Effective Dispersion of Co in Co-Mo/Al_2O_3 Induced by High Pressure Sulfiding by Means of FT-IR Using NO as Surface Probe Molecule

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The surface structure of Co-Mo/Al_2O_3 sulfided *in-situ* at high pressure($\leqq$5 MPa) was characterized by FT-IR/DRA method using NO as a probe molecule. The ratio of the band intensity of NO adsorbed on Co site to that of Mo site increased, when Co-Mo/Al_2O_3 was sulfided at the pressure above 1.1 MPa. Combining the results with those found on catalysts varying the Co/Mo molar ratio, it was suggested that Co site is more effectively dispersed on Mo site by higher pressure sulfiding.

Sulfided Co-Mo/Al_2O_3 catalyst is widely used for hydrotreatment of petroleum fractions, and many efforts have been made to make clear the active sites and to improve the catalyst performance. Since so-called "Co-Mo-S" structure has been proposed by means of Mössbauer emission spectroscopy as the active site for hydrodesulfurization of thiophenes on Co-Mo/Al_2O_3 catalyst,[1] the presence of the similar structure has been suggested in other supported sulfided catalysts, that is, Ni-Mo/active-C,[2] and Ni-W/active-C.[3] On the other hand, it has been reported that "Co-Mo-S" like Mössbauer signal appears even in Co/active-C.[4] Furthermore, it has been reported that "Co-Mo-S" structure is unstable under reaction conditions.[5,6]

Considering the above discrepancies, the following points should be reminded. That is, the characterization techniques adopted so far are mainly Mössbauer and EXAFS, whose information is predominated by the over-all structure of the catalyst, not by the surface structure. And the catalyst pretreating conditions reported so far are limited to an atmospheric pressure. In order to understand the surface structure of the catalyst at its working state, the present work tries to investigate the surface structure of the catalyst sulfided at high pressure($\leqq$5.1 MPa) by means of FT-IR study of adsorbed NO, and to compare it with those sulfided at atmospheric pressure.

Co-Mo/Al_2O_3(4.4 wt% CoO, 15 wt% MoO_3), Mo/Al_2O_3(16 wt% MoO_3) and Co/Al_2O_3(5.2 wt% CoO) examined here were prepared by conventional incipient wetness method, followed by drying at 393 K and calcination at 793 K.

FT-IR spectra of NO adsorbed on the catalysts were measured by means of diffuse reflectance method. Finely powdered catalyst sample was placed in the *in-situ* IR cell and was sulfided with 5% H_2S/H_2 stream at 673 K, for 1 h, in the range of 0.1 to 5.1 MPa. After this procedure, the catalyst was cooled to room temperature, and then exposed to 10% NO/He flow. After flushing the gas-phase NO by He flow, FT-IR measurements were undertaken using Digilab/FTS 165 spectrometer.

Figure 1 a) shows FT-IR spectra of NO adsorbed on Co-Mo/Al_2O_3 sulfided at the pressure of 0.1 to 5.1 MPa. For comparison, FT-IR spectra of NO adsorbed on Mo/Al_2O_3, Co/Al_2O_3 and physical mixture of Mo/Al_2O_3 and Co/Al_2O_3(Co/Mo molar ratio of physical mixture was fixed at 0.56, which is equal to that of Co-Mo/Al_2O_3) are shown in Figure 1 b). From comparison with FT-IR spectra of NO adsorbed on Mo/Al_2O_3 and Co/Al_2O_3, the lower frequency bands(ca. 1800, 1700 cm^{-1}) and higher frequency bands(ca. 1850, 1800 cm^{-1}) in Co-Mo/Al_2O_3 and physical mixture can be assigned to NO adsorbed on Mo and

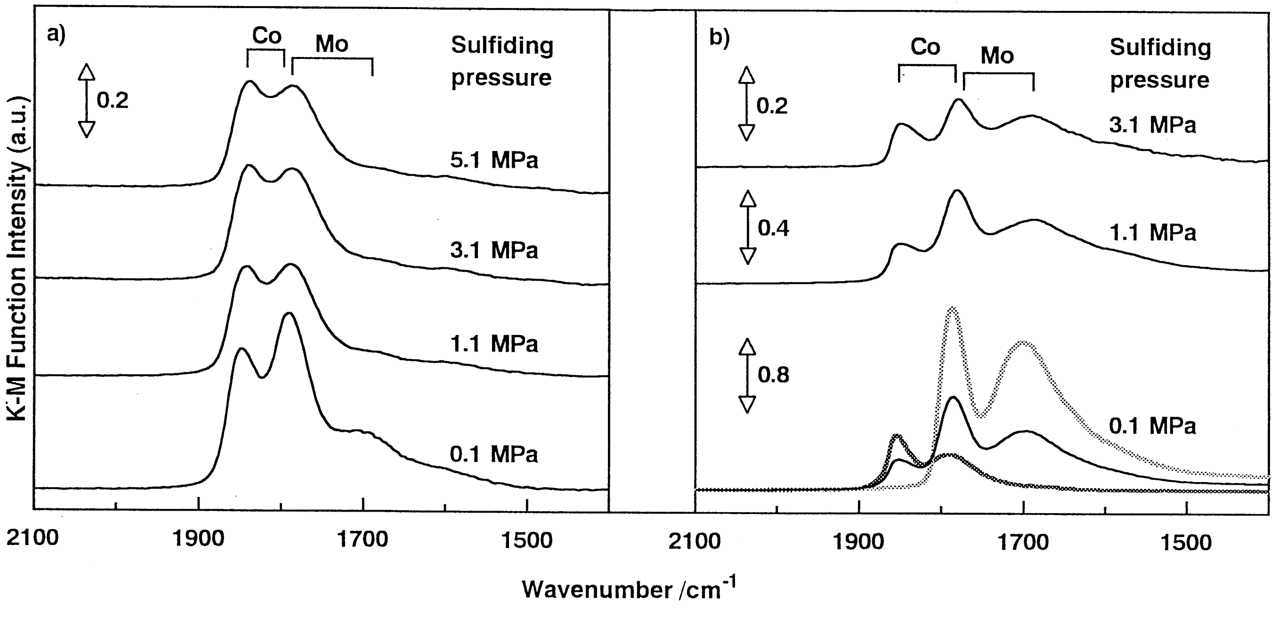

Figure 1. FT-IR spectra of NO adsorbed on the catalyst sulfided at high pressure.
a) Co-Mo/Al_2O_3, b) Mo/Al_2O_3(┈┈), Co/Al_2O_3(━━) and physical mixture of Mo/Al_2O_3 and Co/Al_2O_3(—).

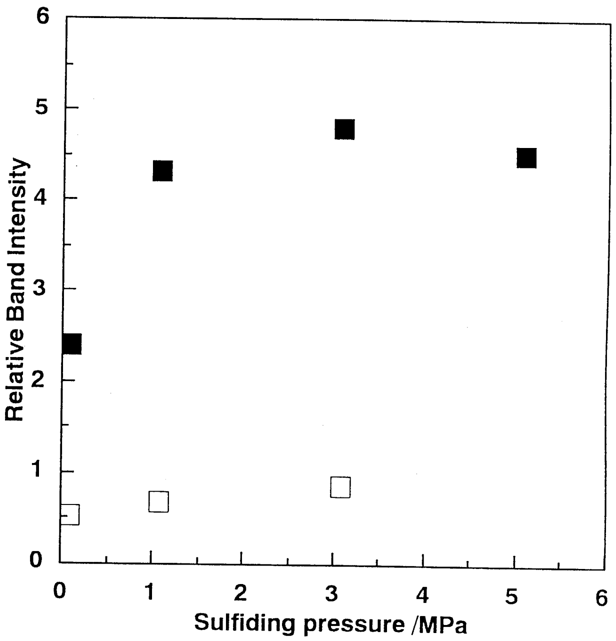

Figure 2. Effect of sulfiding pressure on the intensity ratio of Co site-band to Mo site-band.

(■)Co-Mo/Al_2O_3, (□)physical mixture of Mo/Al_2O_3 and Co/Al_2O_3

Co site respectively.

As shown in Figure 1 a), the intensity of Co site-band is very strong compared to that of Mo site-band, especially when the catalyst is sulfided at higher than 1.1 MPa. This result indicates that Co site is selectively formed compared to Mo site on Co-Mo/Al_2O_3, when Co-Mo/Al_2O_3 is sulfided at the pressure above 1.1 MPa. Figure 1 b) shows that the intensity of Co site-band and Mo site-band of physical mixture are comparable each other and are simple superposition of intensity of Mo/Al_2O_3 and Co/Al_2O_3. Comparing Figure 1 a) and Figure 1b), the intensity ratio of Co site-band to Mo site-band of Co-Mo/Al_2O_3 is much higher than that of physical mixture. This is quantitatively shown in Figure 2.

In order to understand the meaning of Figure 1 from the different point of view, the catalysts varying the Co/Mo molar ratio were also supplied for FT-IR study of adsorbed NO. Figure 3 shows FT-IR spectra of NO adsorbed on the catalysts sulfided at 3.1MPa. With increasing the ratio of Co/Mo, the intensity of Co site-band increases steeply whereas that of Mo site-band decreases and almost disappears. Based on "Co-Mo-S" phase model, which is proposed by Topsøe et al. using Co-Mo/Al_2O_3 sulfided at atmospheric pressure,[1] Figure 3 might be interpreted as follows, that is, coordinatively unsaturated site of Mo is capped by Co.

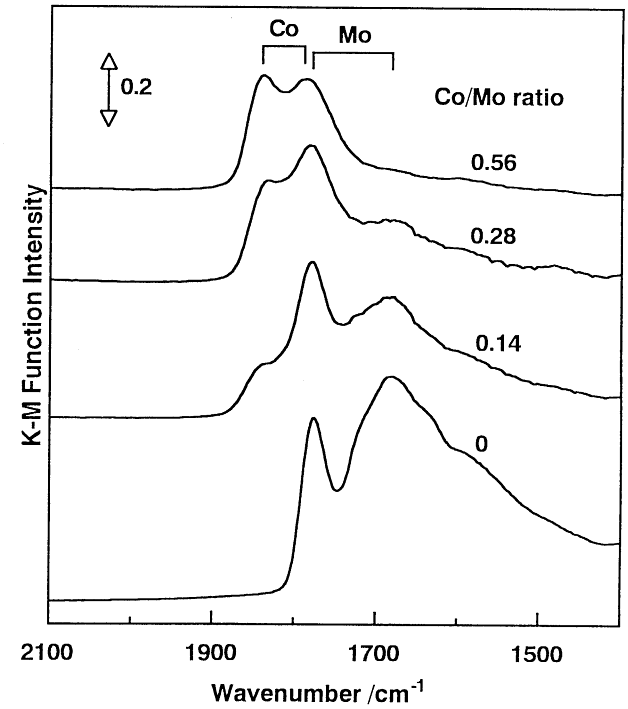

Figure 3. FT-IR spectra of NO adsorbed on Co-Mo/Al_2O_3 with various Co/Mo ratio.

Sulfiding pressure: 3.1MPa

Analogous to Figure 3, Figure 1 a) suggests that "Co-Mo-S" phase is more effectively formed by the higher pressure sulfiding than atmospheric pressure, although it has been reported that "Co-Mo-S" structure is unstable under reaction conditions.[5,6]

References and Notes

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