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Interaction between Mo and Co on Co–Mo/Al_2O_3 sulfided at high pressure (≤5.1 MPa) by means of high pressure DRIFT and EXAFS method

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Abstract

Co–Mo/Al_2O_3 was sulfided at high pressure (≤5.1 MPa) and was supplied for in-situ DRIFT measurement using NO as a surface probe molecule. The IR band of NO adsorbed on Co site was much stronger than that of Mo site, and the IR intensity ratio of Co site band to Mo site band was much higher when Co–Mo/Al_2O_3 was sulfided at the pressure above 1.1 MPa than when it was sulfided at atmospheric pressure. Mo/Al_2O_3, Co/Al_2O_3 and the physical mixture of them were also supplied for the high pressure DRIFT measurement. In the DRIFT spectra of the physical mixture, the intensity of the Mo site band was comparable to that of the Co site band. In the spectra of Ni–Mo/Al_2O_3, only the Ni site band was observed. Mo K-edge EXAFS showed that the dispersion of Mo of Co–Mo/Al_2O_3 is almost the same as that of the physical mixture and does not depend on the sulfiding pressure. Combining the results of the DRIFT spectra with that of Mo K-edge EXAFS, it was suggested that Co–Mo interaction induces selective formation of CUS on Co site on Co–Mo/Al_2O_3 and the interaction is promoted by higher pressure sulfiding. © 1997 Elsevier Science B.V.

Keywords: Co–Mo/Al_2O_3 catalyst; Ni–Mo/Al_2O_3 catalyst; High pressure sulfiding; Coordinatively unsaturated sites; DRIFT of adsorbed NO; Mo K-edge EXAFS

1. Introduction

Co–Mo/Al_2O_3 is widely used for the hydrotreatment of petroleum fractions. In order to meet the severe limitation for the environmental protection, every effort has been made to improve the conversion of HDS, HDN and HGN reactions on Co–Mo/Al_2O_3. For this purpose, the increase of the severity of the reaction conditions is necessary as well as the improvement of the catalyst performance. Not only to make clear the exact surface structure but also to improve catalyst performance further, it is necessary to observe the catalyst surface exposed to the severe reaction conditions.

However, in the characterization of Co–Mo/Al_2O_3, the catalyst pretreating (sulfiding) conditions reported so far are limited to atmospheric pressure, which is far from the working state of Co–Mo/Al_2O_3. It is possible that the structure of Co–Mo/Al_2O_3 sulfided at atmospheric pressure is different from that of Co–Mo/Al_2O_3 sulfided at higher pressure.

Furthermore, the following points should be recalled. That is, the characterization techniques adopted so far are mainly Mössbauer and EXAFS,

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whose information is predominated by the over-all structure of the catalyst, not by the surface structure.

In order to understand the surface structure of the catalyst at its working state, the present work tried to characterize the surface structure of Co–Mo/Al_2O_3 under its working state. That is, CUS distribution on the surface of Co–Mo/Al_2O_3 sulifided at high pressure was investigated by DRIFT study of adsorbed NO using high temperature ($\leq$773 K) and pressure ($\leq$5.1 MPa) in-situ IR cell. Furthermore, fine structure around Mo of Co–Mo/Al_2O_3 was also investigated by Mo K-edge EXAFS using in-situ EXAFS cell. Our special attention was directed to the distribution of CUS on Co sites and Mo sites of Co–Mo/Al_2O_3.

2. Experimental

2.1. *FT–IR/DRA of adsorbed NO*

The catalyst, finely powdered, was placed in the high pressure DRIFT cell and 5% H_2S/H_2 was introduced into the cell at the pressure of 0.1–5.1 MPa, at room temperature. Under flowing 5% H_2S/H_2 (30 ml/min (STP)), the catalyst was heated to 673 K at the rate of 20 K/min. After the temperature reached 673 K, the temperature was held constant for 1 to 10 h. Then, the catalyst was cooled to room temperature, and He was introduced into the IR cell to purge 5% H_2S/H_2. Unless otherwise stated, sulfidation was carried out for 1 h.

10% NO/He was introduced to the IR cell by a pulse method. After flushing the gas-phase NO by He flow, FT–IR/DRA spectrum of NO adsorbed on the catalyst was measured by means of diffuse reflectance method using a FTS6000 (Bio-Rad) spectrometer equipped with mercury–cadmium–telluride detector.

2.2. *Mo K-edge EXAFS*

Finely powdered catalyst was pressed into pellets, which were set in the high pressure EXAFS cell. The EXAFS cell was designed and made according to that reported by Boudart et al. [1] 5% H_2S/H_2 was introduced into the EXAFS cell at the pressure of 0.1–5.1 MPa, at room temperature. Under flowing 5% H_2S/H_2 (150 ml/min (STP)), the catalyst was held at room temperature for 1 h, and then was heated to 673 K at the rate of 10 K/min. This temperature was kept for 2 h. After that, the catalyst was cooled to room temperature, and then He was introduced into the IR cell to flush 5% H_2S/H_2.

After these procedures, X-ray absorption spectra were measured using Laboratory System equipped with double-crystal monochromator [2,3]. The interatomic distances and the coordination numbers were determined by curve fitting techniques [4]. The back-scattering amplitudes and phase shifts reported by McKale et al. [5] were used. MoS_2 powder (supplied by Wako Pure Chemicals) was used as reference for Debye-Waller factor and photoelectron mean free path.

2.3. *Catalyst preparation*

Home-made Co–Mo/Al_2O_3, Mo/Al_2O_3 and Co/Al_2O_3 catalysts were used. Commercial Co–Mo/Al_2O_3 (supplied by Nippon Ketjen) was also used. In the following text, commercial Co–Mo/Al_2O_3 is denoted by Co–Mo/Al_2O_3 (NK) so as to distinguish it from home-made Co–Mo/Al_2O_3.

Home-made Co–Mo/Al_2O_3, Mo/Al_2O_3 and Co/Al_2O_3 were prepared by incipient wetness method. γ-Al_2O_3 (supplied by Nippon Ketjen, 333 m^2/g, 0.76 cm^3/g) was impregnated by $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (supplied by Wako Pure Chemicals) solution followed by drying (393 K, 16 h) and calcination (793 K, 12 h), then Mo/Al_2O_3 (MoO_3:15.8 wt%) was obtained. This was impregnated by $Co(NO_3)_2\cdot 6H_2O$ (supplied by Wako Pure Chemicals) solution, followed by drying (393 K, 16 h) and calcination (793 K, 12 h); finally, Co–Mo/Al_2O_3 was obtained. Co/Mo molar ratio was fixed at that of Co–Mo/Al_2O_3 (NK) (0.56 mol/mol). Co/Al_2O_3 (CoO:5.2 wt%) was prepared as mentioned above.

3. Results and discussions

3.1. *Effect of sulfiding pressure on the surface structure of Co–Mo/Al_2O_3*

3.1.1. *Distribution of CUS on Co–Mo/Al_2O_3, Mo/Al_2O_3 and Co/Al_2O_3*

It is well known that NO adsorbs on CUS of Mo- or Co–Mo/Al_2O_3 catalyst. And it has been sometimes

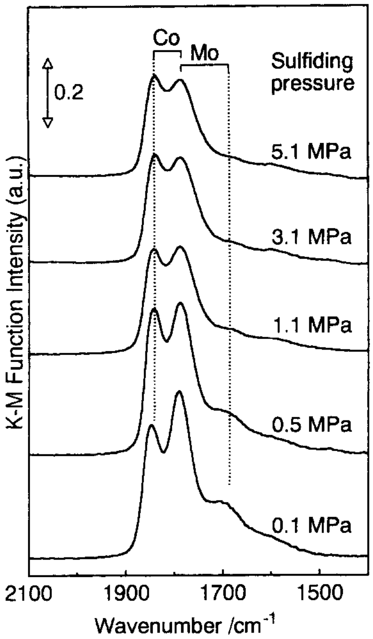

Fig. 1. DRIFT spectra of NO adsorbed on Co–Mo/Al_2O_3 sulfided at high pressure.

reported that the NO uptakes correlate well with the HDS activity. In the present work, in order to investigate the distribution of CUS on the catalyst surface, Co–Mo/Al_2O_3, Mo/Al_2O_3 and Co/Al_2O_3 sulfided at the pressure of 0.1–5.1 MPa were studied by means of high pressure DRIFT method using NO as a probe molecule.

Fig. 1 shows DRIFT spectra of NO adsorbed on Co–Mo/Al_2O_3 sulfided at the pressure of 0.1–5.1 MPa. Two bands appear in the spectrum on Co–Mo/Al_2O_3 at 1850 and 1800 cm^{-1}. A much weaker band also appears around 1700 cm^{-1}. From comparison with the spectra on Mo/Al_2O_3 and Co/Al_2O_3, the lower frequency (1800 and 1700 cm^{-1}) bands and higher frequency(1850 and 1800 cm^{-1}) bands can be assigned to NO adsorbed on Mo site-band and Co site-band, respectively. This assignment is consistent with that in our preceding papers using Co–Mo/Al_2O_3 sulfided at 0.1 MPa [6–8]. From here, we call the higher frequency bands the Co site-band, and the lower frequency bands the Mo site-band.

It is noticed that the spectrum of NO adsorbed on Co–Mo/Al_2O_3 sulfided above 1.1 MPa is different from that on Co–Mo/Al_2O_3 sulfided at 0.1 MPa. That is, increasing the sulfiding pressure above 1.1 MPa, only two bands appear, and the lower frequency Mo site-band seems to disappear. Clearly, the intensity ratio of Co site-band to Mo site-band is much higher when Co–Mo/Al_2O_3 is sulfided over 1.1 MPa than when it is sulfided at 0.1 MPa. It is also noticed that no drastic change appears with increasing sulfiding pressure above 1.1 MPa.

These spectra show that the CUS is selectively formed on Co site of Co–Mo/Al_2O_3 sulfided at every pressure, especially above 1.1 MPa.

Fig. 2(a,b) show the FT–IR/DRA spectra of NO adsorbed on Mo/Al_2O_3 and Co/Al_2O_3, respectively, which are sulfided at 0.1–5.1 MPa. The spectra on Mo- and Co/Al_2O_3 show two bands, respectively. This doublet has been well known and has been assigned to dinitrosyl species adsorbed on Mo site or Co site. Increasing the sulfiding pressure, the shape of the doublet gradually changes. That is, the lower frequency band relatively increases.

Comparing Fig. 1 with Fig. 2(a,b), it is clear that the spectrum of NO adsorbed on Co–Mo/Al_2O_3 is not a simple superposition of those on Mo/Al_2O_3 and Co/Al_2O_3. That is, the IR intensity of Mo site-band in Co–Mo/Al_2O_3 is very weak. However, it is not sure whether the CUS is selectively formed on Co sites, or the CUS on Mo sites selectively disappears.

3.1.2. *Intrinsic effect of sulfiding pressure and the stability of surface structure*

As mentioned above, the sulfiding pressure clearly affects the distribution of CUS on Co–Mo/Al_2O_3. Therefore, the sulfiding pressure may be an important factor influencing the surface structure of the catalyst. In order to confirm this possibility, the effect of the sulfiding pressure was further studied from a different point of view; that is, the effect of sulfiding duration and the stability of the surface structure at its working state.

Concerning the former, FT–IR/DRA spectra of NO adsorbed on Co–Mo/Al_2O_3 sulfided at 0.1 MPa for the time of 1–10 h are shown in Fig. 3. The relative intensity of Co site-band slightly increases with increasing sulfiding time. However, comparing Fig. 1 with Fig. 3, the relative intensity of Co site-band of Co–Mo/Al_2O_3 sulfided at 1.1 MPa (for 1 h) is stronger than that of Co–Mo/Al_2O_3 sulfided at 0.1 MPa for 10 h. These results indicate that the surface structural change induced by 1.1 MPa sulfiding

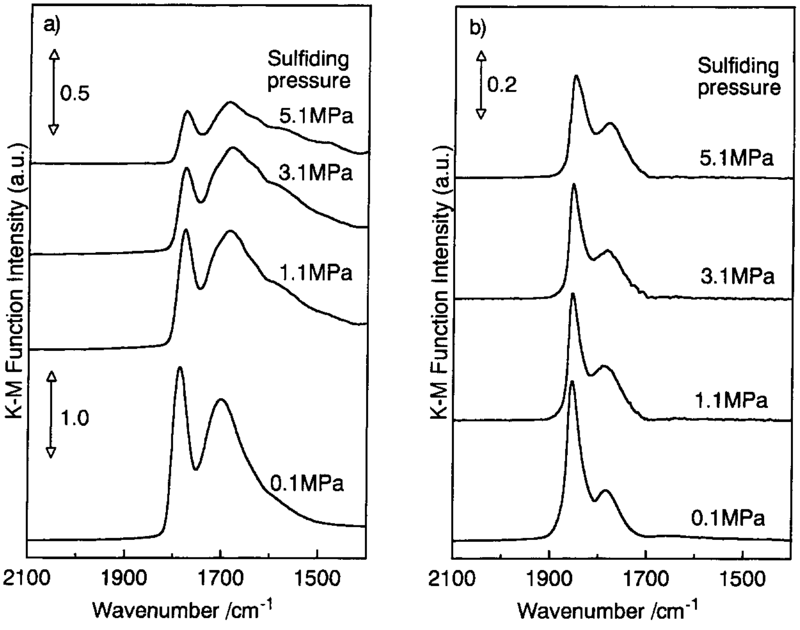

Fig. 2. DRIFT spectra of NO adsorbed on the catalysts sulfided at high pressure. (a) Mo/Al_2O_3 and (b) Co/Al_2O_3.

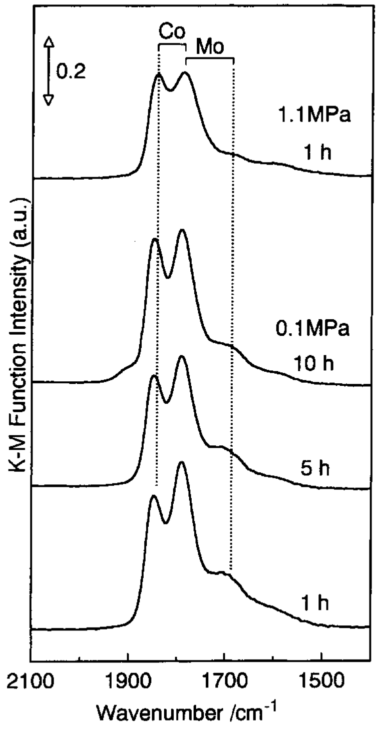

Fig. 3. Comparison of the spectrum on $Co–Mo/Al_2O_3$ sulfided at 1.1 MPa with those on $Co–Mo/Al_2O_3$ sulfided at 0.1 MPa with various sulfiding durations.

can not be attained by simple extension of sulfiding duration at 0.1 MPa.

Concerning the latter, it should be recalled that the catalyst in industrial HDS process is usually exposed to a high pressure hydrogen stream under its working state after presulfiding. It is possible that the surface structure of the catalyst, once sulfided, is changed by this exposing to a hydrogen stream. Here, the CUS of the catalyst which was reduced in the stream of hydrogen after the presulfiding was examined by the same DRIFT method using NO as a probe molecule. Fig. 4 shows the DRIFT spectra of NO adsorbed on $Co–Mo/Al_2O_3$, which was sulfided in 5% H_2S/H_2 stream and then reduced in the stream of H_2 at 673 K under 3.1 MPa. The spectra of adsorbed NO is almost the same as that of the catalyst just sulfided. Even after 10 h of reducing, the spectra is little changed. For comparison, in Fig. 4 are also shown the spectra of the catalyst which was reduced initially in the stream H_2 and then sulfided in the stream of H_2S/H_2 stream. The surface structure of the catalyst reduced initially and then sulfided is different from that of the catalyst sulfided initially and then reduced. It can be said that the catalyst surface is sensitive to the pretreatment, especially presulfiding or prereducing. These spectra suggest that the surface structure of $Co–Mo/Al_2O_3$

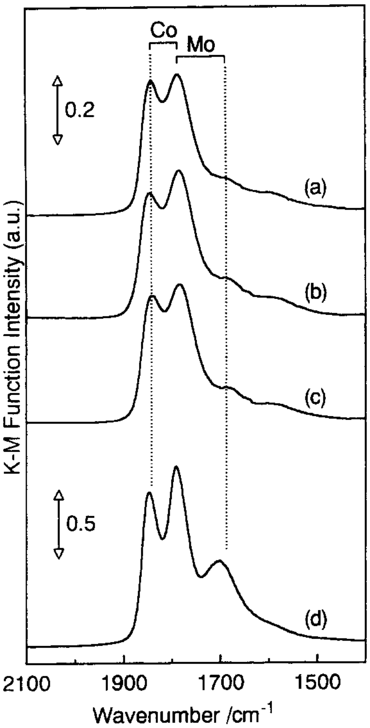

Fig. 4. Comparison of the spectrum on Co–Mo/Al_2O_3 sulfided at 1.1 MPa with those on variously pretreated Co–Mo/Al_2O_3. (a) Sulfided at 1.1 MPa, (b) sulfided at 1.1 MPa then reduced at 3.1 MPa for 2 h, (c) sulfided at 1.1 MPa then reduced at 3.1 MPa for 10 h and (d) reduced at 1.1 MPa then sulfided at 1.1 MPa.

once presulfided is stable under high pressure of hydrogen.

3.1.3. *Effect of loading amount on the interaction between Mo and Co on the support*

What kind of interaction is working between Mo and Co on the support? And how the interaction is changed with increasing the sulfiding pressure.

The interaction between Co and Mo on the support may be affected by the loading amount of Co and Mo. It is possible that higher loading promotes the interaction between Co and Mo.

We prepared the catalyst with half loading, and studied the DRIFT spectra of NO adsorbed on them and studied the effect of loading amount on the interaction between Co and Mo. The results are shown in Fig. 5. As we can see, the DRIFT spectra shows the same pressure dependency as the full loading catalyst. That is, the Mo site-band is very weak at high pressure sulfiding. The results suggest that CUS is selectively formed on Co sites even on the half loading catalyst.

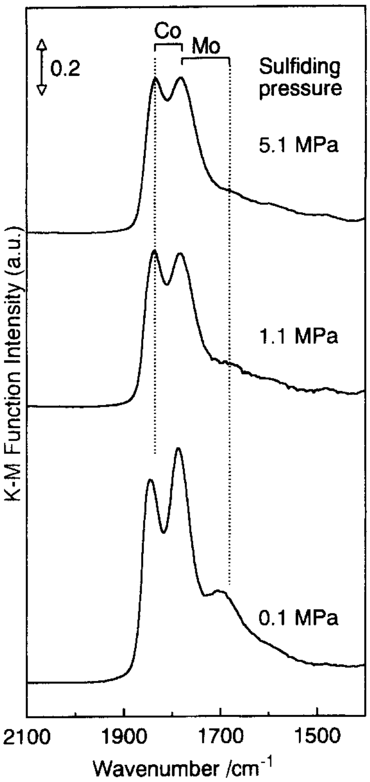

Fig. 5. DRIFT spectra of NO adsorbed on Co–Mo/Al_2O_3 (MoO_3:7.7 wt%,Co/Mo:0.56 mol/mol) sulfided at 0.1, 1.1 and 5.1 MPa.

3.2. *Interaction between Mo and Co on the support*

3.2.1. *Distribution of CUS on a physical mixture of Mo/Al_2O_3 and Co/Al_2O_3*

As mentioned above, the characteristic distribution of CUS observed on Co–Mo/Al_2O_3 sulfided at high pressure is widely observed in other cases, i.e. long time-sulfided catalyst, sulfided then reduced catalyst, and low loading catalyst.

To understand the surface structure of Co–Mo/Al_2O_3 sulfided at high pressure in more detail, we studied the sulfiding pressure dependency of the physical mixture of Mo/Al_2O_3 and Co/Al_2O_3. A physical mixture of Mo/Al_2O_3 and Co/Al_2O_3 was supplied for DRIFT study of adsorbed NO. Co/Mo molar ratio of

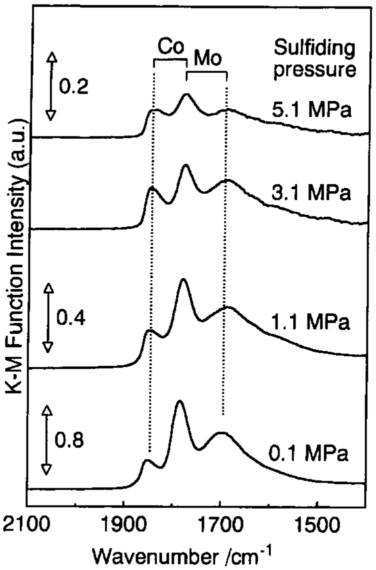

Fig. 6. DRIFT spectra of NO adsorbed on a physical mixture of Mo/Al_2O_3 and Co/Al_2O_3.

the physical mixture was fixed at 0.56, which is equal to that of $Co–Mo/Al_2O_3$. Fig. 6 shows the obtained spectra of NO adsorbed on the physical mixture sulfided at the pressure of 0.1–5.1 MPa. Three bands appear in the range of NO stretching vibration at every pressure of sulfiding. These bands can be assigned to Co and Mo site-band respectively, referring to the spectra of Mo/Al_2O_3 (Fig. 2(a)) and Co/Al_2O_3 (Fig. 2(b)). The intensity of Mo site-band is comparable to that of Co site-band, and does not disappear with increasing sulfiding pressure. In other words, the distribution of CUS of the physical mixture is not affected by sulfiding pressure. Comparing Fig. 6 with Fig. 2(a,b), it is clear that the spectra of NO adsorbed on the physical mixture seems to be a simple superposition of those on Mo/Al_2O_3 and Co/Al_2O_3. This will be discussed in Section 3.2.3.

Here, we will compare the spectra of the physical mixture with that of $Co–Mo/Al_2O_3$. It is easy to point out the difference between them. As we can see, three bands appear in the spectrum of physical mixture. On the other hand, two bands appear in the spectrum of $Co–Mo/Al_2O_3$. The distribution of CUS is clearly different between $Co–Mo/Al_2O_3$ and the physical mixture of Mo- and Co/Al_2O_3. Furthermore, it is noted that the difference became more profound with increasing the sulfiding pressure.

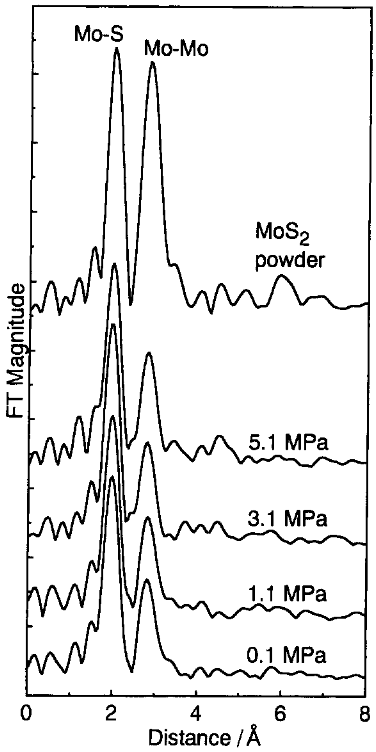

Fig. 7. Fourier transforms of Mo K-edge EXAFS of $Co–Mo/Al_2O_3$ sulfided at high pressure.

3.2.2. *Effect of sulfiding pressure on the morphology of MoS_2-like structure*

As mentioned above, the present results showed that Mo site of $Co–Mo/Al_2O_3$ has a lower number of CUS compared to Mo/Al_2O_3 and the higher pressure of sulfiding decreases the relative ratio of CUS on Mo sites. These two points were investigated from the point of the dispersion of Mo. Because it is possible that the decrease of CUS on Mo site correlates with the morphology of a MoS_2-like structure, that is, the growth of MoS_2-like structure in the lateral direction. Therefore, the change of the dispersion of Mo site accompanied by high pressure sulfiding was examined by means of the Mo K-edge EXAFS method.

Fig. 7 shows the Fourier transforms of Mo K-edge EXAFS spectra (radial structure function) of $Co–Mo/Al_2O_3$ sulfided at the pressure of 0.1–5.1 MPa. Fig. 7 also shows that of MoS_2 powder for reference. As shown in Fig. 7, only Mo–S and Mo–Mo shells clearly appear in the radial structure function of the catalysts sulfided at the pressure of 0.1–5.1 MPa. These two

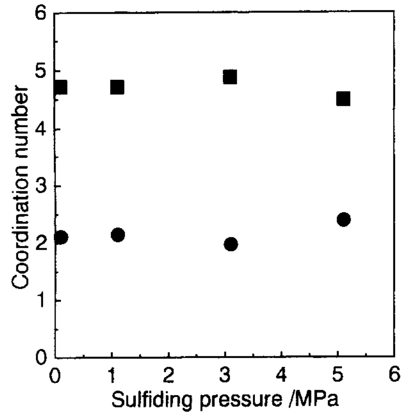

Fig. 8. Dependency of the coordination number of Mo–S shell (■) and Mo–Mo shell (●) on the sulfiding pressure (Co–Mo/Al_2O_3).

peaks suggest that the fine structure around Mo in Co–Mo/Al_2O_3 can be approximated by MoS_2-like structure when Co–Mo/Al_2O_3 is sulfided at the pressure of 0.1–5.1 MPa. It is noticed that the peak intensities of Mo–S and Mo–Mo shells are hardly affected by sulfiding pressure. Coordination numbers calculated about Mo–S and Mo–Mo shells of Co–Mo/Al_2O_3 are shown in Fig. 8. As can be seen from Fig. 8, both Mo–S and Mo–Mo coordination numbers are almost constant in the range of 0.1–5.1 MPa. These results suggest that the morphology of MoS_2-like structure formed in Co–Mo/Al_2O_3 is hardly affected by higher pressure sulfiding.

Fig. 9 shows the radial structure function of the physical mixture sulfided at 0.1, 1.1 and 5.1 MPa. The physical mixture examined here is the same as that for the FT–IR/DRA measurement already mentioned. Mo–S and Mo–Mo coordination numbers of the physical mixture are shown in Fig. 10. Comparing Co–Mo/Al_2O_3 with the physical mixture, Mo–Mo coordination number of Co–Mo/Al_2O_3 is constant, and comparable with that of the physical mixture in the range of 0.1–5.1 MPa. This suggests that the growth of MoS_2-like structure in the lateral direction on Co–Mo/Al_2O_3 is comparable with that on the physical mixture. It can be said that the presence of Co does not affect the morphology of MoS_2-like structure of sulfided Co–Mo/Al_2O_3.

The present Mo K-edge EXAFS studies show that the morphology of MoS_2-like structure of Co–Mo/Al_2O_3 is hardly affected by high pressure sulfiding and the presence of Co. Therefore, it can be said that the surface structural change induced on Co–Mo/Al_2O_3 by high pressure sulfiding is not accompanied by the growth of MoS_2-like structure in the lateral direction.

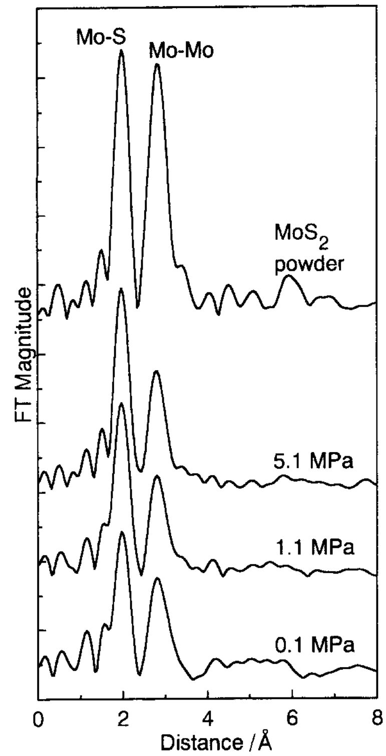

Fig. 9. Fourier transforms of Mo K-edge EXAFS of the physical mixture of Mo/Al_2O_3 and Co/Al_2O_3 sulfided at 0.1, 1.1 and 5.1 MPa.

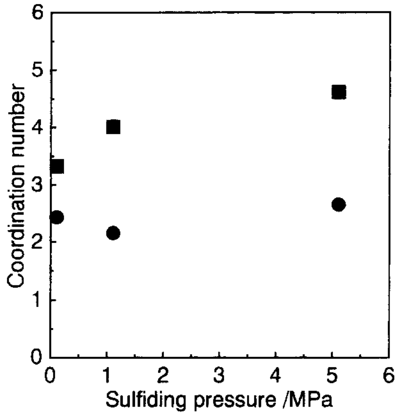

Fig. 10. Dependency of the coordination number of Mo–S shell (■) and Mo–Mo shell (●) on the sulfiding pressure (the physical mixture of Mo/Al_2O_3 and Co/Al_2O_3).

However, the reason why Mo has no CUS on Co–Mo/Al_2O_3 is still unclear. What is the reason of the selective disappearance of CUS on Mo site, or the selective formation of CUS on Co site on Co–Mo/Al_2O_3? Furthermore, what is the reason why the higher pressure of sulfiding increases the selectivity of the disappearance of CUS on Mo site?

The change accompanied by high pressure sulfiding may be due to an interaction between Mo and Co on the support. What kind of interaction is working between Mo and Co on the support?

3.2.3. *Curve fitting analyses of the spectra of the catalysts by linear combination of the spectra of components*

As mentioned above, Mo K-edge EXAFS shows that the dispersion of Mo does not change within this range of sulfiding pressure. Here, in order to investigate the reason why Mo site of Co–Mo/Al_2O_3 has no CUS after high pressure sulfiding, the spectra of Co–Mo/Al_2O_3 were compared with those of Co/Al_2O_3 and Mo/Al_2O_3, and the differences between them were analyzed by a curve fitting method.

Now, we tried to analyze these bands by a linear combination of the IR band of each component (i.e. Mo/Al_2O_3 and Co/Al_2O_3). First of all, in order to obtain the weight of Co site-band, the IR band intensity of Co/Al_2O_3 is adjusted to that of the highest frequency band. Second, the weight of Mo site-band is obtained by adjusting the band intensity of Mo/Al_2O_3 to the lowest frequency band. Then, the spectrum of each component is combined together, depending on each weight. By doing this, we can obtain a good fitting of a linear combination of Mo/Al_2O_3 and Co/Al_2O_3 to that of the physical mixture, as shown in Fig. 11. It can be said that the IR band of the physical mixture is well explained by a linear combination of Mo/Al_2O_3 and Co/Al_2O_3. This result is reasonable because Co and Mo in the physical mixture do not interact.

Then we tried to analyze the IR band of Co–Mo/Al_2O_3 in the same manner as mentioned above. As shown in Fig. 12, the fitting between the IR band of Co–Mo/Al_2O_3 and that of the linear combination of Mo/Al_2O_3 and Co/Al_2O_3 is not good. That is, the spectrum on Co–Mo/Al_2O_3 can not be expressed by the linear combination of those on Mo and Co/Al_2O_3. It is further noted that the discrepancy increases with increasing the sulfiding pressure.

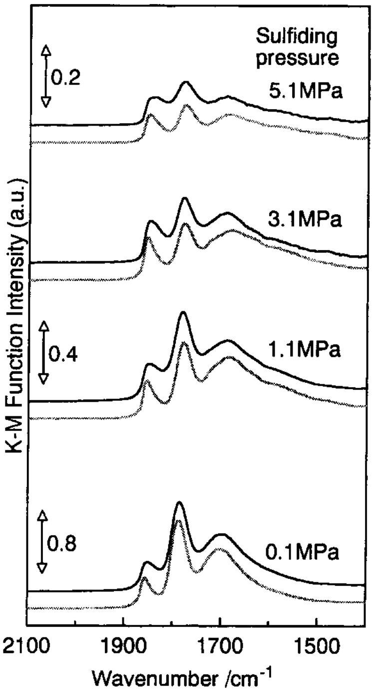

Fig. 11. Curve fitting analysis of the spectra on the physical mixture of Mo/Al_2O_3 and Co/Al_2O_3. The spectra on the physical mixture of Mo/Al_2O_3 and Co/Al_2O_3 (continuous line) and the linear combination of the spectra on Mo/Al_2O_3 and Co/Al_2O_3 (dashed line).

The curve fitting method showed that the distribution of CUS on Co–Mo/Al_2O_3 is different from that of the physical mixture and can not be expressed by a linear combination of the spectra of each component. Especially it is noted that the CUS of Mo/Al_2O_3 drastically disappears when Mo exists with Co on the support.

3.3. *Effect of sulfiding pressure on the surface structure of Ni–Mo/Al_2O_3*

For comparison, Ni–Mo/Al_2O_3 was also supplied for DRIFT measurement. Fig. 13 shows FT–IR/DRA spectra of NO adsorbed on Ni–Mo/Al_2O_3 sulfided at the pressure of 0.1–5.1 MPa. An asymmetric absorption band appears at 1840 cm^{-1} in every pressure of sulfiding. Much weaker and broader band appears around 1700 cm^{-1} in both cases. The spectra of NO

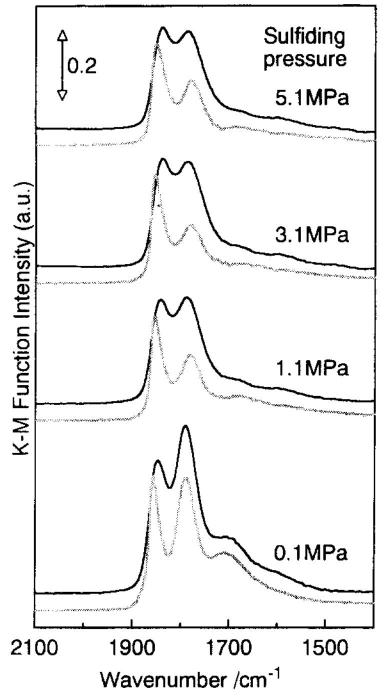

Fig. 12. Curve fitting analysis of the spectra on Co–Mo/Al_2O_3. The spectra on Co–Mo/Al_2O_3 (continuous line) and the linear combination of the spectra on Mo/Al_2O_3 and Co/Al_2O_3 (dashed line).

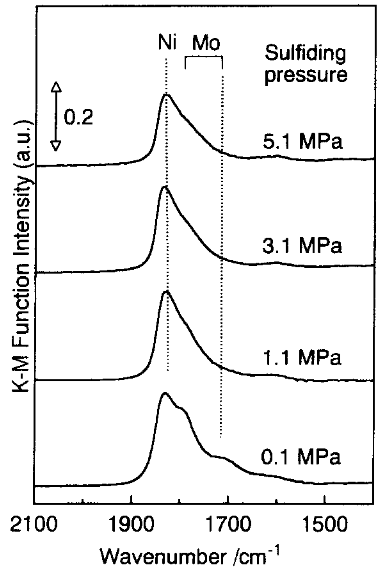

Fig. 13. DRIFT spectra of NO adsorbed on Ni–Mo/Al_2O_3 sulfided at high pressure.

adsorbed on Mo/Al_2O_3 and Ni/Al_2O_3 are also shown in Fig. 14(a,b). Based on the spectra of the reference samples, the asymmetric band in Ni–Mo/Al_2O_3 can be assigned to NO adsorbed on Ni site. The IR intensity of the Ni site-band is insensitive to the change of the sulfiding pressure. On the other hand, two weak bands assigned to NO adsorbed on Mo site appear in the catalyst sulfided at 0.1 MPa but diminish after sulfiding above 1.1 MPa.

The DRIFT spectra of NO adsorbed on Ni–Mo/Al_2O_3 is basically similar to that of Co–Mo/Al_2O_3. That is, CUS is selectively formed on the promoter sites, even at lower pressure of sulfiding.

In the spectra of Ni/Al_2O_3, an asymmetric band appears. This band can be assigned to the dinitrosyl species adsorbed on Ni site. The reason why the band looks like a singlet is due to the molecular structure of dinitrosyl species.

In Fig. 15 are also shown the spectra of a physical mixture of Mo/Al_2O_3 and Ni/Al_2O_3. Ni/Mo molar ratio of the physical mixture was 0.56, which is equal to that of Ni–Mo/Al_2O_3. Both the Ni site-band and Mo site-band clearly appear in every pressure.

Comparing the spectra of Ni–Mo/Al_2O_3 with that of the physical mixture, it is noted that the intensity of Mo-site band of Ni–Mo/Al_2O_3 is much weaker than that of the physical mixture in every pressure of sulfiding. This suggests that Ni interacts with Mo as well as Co.

The DRIFT spectra of Ni–Mo/Al_2O_3 and the physical mixture of Mo/Al_2O_3 and Ni/Al_2O_3 were also analyzed in the same manner. The spectra of the physical mixture can be well expressed by a linear combination of the spectrum of Mo/Al_2O_3 and Ni/Al_2O_3. Ni–Mo/Al_2O_3 is also well expressed by the linear combination, in which the weight of the spectrum of Mo/Al_2O_3 is negligible. It can be said that CUS of Ni–Mo/Al_2O_3 is very selectively formed on Ni site at every pressure of sulfiding.

3.4. Surface structure of Co–Mo/Al_2O_3 formed by high pressure sulfiding

The recent developments of surface analysis techniques contribute to evaluating the surface structure of Co–Mo/Al_2O_3; some models of active sites for HDS reaction are proposed. That is, Topsøe et al. have proposed ‘Co–Mo–S’ model by means of Mössbauer

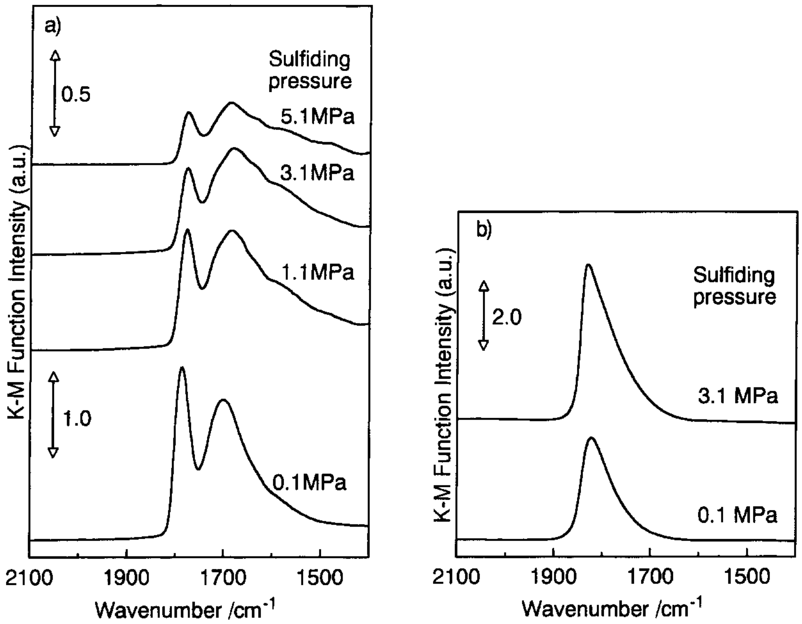

Fig. 14. DRIFT spectra of NO adsorbed on the catalysts sulfided at high pressure. (a) Mo/Al_2O_3 and (b) Ni/Al_2O_3.

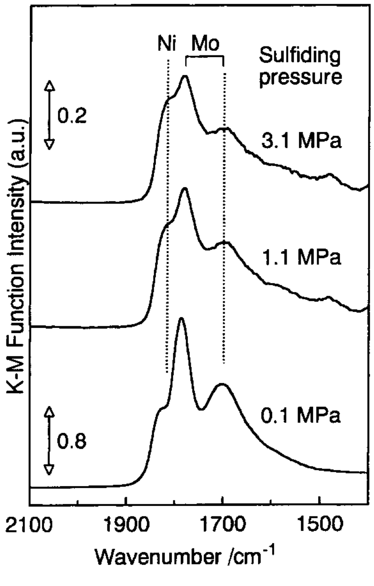

Fig. 15. DRIFT spectra of NO adsorbed on a physical mixture of Mo/Al_2O_3 and Ni/Al_2O_3 sulfided at 0.1, 1.1 and 3.1 MPa.

emission spectroscopy (MES) as the active site for HDS of thiophenes on $Co–Mo/Al_2O_3$ [9,10]. Furthermore, local structure of 'Co–Mo–S' on Co–Mo/active-C has been proposed by means of Mo and Co K-edge EXAFS [11,12].

However, some problems about 'Co–Mo–S' model are pointed out. One is that there is a complexity with signal assignment in MES. That is, it has been reported that 'Co–Mo–S' like Mössbauer signal appears even in Co/active-C [13]. This might make ambiguous the fact that the intensity of 'Co–Mo–S' signal in MES correlates with thiophene HDS activity. The other is concerning the stability of 'Co–Mo–S' in reaction conditions. That is, Breysse et al. have reported the results of MES and XPS of unsupported Co–Mo sulfides using HDS of dibenzothiophene under pressurized conditions [14,15,16]. Based on these results, they speculated that Co in 'Co–Mo–S' on unsupported Co–Mo sulfide was segregated in their reaction condition. This speculation does not necessarily exclude the existence of 'Co–Mo–S' on $Co–Mo/Al_2O_3$, but might limit the role of 'Co–Mo–S' in industrial HDS reaction. Also in relation to this problem, a 'Remote control model' has been proposed by Delmon et al. [17]

These problems indicate the need to recall some points should be reminded about experimental techniques. That is, (i) the characterization techniques adopted so far are mainly MES and EXAFS, whose information is predominated by the over-all structure of the catalysts, not by the surface structure. Therefore, combining these with surface sensitive techniques is necessary to evaluate the surface structure of Co–Mo/Al_2O_3 more clearly. And (ii) the catalyst pretreating (sulfiding) conditions reported so far are limited to atmospheric pressure, which is far from the working state of Co–Mo/Al_2O_3. It is possible that the surface structure of Co–Mo/Al_2O_3 sulfided at atmospheric pressure is different from that of Co–Mo/Al_2O_3 sulfided at higher pressure. In order to clarify the active sites for industrial HDS reaction on Co–Mo/Al_2O_3, it is necessary to characterize the surface structure of Co–Mo/Al_2O_3 under its working state, at least to evaluate in-situ (without exposing the catalyst to the air) the surface structure of Co–Mo/Al_2O_3 sulfided at high pressure.

In relation to problem (i), the authors have characterized the surface structure of Co–Mo/Al_2O_3 by combining NO probe method (NO uptake measurement and FT–IR/DRA study of adsorbed NO) as surface sensitive technique and Mo K-edge EXAFS, and found the new aspects of active site on Co–Mo/Al_2O_3. That is, we have investigated the benzothiophene HDS activity and the surface structure of Co–Mo/Al_2O_3 which is pretreated by combination of sulfiding and reducing, and reported that the formation ratio of Co site to Mo site correlates with the benzothiophene HDS efficiency [6]. In addition, comparing the surface structure of Co–Mo/Al_2O_3 with that of Ni–Mo/Al_2O_3 and Fe–Mo/Al_2O_3 in detail, it was found that the growth of MoS_2-like structure in the lateral direction on Fe–Mo/Al_2O_3, in which synergy effects for HDS of benzothiophene do not appear, is suppressed compared to that on Co–Mo/Al_2O_3 and Ni–Mo/Al_2O_3 [18,19]. However, in these studies, problem (ii) remains unsolved.

In the present work, we tried to study the surface structure of Co–Mo/Al_2O_3 under its working state by high pressure DRIFT method. That is, CUS distribution on the surface of Co–Mo/Al_2O_3 sulfided at high pressure was investigated by FT–IR/DRA study of adsorbed NO using high temperature ($\leq$773 K) and pressure ($\leq$5.1 MPa) in-situ IR cell. Furthermore, the fine structure around Mo of Co–Mo/Al_2O_3 was also investigated by Mo K-edge EXAFS using in-situ EXAFS cell.

As the results, we have found that the sulfiding pressure clearly changes the surface structure. Comparing Co–Mo/Al_2O_3 with the physical mixture, the following two points are noted. (A) The relative intensity of Co site-band of Co–Mo/Al_2O_3 is much stronger than that of the physical mixture in the range of 0.1–5.1 MPa. This suggests that Co site is selectively formed on Co–Mo/Al_2O_3, compared to the physical mixture of Mo/Al_2O_3 and Co/Al_2O_3. (B) it is also noted that the difference of the relative intensity of Co site-band between them is remarkable when the catalysts are sulfided at the pressure above 1.1 MPa. This suggests that Co site is more profoundly formed when Co–Mo/Al_2O_3 is sulfided at the pressure above 1.1 MPa. These two phenomena (A) and (B) suggest that a kind of surface interaction species is effectively formed between Co and Mo when Co–Mo/Al_2O_3 is sulfided at high pressure.

4. Conclusion

In order to evaluate the surface structure of Co–Mo/Al_2O_3 under its working state, the distributions of CUS of Co–Mo/Al_2O_3 and the physical mixture of Mo/Al_2O_3 and Co/Al_2O_3 sulfided at high pressure ($\leq$5.1 MPa) were investigated in-situ by FT–IR/DRA study of adsorbed NO. It was found that the CUS was selectively formed on Co site of Co–Mo/Al_2O_3, and the selectivity was clearly increased by higher pressure of sulfiding. On the other hand, Mo K-edge EXAFS measurement indicated that the dispersion of Mo does not change by higher pressure of sulfiding. Therefore, the selective formation of CUS on Co site is not due to the selective sintering of Mo site of Co–Mo/Al_2O_3. Based on these results, it was suggested that Co–Mo interaction species is effectively formed by higher pressure sulfiding. The present work shows more straightforward results, based on which one can discuss about the surface structure of Co–Mo/Al_2O_3 under its working state with respect to Co and Mo site distribution.

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