

In situ DRIFT studies of sulfided K-Mo/ γ -Al₂O₃ catalysts

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Abstract

Sulfided Mo/ γ -Al₂O₃ catalyst and K-Mo/ γ -Al₂O₃ catalysts with K/Mo = 0.4 and 0.8 were investigated by in situ diffuse reflectance infrared Fourier transform (DRIFT) with NO and syngas adsorption and with high-pressure CO hydrogenation from syngas. On the sulfided Mo/ γ -Al₂O₃ catalyst NO adsorption gives bands at 1790 and 1690 cm⁻¹ and syngas adsorption gives bands at 2095, 2065 and 2010 cm⁻¹. They are assigned to NO and CO adsorbed on the MoS₂-like species on the surface, respectively. However, on the sulfided K-Mo/ γ -Al₂O₃ catalysts, NO adsorption gives the only band at 1252 cm⁻¹ because of the formation of NO₂ or NO₃⁻ species; no band was observed by syngas adsorption. These results suggest that on the sulfided K-Mo/ γ -Al₂O₃ catalysts, the sites for NO and CO adsorption over the MoS₂-like species are addressed by K atoms to form K-MoS₂ species, which effectively inhibits NO and CO adsorption. In addition, the K-MoS₂ species are more likely to be oxidized than the MoS₂-like species. DRIFT spectra recorded after the sulfided catalysts were used for high-pressure CO hydrogenation indicated that formate species are present on both the sulfided Mo/ γ -Al₂O₃ catalysts and the sulfided K-Mo/ γ -Al₂O₃ catalysts. They yielded bands at 1590, 1420 and 1385 cm⁻¹ and at 1590, 1415 and 1352 cm⁻¹, respectively. During high-pressure CO hydrogenation, formate species on the sulfided Mo/ γ -Al₂O₃ catalyst are converted to CO₂ and methane, whereas those on the sulfided K-Mo/ γ -Al₂O₃ catalysts are converted to methanol, CO₂, or CH₄. On the sulfided K-Mo/ γ -Al₂O₃ catalysts, the amounts of formate species increase with time through the initial 8 h of reaction. If 5000 ppm H₂S in syngas is introduced on to the catalyst bed as an impurity during reaction, the amounts of the formate species greatly decrease, resulting in an increase in selectivity to hydrocarbons and a decrease in selectivity to mixed alcohols. Therefore, the loss of sulfur and partial oxidation of the K-MoS₂ species are necessary for formation of active sites for alcohols synthesis. Our results indicate that during high-pressure CO hydrogenation, active sites for alcohol synthesis are on the partly oxidized K-MoS₂ species. © 2003 Elsevier B.V. All rights reserved.

Keywords: Sulfided K-Mo/ γ -Al₂O₃ catalysts; NO and syngas adsorption; High-pressure CO hydrogenation; DRIFT

1. Introduction

Sulfided Mo-based catalysts have been used widely in many hydrotreating processes because of their high activities for hydrodesulfurization and hydrodenitrogenation. After modification by alkali promoter, Mo-based catalysts also show excellent properties for mixed alcohol synthesis from CO hydrogenation. Sulfided Mo-based catalysts have received great attention for mixed alcohol synthesis because of their advantage of being S tolerant. Various groups have investigated both unsupported and supported MoS₂-based catalysts [1–6].

A variety of techniques have been used to study Mo-based catalysts to determine their structural features and to relate structural features to catalytic performance. For unsupported MoS₂-based catalysts, Lee et al. reported that high selectivity to mixed alcohols is obtained when K species spread uniformly over the MoS₂ surface [3]. For supported catalysts, it has been claimed that K-Mo interaction species are formed on oxidized catalyst precursors [6–9] and that some K-Mo-S and/or K-Mo-S-O species are formed after sulfidation of the oxidized catalyst precursors, which are correlated with active sites for mixed alcohol synthesis as well [10,11]. However, morphological structures of K-promoter on the catalyst surface remain unclear.

It has been reported that initial activity for mixed alcohol synthesis is low over K-promoted MoS₂-based catalyst. However, activity obviously increases with reaction time in the first 15 h and then gradually becomes horizontal [9,12]. Structural studies show that, during mixed alcohol synthesis, some sulfur species, including those coordinated with

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the Mo atoms, are lost and that a part of Mo^{4+} species is oxidized to Mo^{5+} or Mo^{6+} species [12]. However, it is unclear whether these changes directly affect enhancement of the activity of the sample for mixed alcohol synthesis.

Mechanistic study on mixed alcohol synthesis over the MoS_2 -based catalysts indicates that during high-pressure CO hydrogenation, the primary product is methanol and that secondary reactions of the methanol to produce methane, H_2O and CO_2 may take place before the methanol desorbs from the surface [4,6]. It has also been suggested that acyl intermediates are formed on the catalyst surface by CO insertion into the adsorbed alkyls during mixed alcohol synthesis from CO hydrogenation. These acyl intermediates can be hydrogenated to form alcohols or be hydrogenated and dehydrated to produce hydrocarbons, depending on the nature of the active sites and on the reaction conditions [1,13,14]. However, in situ observations of the intermediate species on the K-MoS₂-based catalysts have not been reported.

Among the numerous studies devoted to sulfided Mo-based catalysts, a few deal with investigations of adsorption properties of surface species. It was demonstrated that both the number and the type of surface sites present on sulfided Mo-based catalysts can be quantified by NO and CO adsorption [15–25]. However, the reports usually address surface adsorption properties of Mo catalysts and Co- or Ni-promoted Mo catalysts. Investigations of NO and CO adsorption on freshly sulfided and used K-Mo catalysts may be helpful to elucidate morphological structures of K-promoter on the catalyst surface and the structural changes during reactions. Moreover, whereas the used samples are conducted to NO adsorption, those intermediate species on the surface may react with the adsorbed NO [26–29]. Observations of these reactions may deepen understanding of the reaction mechanism.

The present work reports our recent study with in situ diffuse reflectance infrared Fourier transform of NO and syngas adsorption and of high-pressure CO hydrogenation on several sulfided K-Mo/ γ -Al₂O₃ catalysts. Influences of K-promoter and small amount of H₂S as an impurity in syngas are investigated. Results are also compared with the activity data.

2. Experimental

2.1. Preparation of oxidized catalyst precursors

Oxidized K-Mo/ γ -Al₂O₃ samples were prepared by impregnation method, as described in our previous work [11,12], using γ -Al₂O₃, KCl (99%) and $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ (99%). Before drying at 120 °C for 12 h and calcination in air at 300 °C for 1 h, γ -Al₂O₃ support was initially impregnated with the aqueous solution of KCl. Obtained samples were then impregnated with an aqueous solution of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$, followed by drying and calcination in air at 500 °C for 12 h. Finally,

the samples were calcined in air at 800 °C for 12 h. An oxidized Mo/ γ -Al₂O₃ sample was prepared by directly impregnating the γ -Al₂O₃ support with an aqueous solution of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$, followed by drying at 120 °C for 12 h, calcination in air at 500 °C for 12 h and calcination in air at 800 °C for 12 h. Molybdenum contents of all samples, calculated as the weight ratio of MoO₃/Al₂O₃, were maintained at 0.24; K contents, as K/Mo atomic ratio, are 0, 0.4 and 0.8.

When the catalysts were calcined at 800 °C, the K-Mo/ γ -Al₂O₃ samples had weight losses of about 1% and the Mo/ γ -Al₂O₃ sample had weight loss of about 5%. Therefore, the K and Mo species on the K-Mo/ γ -Al₂O₃ samples were not sublimated, but a small part of the Mo species on the Mo/ γ -Al₂O₃ sample was sublimated. As a result of calcination at 800 °C, BET surface areas of the samples decreased from about 130 m²/g to about 25 m²/g.

2.2. Diffuse reflectance infrared Fourier transform (DRIFT) with NO and syngas adsorption

Spectra were recorded with a resolution of 4 cm⁻¹ and accumulation of 100 on a Bio-Rad FTS 575C FTIR spectrometer supplied with a MCT detector and diffuse reflectance attachment. One set of stainless steel gas lines was connected to the cell with CaF₂ windows, which allows in situ sulfidation and high-pressure CO hydrogenation before NO or syngas adsorption.

For each experiment, approximately 0.1 g of oxidized sample was filled into the sample holder in the cell. The oxidized sample was initially sulfided in situ in a stream of 5% H₂S/H₂ (30 ml/min) at atmospheric pressure and 400 °C for 6 h. After sulfidation, the sample was cooled to room temperature and flushed in He flow for 1 h. Thereafter, if the sample was conducted to NO adsorption, it was kept in the He flow and 10% NO/He was injected into the cell with a dose of 5 ml. DRIFT spectra were recorded simultaneously. Injection was repeated until intensities of the IR bands occurring from NO adsorption remained unchanged. If the sample was conducted to syngas adsorption, He flow was replaced by a syngas flow at atmospheric pressure and room temperature. After the sample was kept in the syngas flow for 1 h, it was flushed with the He flow again. DRIFT spectra were recorded after He flushing for 30 min.

Sulfided samples were also employed for in situ high-pressure CO hydrogenation in a syngas flow (H₂/CO = 2.0) at 340 °C and 4.1 MPa and monitored with DRIFT. To investigate the influence of small amount of H₂S as an impurity in the syngas flow, after the K-Mo/ γ -Al₂O₃ catalyst with K/Mo = 0.8 was used for high-pressure CO hydrogenation for 4 h, 5% H₂S/H₂ was mixed with the syngas and fed to the catalyst bed. Flow rate of the H₂S/H₂ was adjusted so that the content of H₂S in the inlet gas became 5000 ppm. The catalyst was further used in the syngas flow with 5000 ppm H₂S for 1 h. After reaction, the catalysts were cooled to room temperature in the reaction gas flow and

then flushed with He flow at atmospheric pressure for 1 h. Finally, all used samples were conducted to NO adsorption by the procedures mentioned above.

2.3. Activity test

Activities for high-pressure CO hydrogenation of the sulfided Mo/ γ -Al₂O₃ and K-Mo/ γ -Al₂O₃ catalysts were measured using a conventional fixed-bed reactor equipped with an on-line gas chromatograph (Shimadzu Corp.). The reactor was a 360 mm long stainless tube with 7.5 mm internal diameter. For each experiment, 0.5 g of catalyst sample, which had been sulfided *ex situ* with a flow of 5% H₂S/H₂ (30 ml/min) at 400 °C for 6 h, was charged in the reactor and then exposed to the syngas stream without pre-treatment. Reaction was performed at 340 °C, 4.1 MPa and 6000 ml g-cat⁻¹ h⁻¹. Catalyst bed temperature was measured with a thermocouple inserted into the catalyst bed. A mass flow controller (Brooks Instrument) fed the syngas, composed of CO 33%, H₂ 62% and Ar 5%, to the reactor. A backpressure regulator (Tescom Corp.) maintained the reaction pressure. After the reaction was performed for 20 h, 1000 or 50 000 ppm H₂S/H₂ was mixed with the syngas and fed to the catalyst bed to investigate the influence of a small amount of H₂S as an impurity in syngas on the catalytic property of the sulfided samples. A mass flow controller adjusted the flow rate of the H₂S/H₂ so that the content of H₂S in the inlet gas became 100, 200 and 5000 ppm, respectively.

Contents of Ar, CO, CO₂ and CH₄ in the outlet gas were quantified by TCD with a 2 m active carbon column. Hydrocarbons and alcohols were quantified by FID with a 2 m alumina column.

3. Results and discussion

3.1. DRIFT spectra of NO and CO adsorbed on the freshly sulfided catalysts

Oxidized catalyst samples were sulfided *in situ* by 5% H₂S/H₂ at 400 °C for 6 h and flushed with a flow of He at atmospheric pressure and room temperature for 1 h. Then they were subjected to NO or syngas adsorption. While the sample was subjected to NO adsorption, it was kept in the He flow and NO was injected into the catalyst bed. Fig. 1 depicts spectra recorded from NO adsorption on the sulfided Mo/ γ -Al₂O₃ catalyst and K-Mo/ γ -Al₂O₃ catalysts with K/Mo = 0.4 and 0.8.

It is seen that NO adsorption on the sulfided Mo/ γ -Al₂O₃ catalyst gives rise to two bands at 1790 and 1690 cm⁻¹. These bands are assigned to NO adsorbed on MoS₂-like species over the catalyst [22–25]. According to the literature [15–17,22–25,30], the bands of gas phase NO doublet are centered at 1875 cm⁻¹. They shift to near 1800 and 1700 cm⁻¹, respectively, after NO is adsorbed on sulfided

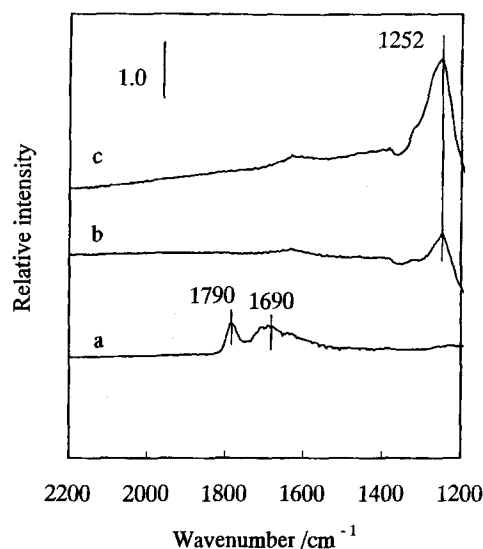


Fig. 1. DRIFT spectra of NO adsorbed on freshly sulfided samples: (a) Mo/ γ -Al₂O₃, (b) K-Mo/ γ -Al₂O₃ with K/Mo = 0.4, and (c) K-Mo/ γ -Al₂O₃ with K/Mo = 0.8.

Mo-based catalysts. It is also seen that NO adsorption on the sulfided K-Mo/ γ -Al₂O₃ samples gives the only band at 1252 cm⁻¹. The band intensity at 1252 cm⁻¹ for the sample with K/Mo = 0.8 is stronger than that for the sample with K/Mo = 0.4. This band is caused by formation of NO₂ or NO₃⁻ species [31].

Our previous work found that MoS₂-like species are formed both on the sulfided Mo/ γ -Al₂O₃ catalyst and on the sulfided K-Mo/ γ -Al₂O₃ catalysts [11,12]; however, the bands caused by NO adsorbed on MoS₂-like species are not observed from NO adsorption on the sulfided K-Mo/ γ -Al₂O₃ samples. Therefore, over the sulfided K-Mo/ γ -Al₂O₃ samples, the sites for NO adsorption on the MoS₂-like species may be addressed by K atoms, which effectively inhibit NO adsorption on the catalysts. The nature of the MoS₂-like species may change after K atoms address them; here we refer to the MoS₂-like species addressed by K atoms as K-MoS₂ species.

It is known that NO is a reactive probe molecule that may oxidize the surface MoS₂-like species during NO exposure [32,33]. However, the band at 1252 cm⁻¹ is not observed from NO adsorption on sulfided Mo-based catalysts. On the sulfided K-Mo/ γ -Al₂O₃ catalysts, K atoms should be coordinated with S atoms. This is supported by results from total sulfur analysis, as shown in our previous work [12], which indicate that on freshly sulfided K-Mo/ γ -Al₂O₃ catalyst, the S/Mo atomic ratio is greatly higher than the values for freshly sulfided Mo/ γ -Al₂O₃ catalysts and for MoS₂ crystalline [34,35]. Existing of NO₂ or NO₃⁻ species on the sulfided K-Mo/ γ -Al₂O₃ catalysts may suggest that the sulfided K species were oxidized during NO exposure; thereafter, the oxidized K species reacted with NO to produce NO₂ or NO₃⁻ species. Intensity of the band at 1252 cm⁻¹ is stronger for the sample with K/Mo = 0.8, indicating that

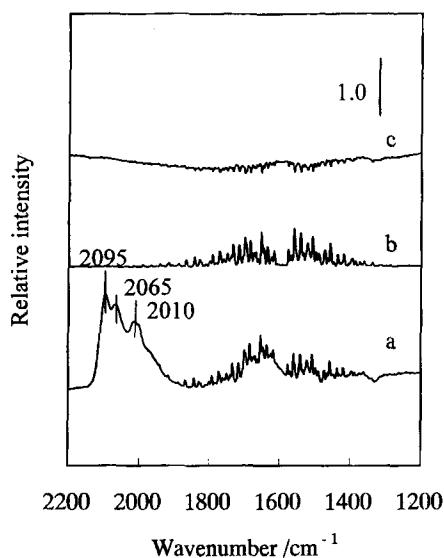


Fig. 2. DRIFT spectra of syngas adsorbed on freshly sulfided samples: (a) Mo/ γ -Al₂O₃, (b) K-Mo/ γ -Al₂O₃ with K/Mo = 0.4, and (c) K-Mo/ γ -Al₂O₃ with K/Mo = 0.8.

more K species on the surface are oxidized. Although NO is able to oxidize the surface MoS₂-based catalysts during NO exposure, NO₂ or NO₃⁻ species are not detected on the sulfided Mo/ γ -Al₂O₃ catalyst. Therefore, the sulfided K species are more easily oxidized than the sulfided Mo species, which suggests that the K component connects with O atoms more strongly than with the Mo component. This may be the reason why the K-Mo-O species on K-Mo/ γ -Al₂O₃ catalysts are less readily reduced and sulfided than those on Mo/ γ -Al₂O₃ catalyst [9,10].

The sulfided catalyst was exposed to syngas flow at room temperature and atmospheric pressure for 1 h. This process causes syngas adsorption. Then the sample was flushed with the He flow again. Fig. 2 shows spectra recorded after He flushing for 30 min; each spectrum is referencing to the spectrum recorded before the same sample was exposed to the syngas flow.

Syngas adsorption on the sulfided Mo/ γ -Al₂O₃ catalyst yields three bands at 2095, 2065 and 2010 cm⁻¹. These bands are caused by CO adsorbed on the MoS₂-like species. According to the literature [18–20,36,37], the band at 2100–2090 cm⁻¹ corresponds to CO adsorption on some reduced Mo centers, such as five-fold coordinated Mo atoms, whereas the band at 2070–2060 cm⁻¹ with a tail at 2000–2020 cm⁻¹ is attributed to more reduced Mo atoms, such as four-fold coordinated Mo atoms.

On the other hand, syngas adsorption on the sulfided K-Mo/ γ -Al₂O₃ catalysts with K/Mo = 0.4 and 0.8 yields no bands caused by CO adsorbed on the MoS₂-like species. These results support the inference that K atoms address the sites for probe molecule adsorption over the MoS₂-like species.

Many authors have noted that Mo coordinately unsaturated sites (CUSs) located at the edges of the MoS₂-like

species play a major role in the adsorption and activation of some reactants. A convenient way to characterize such sites is the use of NO and CO adsorption. NO has been found particularly suitable because it specifically adsorbs on the sulfide phase. It has been verified for Co- and Ni-promoted Mo-based catalysts that the Co and Ni species also provide sites for CO and NO adsorption and that the number of promoted sites increases at the expense of Mo sites [16]. However, for K-promoted Mo-based catalysts, K species do not provide sites for CO and NO adsorption. Moreover, although the dispersion of the K species on the sulfided K-Mo/ γ -Al₂O₃ catalyst with K/Mo = 0.4 expands almost all Mo sites, the number of K sites further increases with increasing K loading to K/Mo = 0.8.

3.2. DRIFT spectra recorded from the sulfided catalysts used for CO hydrogenation

The sulfided Mo/ γ -Al₂O₃ and K-Mo/ γ -Al₂O₃ catalysts were also subjected to in situ high-pressure CO hydrogenation at 340 °C and 4.1 MPa and monitored by DRIFT. During the reaction, the bands caused by gaseous CH₄, CO₂ and methanol, which are at 3015, 2360 and 1030 cm⁻¹, respectively [38,39], were seen clearly for the sulfided K-Mo/ γ -Al₂O₃ catalysts; whereas only the bands caused by gaseous CH₄ and CO₂ were visible for the sulfided Mo/ γ -Al₂O₃ catalysts (not shown). After reaction for 4 h, samples were cooled to room temperature. The bands caused by gaseous CH₄, CO₂ and methanol disappeared at that time. Thereafter, pressure was reduced and the syngas flow was replaced by He flow at atmospheric pressure. Spectra recorded after He flushing for 1 h are shown in Fig. 3, each spectrum is referencing to the spectrum recorded before the same sample was exposed to the syngas.

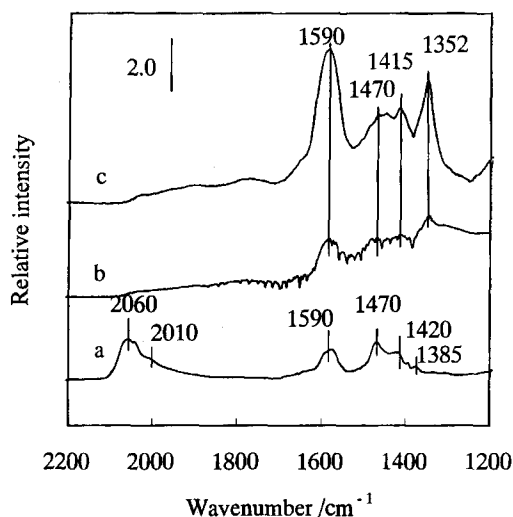


Fig. 3. DRIFT spectra recorded after the sulfided samples were used for high-pressure CO hydrogenation at 4.1 MPa and 340 °C for 4 h, followed by He flushing at room temperature for 1 h: (a) Mo/ γ -Al₂O₃, (b) K-Mo/ γ -Al₂O₃ with K/Mo = 0.4, and (c) K-Mo/ γ -Al₂O₃ with K/Mo = 0.8.

A strong band at 2060 cm^{-1} and a weak band at 2010 cm^{-1} are observed for the sulfided $\text{Mo}/\gamma\text{-Al}_2\text{O}_3$ sample. These bands are caused by CO adsorption on the MoS_2 -like species. In comparison with the spectra recorded from syngas adsorption on the freshly sulfided $\text{Mo}/\gamma\text{-Al}_2\text{O}_3$ sample, the band at 2095 cm^{-1} disappears. This indicates that during the reaction, those five-fold coordinated Mo atoms on the surface were converted to four-fold coordinated Mo atoms, which is in agreement with the observations that some sulfur species are gradually lost during the reaction.

In addition to the bands caused by CO adsorption on MoS_2 -like species, broad bands at 1590 and 1470, 1420 and 1385 cm^{-1} are observed. The bands at 1590, 1420 and 1385 cm^{-1} may be assigned to formate species (HCOO^-). According to the literature [40], formate species yield two bands at 1590 and 1395 cm^{-1} , but the 1395 cm^{-1} band may split in two [40,41], producing the bands at 1420 and 1385 cm^{-1} . The band at 1470 cm^{-1} may be assigned to acetate (CH_3COO^-), methoxide (CH_3O^-) or carbonate (CO_3^-) species [28,31,42].

For sulfided $\text{K-Mo}/\gamma\text{-Al}_2\text{O}_3$ samples, bands caused by CO adsorption on the MoS_2 -like species are not observed, but strong bands at 1590, 1470, 1415 and 1352 cm^{-1} are clearly visible. Bands at 1590, 1415 and 1352 cm^{-1} are assigned to formate species, and the band at 1470 cm^{-1} is assigned to acetate (CH_3COO^-), methoxide (CH_3O^-) or carbonate (CO_3^-) species. On the sulfided $\text{K-Mo}/\gamma\text{-Al}_2\text{O}_3$ catalyst the 1395 cm^{-1} band caused by formate species split in two: 1415 and 1352 cm^{-1} .

Subsequent experiments investigated the formation of formate species during the reaction on the sulfided $\text{K-Mo}/\gamma\text{-Al}_2\text{O}_3$ catalyst with $\text{K/Mo} = 0.8$. Fig. 4 clearly shows the bands caused by formate species from the spectrum recorded after the catalyst was used for high-pressure

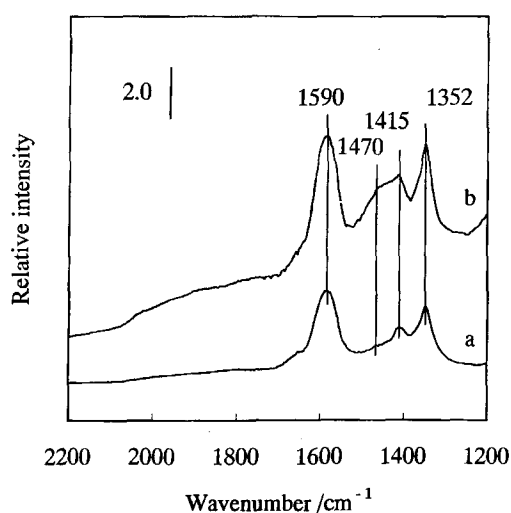


Fig. 4. DRIFT spectra recorded after the sulfided $\text{K-Mo}/\gamma\text{-Al}_2\text{O}_3$ catalyst ($\text{K/Mo} = 0.8$) used for high-pressure CO hydrogenation at 4.1 MPa and 340°C for (a) 1 h or (b) 8 h was flushed with a flow of He at room temperature for 1 h.

CO hydrogenation for 1 h. The bands attributed to formate species become stronger after the catalyst was used for high-pressure CO hydrogenation for 8 h.

Although formate species are formed both on sulfided $\text{Mo}/\gamma\text{-Al}_2\text{O}_3$ and on sulfided $\text{K-Mo}/\gamma\text{-Al}_2\text{O}_3$ catalysts, wavenumbers of the bands caused by formate species are different. These results suggest that formate species are present on various sites. On the sulfided $\text{Mo}/\gamma\text{-Al}_2\text{O}_3$ catalyst, formate species should be present on the MoS_2 -like species. On the other hand, formate species on the sulfided $\text{K-Mo}/\gamma\text{-Al}_2\text{O}_3$ catalysts, which yield bands at 1590, 1415 and 1352 cm^{-1} , are present on the partly oxidized K-MoS_2 species because the MoS_2 -like species on sulfided $\text{K-Mo}/\gamma\text{-Al}_2\text{O}_3$ catalysts are addressed by K atoms; also, they may be partly oxidized during the reaction, as shown in our previous work [9,12]. Results of that work agree with results reported by various groups [6,9]. This suggestion is supported by observations that the amounts of formate species on the sulfided $\text{K-Mo}/\gamma\text{-Al}_2\text{O}_3$ catalysts greatly increase with time at the initial time of reaction. In addition, as described later, formate species are suppressed drastically by introducing a small amount of H_2S as an impurity in syngas into the catalyst bed while performing high-pressure CO hydrogenation.

The literature [13,14] cites formate species as intermediates for methanol synthesis from CO hydrogenation; methane may be produced by a secondary reaction of methanol [4,6]. In addition, formate species are the intermediates for CO_2 formation from a water-gas shift reaction ($\text{CO} + \text{H}_2\text{O}$) and intermediates for CO formation from reverse water-gas shift ($\text{CO}_2 + \text{H}_2$) [40,42]. Therefore, during the reaction, the formate species may be converted to methanol, methane or CO_2 , depending on the nature of the active sites and on reaction conditions. After the sulfided $\text{Mo}/\gamma\text{-Al}_2\text{O}_3$ catalyst and the sulfided $\text{K-Mo}/\gamma\text{-Al}_2\text{O}_3$ catalyst with $\text{K/Mo} = 0.8$ were used for CO hydrogenation for 8 h, they were cooled to room temperature and then treated in a H_2 flow at 2.5 MPa, respectively. Increasing the temperature to above 100°C decreased the bands caused by the formate species. In the meantime, for the sulfided $\text{Mo}/\gamma\text{-Al}_2\text{O}_3$ catalyst, the bands caused by CO_2 (2360 cm^{-1}) and CH_x species ($x = 2-4$, $2855-3015\text{ cm}^{-1}$) increased. For the sulfided $\text{K-Mo}/\gamma\text{-Al}_2\text{O}_3$ catalyst, the bands caused by methanol (1030 cm^{-1}), CO_2 and CH_x species increased. Increasing the temperature to above 300°C , these bands became very strong (not shown here). Therefore, during the reaction, the formate species on the sulfided $\text{Mo}/\gamma\text{-Al}_2\text{O}_3$ catalyst are converted to CO_2 and CH_4 and those on the sulfided $\text{K-Mo}/\gamma\text{-Al}_2\text{O}_3$ catalyst are converted to methanol, CO_2 and CH_4 . Different features of the formate species over the sulfided $\text{Mo}/\gamma\text{-Al}_2\text{O}_3$ catalyst and those over the sulfided $\text{K-Mo}/\gamma\text{-Al}_2\text{O}_3$ catalysts may reflect the role of K-promoter in enhancing activity for mixed alcohol synthesis.

Although CO_2 is usually considered to be a product of the water-gas shift reaction, it can be formed from methanol on K-Mo -based catalysts [4,6]. This fact supports the idea that

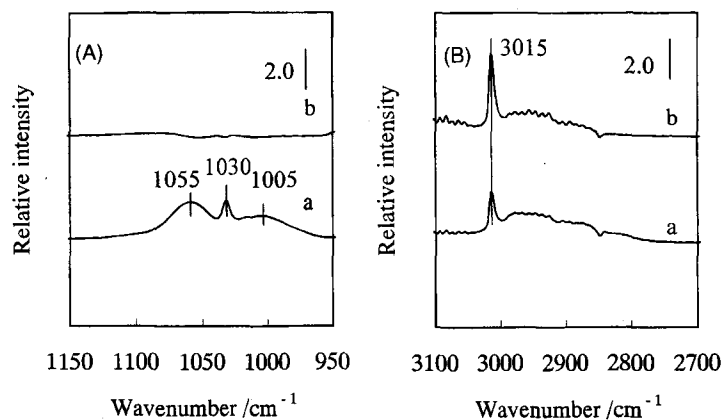


Fig. 5. DRIFT spectra recorded after the sulfided K-Mo/ γ -Al₂O₃ catalyst with K/Mo = 0.8 was used for high-pressure CO hydrogenation for 4 h (a), followed by introducing 5000 ppm H₂S into the catalyst bed (b).

methanol and CO₂ are produced from the same intermediates during high-pressure CO hydrogenation.

It is worth noting that intensities of the bands caused by formate species are drastically stronger than for the sulfided Mo/ γ -Al₂O₃ catalyst for the sulfided K-Mo/ γ -Al₂O₃ catalyst with K/Mo = 0.8. However, over the sulfided Mo/ γ -Al₂O₃ catalyst, the specific activity is greatly higher, as shown later, indicating that the amounts of formate species formed during the reaction should be larger. Therefore, over the sulfided K-Mo/ γ -Al₂O₃ catalyst, formate species may be strongly adsorbed on the surface and their desorption becomes slower, so that more formate species are detected on the surface.

Influences of a small amount of H₂S as an impurity in syngas on catalytic properties of the sulfided K-Mo/ γ -Al₂O₃ catalysts were also investigated to elucidate effects of K-promoter on mixed alcohol synthesis from high-pressure CO hydrogenation. After the sulfided K-Mo/ γ -Al₂O₃ catalyst with K/Mo = 0.8 was used for mixed alcohol synthesis at 4.1 MPa and 340 °C for 4 h, a 5% H₂S/H₂ flow was mixed with the syngas and introduced into the catalyst bed. Flow rate of the H₂S/H₂ was adjusted to 1/10 of that of the syngas, so that the content of H₂S in the inlet gas became 5000 ppm. As shown in Fig. 5, after the 5000 ppm H₂S is introduced into the catalyst bed, intensities of the bands caused by CH₄ (3015 cm⁻¹) greatly increase and bands caused by methanol (1055, 1030 and 1005 cm⁻¹) sharply decrease. This result indicates that 5000 ppm H₂S in the syngas flow decreased activity for mixed alcohol synthesis and increased activity for CH₄ synthesis. After the catalyst was used in the syngas flow with 5000 ppm H₂S for 1 h, the temperature was reduced and the sample was flushed with He flow at room temperature. Spectra recorded after He flushing show that intensities of the bands caused by formate species weakened (not shown). This result may indicate that the 5000 ppm H₂S in the syngas flow resulfided the partly oxidized K-MoS₂ species, so that the formate species on the surface became weakly adsorbed and easily desorbed. Therefore, features of the sulfided K-MoS₂

species are quite different from those of the partly oxidized sulfided K-MoS₂ species, but similar to those of the MoS₂-like species on the sulfided Mo/ γ -Al₂O₃ catalyst.

3.3. NO adsorption on the sulfided samples used for high-pressure CO hydrogenation

After the sulfided Mo/ γ -Al₂O₃ and K-Mo/ γ -Al₂O₃ catalysts were used for high-pressure CO hydrogenation at 4.1 MPa, 340 °C for 4 h, temperature was reduced and the sample was flushed in a He flow at room temperature for 1 h. Thereafter, NO was injected into the catalyst bed. Fig. 6 shows spectra recorded after NO adsorption, referencing to the spectrum recorded before NO was injected.

NO adsorption on the sulfided Mo/ γ -Al₂O₃ sample after use for the high-pressure CO hydrogenation produces bands

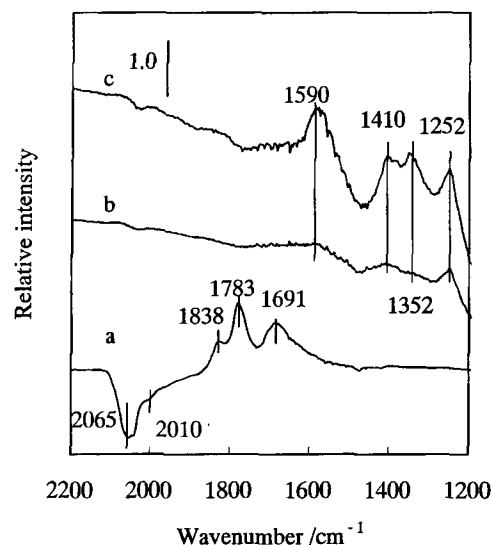


Fig. 6. DRIFT spectra of NO adsorbed on sulfided samples after mixed alcohol synthesis at 4.1 MPa and 340 °C for 4 h: (a) Mo/ γ -Al₂O₃, (b) K-Mo/ γ -Al₂O₃ with K/Mo = 0.4, and (c) K-Mo/ γ -Al₂O₃ with K/Mo = 0.8.

at 1838, 1783 and 1691 cm^{-1} . A larger band at 1838 cm^{-1} is observed compared with the spectrum recorded from NO adsorption on freshly sulfided $\text{Mo}/\gamma\text{-Al}_2\text{O}_3$ sample. In addition, with NO adsorption on the surface, adsorbed CO species partly desorb from the surface.

The literature [15,17] indicates that NO adsorption on reduced $\text{Mo}/\gamma\text{-Al}_2\text{O}_3$ catalysts gives bands with higher wavenumbers than NO adsorption on sulfided $\text{Mo}/\gamma\text{-Al}_2\text{O}_3$ catalysts; therefore, appearance of the band at 1838 cm^{-1} suggests that some sulfided Mo sites on the surface are converted to reduced Mo sites. This result agrees with observations that sulfur species are partly lost during CO hydrogenation.

Fig. 6 also shows that NO adsorption on sulfided $\text{K-Mo}/\gamma\text{-Al}_2\text{O}_3$ samples after use for high-pressure CO hydrogenation gives rise to bands at 1590, 1410, 1352, and 1252 cm^{-1} . Bands at 1590, 1410 and 1352 cm^{-1} are assigned to formate species and the band at 1252 cm^{-1} is assigned to NO_2 or NO_3^- species. For the sample with $\text{K/Mo} = 0.8$, the bands of formate species are stronger than for the sample with $\text{K/Mo} = 0.4$. These results indicate that some surface species formed during the reaction, which may not be detected by DRIFT, have reacted with adsorbed NO to produce the formate species. During the reaction, surface species may attach to the oxygen atoms in NO molecules. According to published research results, oxygenated organic species like alcohols, aldehydes and carboxylates have a role in NO reduction [43]. No formate species are formed during NO adsorption on the sulfided $\text{Mo}/\gamma\text{-Al}_2\text{O}_3$ catalyst. This fact suggests that those surface species on the sulfided $\text{Mo}/\gamma\text{-Al}_2\text{O}_3$ catalyst have relatively lower ability to attach to oxygen atoms from adsorbed NO.

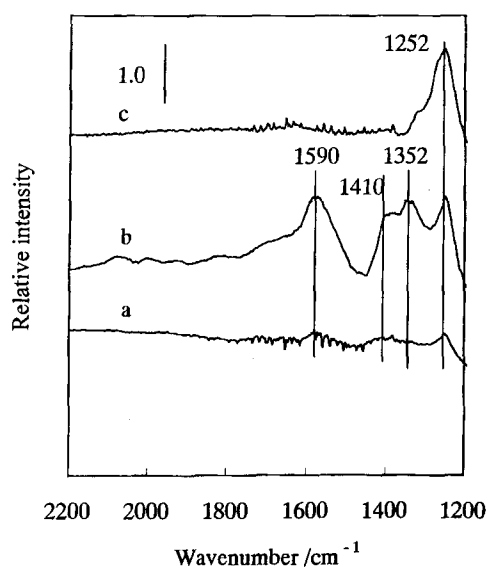


Fig. 7. DRIFT spectra of NO adsorbed on the sulfided $\text{K-Mo}/\gamma\text{-Al}_2\text{O}_3$ ($\text{K/Mo} = 0.8$) catalyst after mixed alcohol synthesis in the absence of H_2S at 4.1 MPa and 340 °C are shown for (a) 1 h and (b) 8 h, (c) after mixed alcohol synthesis in the absence of H_2S for 4 h, and in the presence of H_2S (5000 ppm) for 1 h.

The sulfided $\text{K-Mo}/\gamma\text{-Al}_2\text{O}_3$ catalyst with $\text{K/Mo} = 0.8$ used for the high-pressure CO hydrogenation was also investigated by NO adsorption for various times. Fig. 7 shows that on a sample used for high-pressure CO hydrogenation for 1 h, NO adsorption produces weak bands at 1590, 1410, 1352, and 1252 cm^{-1} . On the sample used for CO hydrogenation for 8 h, NO adsorption yields similar bands, but with stronger intensities. Fig. 7 also shows that NO adsorption yields only the band at 1252 cm^{-1} if the sulfided $\text{K-Mo}/\gamma\text{-Al}_2\text{O}_3$ catalyst used for high-pressure CO hydrogenation for 4 h was further used for CO hydrogenation in the syngas with 5000 ppm H_2S for 1 h on the used sample. The bands in the region of 1600–1350 cm^{-1} disappear, in contrast to data of NO adsorption on the same sample used for high-pressure CO hydrogenation from syngas without H_2S .

3.4. Activities of the sulfided catalysts for high-pressure CO hydrogenation

High-pressure CO hydrogenation over sulfided catalysts was performed at 4.1 MPa, 340 °C and $\text{SV} = 6000 \text{ ml g-cat}^{-1} \text{ h}^{-1}$. Figs. 8 and 9 show changes of CO conversion and yields of products with reaction time over the sulfided $\text{Mo}/\gamma\text{-Al}_2\text{O}_3$ catalyst and over the sulfided $\text{K-Mo}/\gamma\text{-Al}_2\text{O}_3$ catalyst with $\text{K/Mo} = 0.8$, respectively.

Fig. 8 indicates that the main products from CO hydrogenation over the sulfided $\text{Mo}/\gamma\text{-Al}_2\text{O}_3$ catalyst are hydrocarbons and CO_2 . During the whole 20 h reaction, CO conversion slightly decreases and selectivity to hydrocarbons remains unchanged.

Fig. 9 shows that high-pressure CO hydrogenation produces mixed alcohols, hydrocarbons and CO_2 over the sulfided $\text{K-Mo}/\gamma\text{-Al}_2\text{O}_3$ catalyst with $\text{K/Mo} = 0.8$. The CO conversion and selectivities to hydrocarbons and CO_2 decrease drastically with reaction time. However, selectivity to

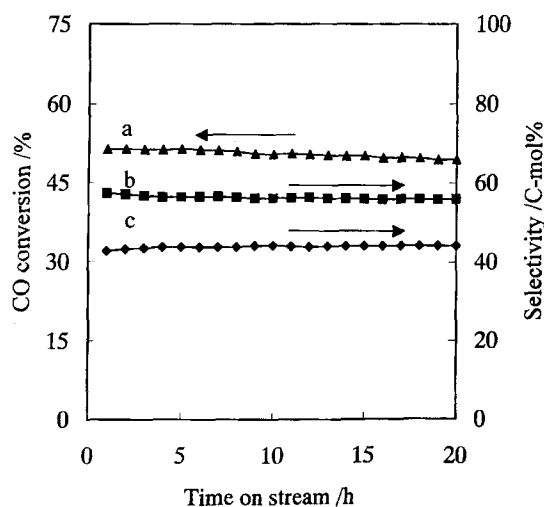


Fig. 8. Changes in (a) CO conversion and in selectivities to (b) hydrocarbons and (c) CO_2 with time-on-stream over the sulfided $\text{Mo}/\gamma\text{-Al}_2\text{O}_3$ sample for high-pressure CO hydrogenation at 4.1 MPa, 340 °C, and $\text{SV} = 6000 \text{ ml g-cat}^{-1} \text{ h}^{-1}$.

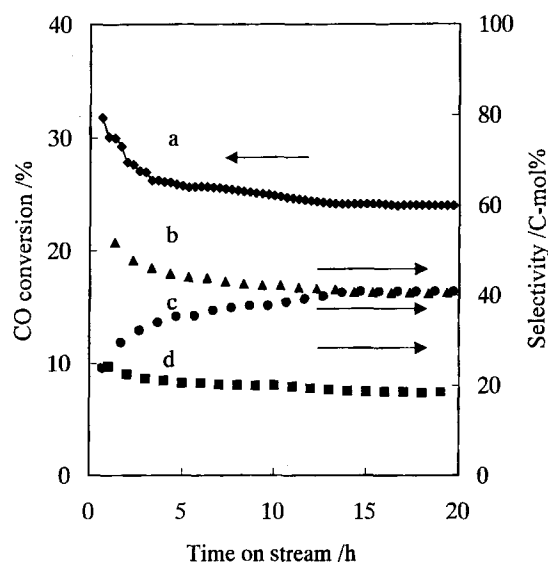


Fig. 9. Changes in (a) CO conversion and in selectivities to (b) CO₂, (c) mixed alcohols, and (d) hydrocarbons with time-on-stream over the sulfided K-Mo/ γ -Al₂O₃ sample (K/Mo = 0.8) for high-pressure CO hydrogenation at 4.1 MPa, 340 °C and SV = 6000 ml g-cat⁻¹ h⁻¹.

mixed alcohols gradually increases and reaches 42% after reaction for 20 h. The literature reports similar results [9,12].

After high-pressure CO hydrogenation was performed for 20 h, a flow of 1000 ppm H₂S/H₂ was mixed with the syngas flow and then introduced into the catalyst bed as an impurity. Flow rate of the H₂S/H₂ was adjusted to 1/10 and 1/5 of that of the syngas, so that the content of H₂S in the inlet gas became 100 or 200 ppm. After H₂S was introduced into the catalyst bed, CO conversion slightly decreased and selectivities to the products did not change. This result indicates that 200 ppm H₂S in the inlet gas has little effect on catalytic properties of the samples.

To investigate the influence of a higher level of H₂S in the inlet gas on catalytic properties for CO hydrogenation, a flow of 5% H₂S/H₂ was mixed with the syngas. The flow rate of the H₂S/H₂ was adjusted to 1/10 of that of the syngas, so that the content of H₂S in the inlet gas became 5000 ppm. In this manner, activities were changed markedly. Fig. 10 shows changes in yields of hydrocarbons, CO₂, and alcohols by introducing 5000 ppm H₂S into the catalyst bed.

For the sulfided Mo/ γ -Al₂O₃ catalyst, both the yield of hydrocarbons and the yield of CO₂ obviously decrease after H₂S is introduced into the catalyst bed, but the selectivity to hydrocarbons does not change. For the sulfided K-Mo/ γ -Al₂O₃ catalysts, yields of hydrocarbons and CO₂ greatly increase and yield of mixed alcohols sharply decreases. As a result, for the sample with K/Mo = 0.4, CO conversion increases from 26.6 to 33.3%, but the selectivity to mixed alcohols decreases from 16 to 3%. For the sample with K/Mo = 0.8, CO conversion increased from 23.9 to 28.5%, but the selectivity to mixed alcohols decreases from 42 to 13%. In addition, once we stopped introducing H₂S into the catalyst bed, CO conversion quickly decreased and

the selectivity to mixed alcohols sharply increased (data not shown).

3.5. New understanding of the reaction mechanism

Reportedly, H₂ uptakes over sulfided K-Mo/ γ -Al₂O₃ catalysts are drastically lower than those over the sulfided Mo/ γ -Al₂O₃ catalyst [9]. The present study clearly indicated that CO adsorption over the sulfided K-Mo/ γ -Al₂O₃ catalysts is inhibited compared to that over the sulfided Mo/ γ -Al₂O₃ catalyst. These changes may be the main reason why sulfided K-Mo/ γ -Al₂O₃ catalysts show lower specific activity for high-pressure CO hydrogenation than sulfided Mo/ γ -Al₂O₃ catalyst. Mixed alcohols are produced only on K-promoted Mo/ γ -Al₂O₃ catalysts, which indicates that the K component played an important role in formation of mixed alcohols. Formate species should be intermediates for methanol synthesis, but the formate species may be converted to methane or CO₂ by secondary reactions of methanol. The K-promoter may affect reaction paths: methane synthesis and CO₂ formation were effectively inhibited on partly oxidized K-MoS₂ species. It was reported that K-promoter inhibits the formation of hydrocarbons by suppressing acidity of active sites because acidic sites favor alcohol dehydration [11]. Furthermore, during water-gas shift reaction over MoS₂-based catalysts, CO₂ desorption is reported to be the rate determining step [44]; our results indicate that the partly oxidized K-MoS₂ species have relatively strong interaction with the formate species, which may inhibit CO₂ formation to some degree.

It is worth mentioning that, at the initial time of the CO hydrogenation reaction, the activity for mixed alcohol synthesis is low but the activities for hydrocarbon synthesis and CO₂ formation are rather high for sulfided K-Mo/ γ -Al₂O₃ catalysts. Consequently, active sites for hydrocarbon synthesis and CO₂ formation are transformed gradually during the reaction to active sites for mixed alcohol synthesis. Those observations imply that sulfided K-MoS₂ species are unfavorable for mixed alcohol synthesis. Our previous work [12] showed that sulfur loss and partial oxidization of sulfided K-MoS₂ species during reaction are necessary for formation of active sites for mixed alcohol synthesis.

Moreover, activity for mixed alcohol synthesis sharply decreases and that for hydrocarbon synthesis and for CO₂ formation drastically increases when the sulfided K-Mo/ γ -Al₂O₃ catalyst was used in high-pressure syngas with 5000 ppm H₂S. Thereby, active sites for mixed alcohol synthesis are transformed back to active sites for hydrocarbon synthesis and CO₂ formation. Effects of K-promoter on increasing activities for mixed alcohol synthesis are suppressed by introduction of 5000 ppm H₂S into the catalyst bed. This may occur because the partly oxidized K-MoS₂ species are resulfided and converted back to sulfided K-MoS₂ species when H₂S is present. On the K-MoS₂ species, methane synthesis and CO₂ formation are promoted as a result of higher ability for hydrogenation and

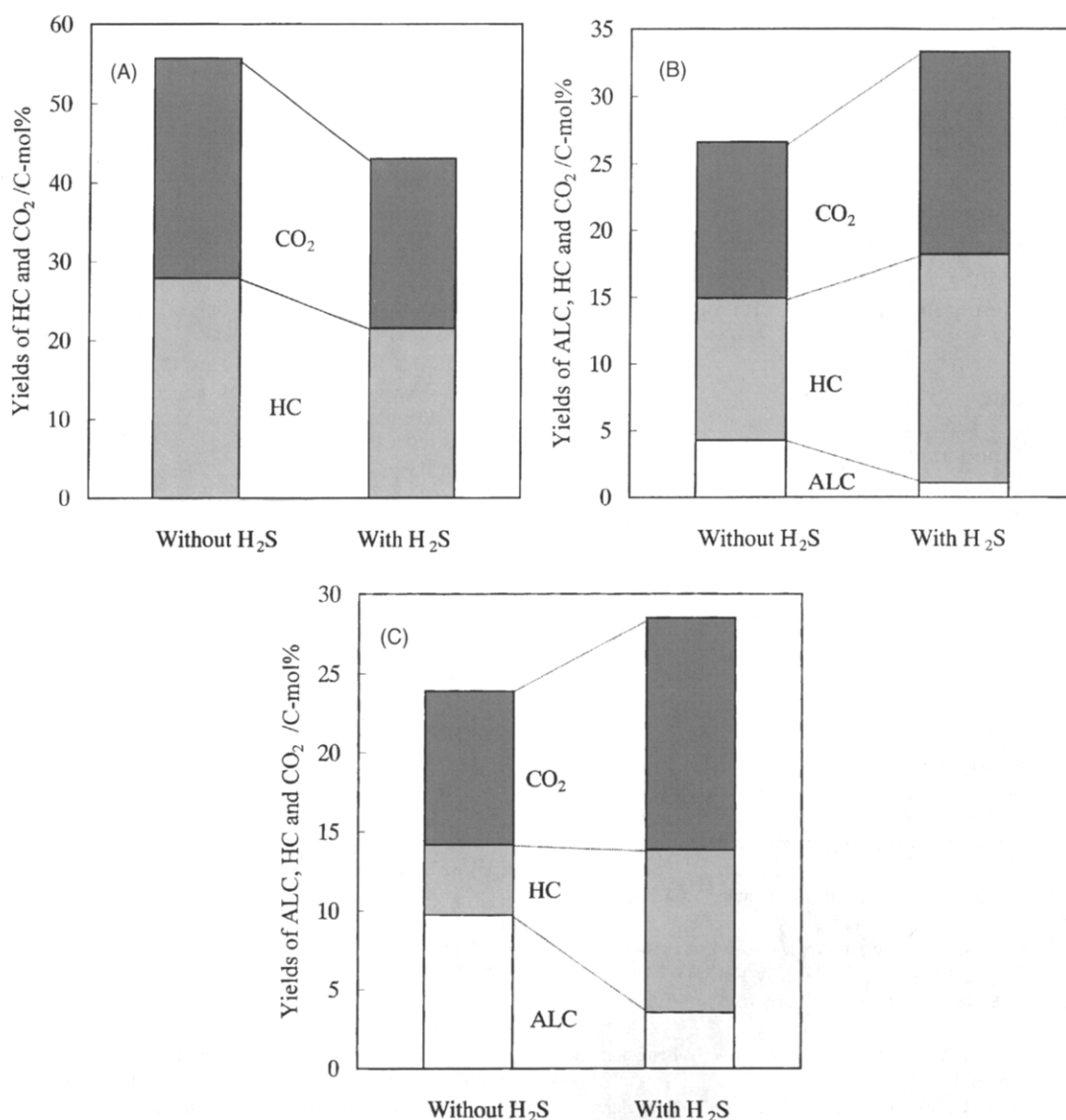


Fig. 10. Changes in activity over sulfided catalysts for high-pressure CO hydrogenation at 4.1 MPa, 340°C and SV = 6000 ml g-cat⁻¹ h⁻¹ by adding 5000 ppm H₂S into the feed gas: (A) Mo/γ-Al₂O₃, (B) K-Mo/γ-Al₂O₃ (K/Mo = 0.4), and (C) K-Mo/γ-Al₂O₃ (K/Mo = 0.8).

faster desorption of CO₂. Hou et al. reported that desorption of CO₂ became faster as small amounts of H₂S were introduced into the catalyst bed when MoS₂-based catalyst was used for water-gas shift reaction [45]. These observations strongly suggest that the active sites for alcohol synthesis are not on the K-MoS₂ species, but on the partly oxidized K-MoS₂ species during high-pressure CO hydrogenation.

Introduction of 5000 ppm H₂S in syngas into catalyst bed does not affect transformation of active sites for mixed alcohol synthesis to active sites for hydrocarbon synthesis and CO₂ formation because K species are absent during high-pressure CO hydrogenation over sulfided Mo/γ-Al₂O₃ catalyst. However, CO₂ and hydrocarbon synthesis activity of sulfided Mo/γ-Al₂O₃ are lower in the presence of H₂S because concentration of CO in the feed gas (H₂S/CO/H₂/Ar) is slightly lower than in the syngas.

4. Summary

DRIFT spectra of NO and syngas adsorption on freshly sulfided Mo/γ-Al₂O₃ and K-Mo/γ-Al₂O₃ catalysts indicate that sites for NO and CO adsorption over the MoS₂-like species are addressed by K species to form K-MoS₂ interaction species. The K-MoS₂ species are relatively more likely to be oxidized. DRIFT spectra of catalysts used for high-pressure CO hydrogenation show that formate species are formed on MoS₂-like species over the sulfided Mo/γ-Al₂O₃ catalyst. On the other hand, formate species are formed on partly oxidized K-MoS₂ species over the sulfided K-Mo/γ-Al₂O₃ catalysts. The formate species on the sulfided Mo/γ-Al₂O₃ catalyst are converted to CO₂ and methane and those on the sulfided K-Mo/γ-Al₂O₃ catalysts are converted to methanol, CO₂ or CH₄ during

high-pressure CO hydrogenation. The amounts of formate species increase with time at the initial 8 h of reaction on the sulfided K-Mo/ γ -Al₂O₃ catalysts; the formate species amounts become greatly decreased if 5000 ppm H₂S in syngas is introduced on to the catalyst bed as an impurity during the reaction. This results in an increase in selectivity to hydrocarbons and a decrease in selectivity to mixed alcohols. Our results indicate that active sites for alcohol synthesis are not on the K-MoS₂ species, but on the partly oxidized K-MoS₂ species during high-pressure CO hydrogenation.

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