two main formation pathways of alkyl species, dehydrogenation of oxygenated intermediates and hydrogenation of dissociated C species. The former reaction would be suppressed with fewer acid sites. Therefore, the decrease in acid sites resulted in fewer sites for hydrocarbon formation and relatively higher selectivity for alcohols. In the present study, ethers were detected in trace amounts because the condensation of oxygenated intermediates and alkyl species hardly occurred.

The selectivity for C2+ alcohols was higher on the silica-supported catalyst than on the unsupported catalyst. The surface area of the supported catalysts was higher than that of the unsupported catalyst, as shown in Table 1. The number of active sites on the catalysts would depend on the extent of dispersion of the metal on the catalysts, which favors C2+ alcohol synthesis. XPS analyses showed that the ratio of the CoMoS phase to all Co species decreased in the order of K02Co06MoS, K02Co06Mo/Si, and K02Co06Mo/Al, as shown in Table 3. This order was identical with the order of the selectivity for methanol. The formation of methanol is considered to involve reaction of the non-dissociatively adsorbed CO* species with the dissociative H* species, as shown in Scheme 1. Additionally, infrared spectroscopy (IR) measurements have shown that part of the CoMoS phase carries non-dissociatively adsorbed CO species52,55). Therefore, the formation of the CoMoS phase on the catalysts would favor the formation of alcohols, especially methanol.

The present study suggested that excessive Co/Mo ratio inhibited the formation of CO2 due to the formation of metal sulfides, or Co9S8 species, at the dissociative CO adsorption sites, but was favorable for the formation of hydrocarbons. CO2 as well as C2+ alcohols would be formed via non-dissociatively adsorbed CO species, as in Scheme 1. Furthermore, CO insertion into alkyl intermediates resulting in growth of the carbon chain in alcohols was competitive against hydrogenation of alkyl species. Therefore, for growth of the carbon chain of alcohol, active sites must facilitate the insertion of non-dissociatively adsorbed CO species into alkyl intermediates.

Presumably both dissociated O species and adsorbed CO reacted to form CO2. To suppress dissociated O species, the formation of CO2 could be also inhibited by using cerium oxide, which can store a large amount of oxygen (high oxygen-storage capacity). Cerium oxide can also act as a support for catalysts in exhaust-gas treatment and steam reforming reactions, and is known to be a strong reducing agent56,57).

5. Conclusions

The main products formed over the bulk MoS2 catalysts were hydrocarbons and CO2, whereas addition of Co to the MoS2 catalyst promoted selectivity for C2+ alcohol and total alcohols, and highly inhibited selectivity for hydrocarbons. Co/Mo ratio in the range from 0.2 to 0.6 provided the highest CO conversion and selectivity for C2+ alcohols at a Co/Mo ratio of 0.4. As the Co/Mo ratio increased, selectivity for CO2 was suppressed and the distribution of alcohols shifted to higher carbon number. Addition of K to the Co04MoS catalyst resulted in improved selectivity for total alcohols and considerably reduced formation of hydrocarbons compared to Co04MoS. Higher K/Mo ratio for KCuMoS increased selectivities for methanol and C2+ alcohol, and slightly decreased CO formation. Higher loading of K also promoted the chain propagation of alcohols, but markedly decreased selectivity for hydrocarbons even at higher temperatures. The alumina-supported catalyst was the most favorable for F-T synthesis and unfavorable for C2+ alcohol synthesis, whereas the silica-supported catalyst was more favorable for the synthesis of C2+ alcohols. The selectivity for methanol was improved with higher ratio of CoMoS phase to all Co species. The CoMoS phase of the catalysts is important for the formation of alcohols, especially methanol.

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要旨

MoS₂系触媒を用いた混合アルコール合成におけるコバルトおよびカリウムの添加効果

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いくつかの非担持および担持モリブデン系触媒を沈殿法や含浸法で調製した。調製された触媒は N₂吸着、XRD、H₂-TPR や XPS 測定により解析された。アルコール合成触媒活性は高圧固定床流通式反応器を用いて次の反応条件で評価された。250 ～350 ℃, 5.0 MPa, GHSV: 5000 h⁻¹, H₂/CO 比: 1.0。バルク状非担持 MoS₂触媒に Co を添加することで、C₂⁺アルコールおよび総アルコール類の選択性が促進した。同時に対し、炭化水素類の選択性が減少した。さらに、Co₂MoS₄ に K を添加すると、総アルコール類の選択性が改善され、炭化水素類は抑制された。その一方、メタノールおよび CO₂選択性は増加し、炭素生成率も減少した。非担持触媒およびシリカ、アルミナ担持触媒を比較すると、アルミナ担持触媒は Fischer-Tropsch 合成が最も有利となり、C₂⁺アルコール合成が不利となった。シリカ担持触媒は非担持触媒よりも C₂⁺アルコール合成反応により選択的な触媒であった。