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Catalysis Today 50 (1999) 3–8

CATALYSIS TODAY

High pressure ($\leq$5.1 MPa) DRIFT study on surface structure of Co–Mo/Al_2O_3 and Ni–Mo/Al_2O_3 using NO as probe molecule[1]

Muneyoshi Yamada*, Naoto Koizumi, Masato Yamazaki

Department of Applied Chemistry, Graduate School of Engineering, Tohoku University, Aoba, Aramaki, Aoba-ku, Sendai, 980-8579, Japan

Abstract

The surface structures of Co–Mo/Al_2O_3 and Ni–Mo/Al_2O_3 sulfided at 0.1–5.1 MPa were investigated by the in situ DRIFT of adsorbed NO and Mo K-edge EXAFS. The relative intensities of IR bands of NO adsorbed on Co–Mo/Al_2O_3 and Ni–Mo/Al_2O_3 changed depending on the pressure of sulfiding. It was indicated that CUS were selectively formed on the promoters of Co–Mo/Al_2O_3 and Ni–Mo/Al_2O_3 when the catalysts were sulfided above 1.1 MPa. In other words, CUS of Mo disappeared by higher pressure of sulfiding. On the other hand, Mo K-edge EXAFS indicated that MoS_2-like structure of Co–Mo/Al_2O_3 was not sintered by higher pressures of sulfiding. Based on these results, it is concluded that the selective formation of CUS on the promoters of Co–Mo/Al_2O_3 and Ni–Mo/Al_2O_3 is caused by Co–Mo and Ni–Mo interaction by higher pressure of sulfiding resulting in the selective capping of CUS on Mo by the promoters. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Hydrotreating catalysts; Working state; Surface fine structure; Coordinatively unsaturated sites; High pressure DRIFT of adsorbed NO; High pressure EXAFS

1. Introduction

Co–Mo/Al_2O_3 and Ni–Mo/Al_2O_3 are 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 the catalysts. For this purpose, the high severity of the reaction conditions is necessary as well as the improvement of the catalyst performance. Not only to make clear the surface structure but also to improve the activity and selectivity of the catalysts, it is necessary to characterize the catalyst exposed to the severe reaction conditions.

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

In the present work, we tried to study the surface structure of Co–Mo/Al_2O_3 and Ni–Mo/Al_2O_3 by high pressure in situ methods. That is, the distribution of coordinatively unsaturated site (CUS) on these catalysts sulfided at high pressure was investigated by FT-IR/DRA study of adsorbed NO using high temperature

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*Corresponding author. Tel.: +81-22-217-7214; fax: +81-22-217-7293.

[1] Symposium on Catalysis in Fuel Processing and Environmental Protection. Sponsored by ACS, Divisions of Fuel Chemistry, Petroleum Chemistry and Environmental Chemistry, 214th ACS National Meeting, Las Vegas. NV, 7–11 September 1997.

PII: S0920-5861(98)00475-1

($\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.

One of the characteristic points of sulfided Co–Mo/Al_2O_3 and Ni–Mo/Al_2O_3 is the promoting effect of Co and Ni. That is, the addition of small amount of Co or Ni to Mo/Al_2O_3 drastically improves the HDS activity. The present work also aims to make clear this promoting effect through observing the fine structure of the catalysts which are exposed to high pressure sulfiding atmosphere.

2. Experimental

2.1. DRIFT measurement 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. After the temperature reached 673 K, the temperature was held for 1–10 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.

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

3. Mo K-edge EXAFS

Finely powdered catalyst was pressed into pellets, and was set in the high pressure EXAFS cell, which was made referring 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 heated to 673 K. 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 backscattering amplitudes and phase shifts reported by McKale et al. [5] were used. MoS_2 powder (supplied by Wako Pure Chemical Industries) was used as reference for Debye–Waller factor and photoelectron mean free path.

3.1. Catalyst preparation

Home-made Co–Mo/Al_2O_3, Mo/Al_2O_3 and Co/Al_2O_3 were used. Commercial Co–Mo/Al_2O_3 was also used. From here, the commercial Co–Mo/Al_2O_3 is denoted by Co–Mo/Al_2O_3 (CM) 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 (commercial, 333 m^2/g) was impregnated by $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (supplied by Wako Pure Chemical Industries) solution followed by drying (393 K, 16 h) and calcination (793 K, 12 h), and then Mo/Al_2O_3 (MoO_3: 15.8 wt%) was obtained. This Mo/Al_2O_3 was further impregnated by $Co(NO_3)_2\cdot 6H_2O$ (supplied by Wako Pure Chemical Industries) solution followed by drying (393 K, 16 h) and calcination (793 K, 12 h), and Co–Mo/Al_2O_3 was obtained. Co/Mo molar ratio was fixed at that of Co–Mo/Al_2O_3 (CM) (0.56 mol/mol). Co/Al_2O_3 (CoO: 5.2 wt%) was prepared as mentioned above.

4. Results and discussion

4.1. Distribution of CUS on Co–Mo/Al_2O_3 sulfided at high pressure

It is well known that NO adsorbs on CUS of Mo– or Co–Mo/Al_2O_3 catalyst. And it has been sometimes reported that the NO uptake correlates well with the HDS activity.

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}. Much weaker band also appears around 1700 cm^{-1}. From comparison with the spectra on Mo/Al_2O_3 and Co/Al_2O_3 (Fig. 3), the lower frequency (1800 and 1700 cm^{-1}) bands and higher frequency (1850 and 1800 cm^{-1}) bands can be assigned

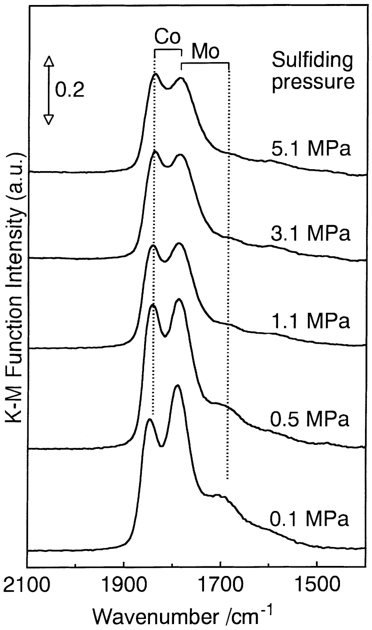

Fig. 1. DRIFT spectra of NO adsorbed on Co–Mo/Al_2O_3 sulfided at high pressure.

to NO adsorbed on Mo site and Co site, 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 name the higher frequency bands, Co site-band, and the lower frequency bands, Mo site-band.

It is noticed that the spectra of NO adsorbed on Co–Mo/Al_2O_3 sulfided above 1.1 MPa are different from that sulfided at 0.1 MPa. That is, increasing the sulfiding pressure above 1.1 MPa, lower frequency Mo site-band does not appear, and only two bands appear. Clearly, the relative intensity 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.

4.2. Effect of sulfiding duration and the stability of surface structure

The DRIFT spectra characteristic of the high pressure sulfided Co–Mo/Al_2O_3 was further examined from the different point of view, that is the effect of sulfiding duration and the stability to H_2 exposure.

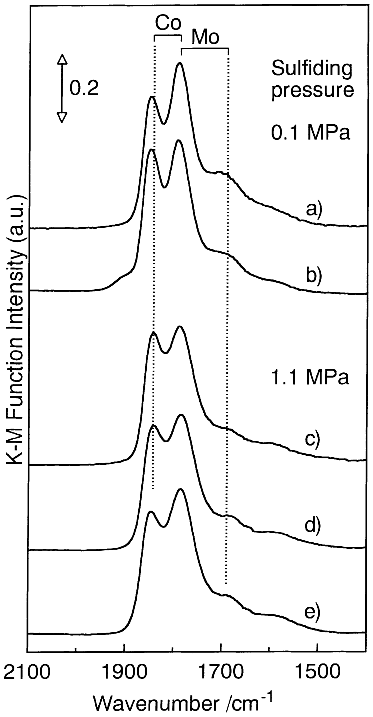

Fig. 2. DRIFT spectra of NO adsorbed on Co–Mo/Al_2O_3: (a) sulfided (0.1 MPa, 1 h); (b) sulfided (0.1 MPa, 10 h); (c) sulfided (1.1 MPa, 1 h); (d) sulfided (1.1 MPa, 1 h) and then reduced (3.1 MPa, 2 h); and (e) sulfided (1.1 MPa, 1 h) and then reduced (3.1 MPa ,10 h).

DRIFT spectra of NO adsorbed on Co–Mo/Al_2O_3 sulfided at 0.1 MPa for 1 h and 10 h are shown in Fig. 2. The relative intensity of Co site-band of 10 h sulfiding is a little stronger than that of 1 h. However, comparing Fig. 1 with Fig. 2, 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 change of the catalyst surface structure induced by 1.1 MPa sulfiding cannot be attained by simple extension of sulfiding duration at 0.1 MPa.

Furthermore, the stability of the catalyst surface to H_2 exposure was studied. Because the catalyst in industrial HDS process is usually exposed to a high pressure of hydrogen stream under its working state after presulfiding. Here, the catalyst, which was sulfided at 673 K under 1.1 MPa and then reduced in the

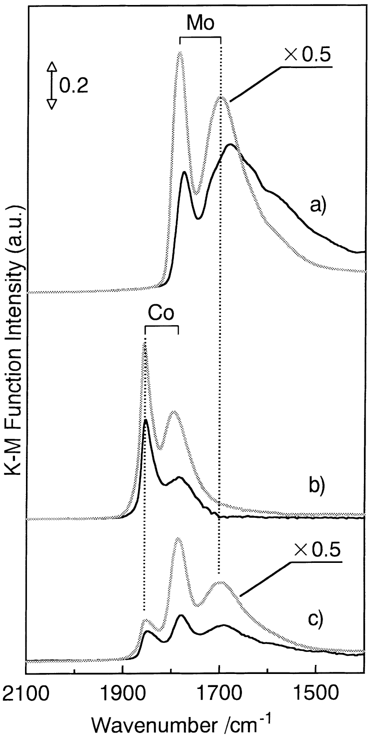

Fig. 3. DRIFT spectra of NO adsorbed on Mo/Al_2O_3 (a), Co/Al_2O_3 (b) and the physical mixture of Mo/Al_2O_3 and Co/Al_2O_3 (c).(▒▒▒▒) sulfided at 0.1 MPa, (———) sulfided at 3.1 MPa.

stream of hydrogen at 673 K under 3.1 MPa, was supplied for the same DRIFT measurement. The result is shown also in Fig. 2. The spectra of adsorbed NO are almost the same as that of the catalyst just sulfided. Even after 10 h reducing, the spectra are little changed. The present spectra suggest that the surface structure of Co–Mo/Al_2O_3, once presulfided, is stable under high pressure of hydrogen.

4.3. *Distribution of CUS of Mo/Al_2O_3, Co/Al_2O_3 and physical mixture of them*

Fig. 3 shows the DRIFT spectra of NO adsorbed on Mo/Al_2O_3 and Co/Al_2O_3, respectively, which were sulfided at 0.1 and 3.1 MPa. The spectra on Mo- and Co/Al_2O_3 show two bands, respectively. This doublet has been well known and been assigned to dinitrosyl species adsorbed on Mo site or Co site. Increasing the sulfiding pressure, the shape of doublet gradually changes. That is, the relative intensity of the lower frequency band increases compared to that of the higher frequency band.

Comparing Fig. 1 with Fig. 3, 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.

For understanding 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 in which Co/Mo molar ratio was fixed at 0.56, being equal to that of Co–Mo/Al_2O_3. Fig. 3 also shows the spectra of NO adsorbed on the physical mixture sulfided at 0.1 and 3.1 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 and Co/Al_2O_3. 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. It is clear that the spectra of NO adsorbed on the physical mixture seem to be a simple superposition of those on Mo/Al_2O_3 and Co/Al_2O_3.

Comparing the spectra of the physical mixture with that of Co–Mo/Al_2O_3, it is easy to point out the difference between them. That is three bands appear in the spectrum of the physical mixture, while 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 becomes more profound with increasing the sulfiding pressure.

However, it is not sure whether the CUS is selectively formed on Co site or the CUS on Mo site selectively disappear.

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

As mentioned above, the present results may indicate that Mo site of Co–Mo/Al_2O_3 has less number of

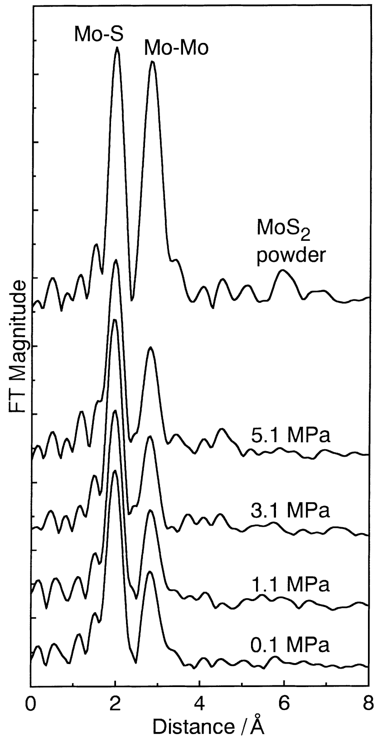

Fig. 4. Fourier transforms of Mo K-edge EXAFS of Co–Mo/Al_2O_3 sulfided at high pressure.

CUS compared to Mo/Al_2O_3 and the higher pressure of sulfiding decreases the relative ratio of CUS on Mo site. 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 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 Mo K-edge EXAFS method.

Fig. 4 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. 4 also shows that of MoS_2 powder for reference. As is shown, both 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 peaks suggest that fine structure around Mo in Co–Mo/Al_2O_3 is similar to MoS_2-like structure when Co–Mo/Al_2O_3 is sulfided at the pressure of 0.1–5.1 MPa. The coordination numbers calculated about Mo–S and Mo–Mo shells of Co–Mo/Al_2O_3 are shown in Fig. 5.

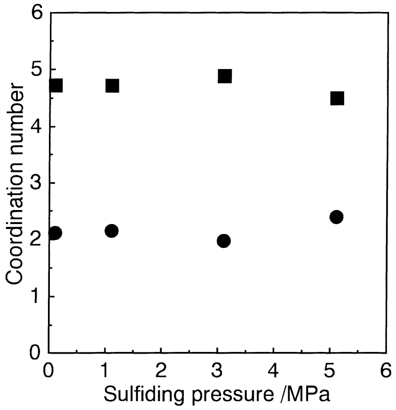

Fig. 5. Coordination number of Mo–S(■) and Mo–Mo(●) shell calculated from Fig. 4.

As can be seen from this Figure, 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. In other words, the surface structural change observed by IR 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.

However, the reason why Mo site 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, the reason why the higher pressure of sulfiding increases the selectivity of the disappearance of CUS on Mo site is also unclear.

4.5. *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. 6 shows DRIFT spectra of NO adsorbed on Ni–Mo/Al_2O_3 sulfided at the pressure of 0.1 and 3.1 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}. The similar asymmetric band also appears in the spectra of Ni/Al_2O_3 sulfided at the same pressure. Comparing with the reference samples (i.e., Mo/Al_2O_3 and Ni/Al_2O_3), the asymmetric band in Ni–Mo/Al_2O_3 can be assigned to NO adsorbed on Ni site.

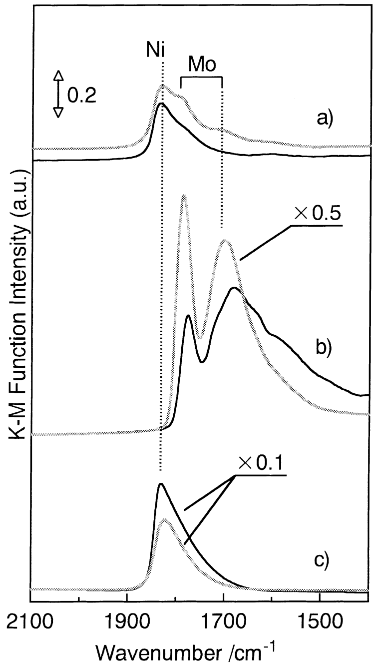

Fig. 6. DRIFT spectra of NO adsorbed on Ni–Mo/Al_2O_3 (a), Mo/Al_2O_3 (b) and Ni/Al_2O_3 (c). (············) sulfided at 0.1 MPa, (———) sulfided at 3.1 MPa.

The reason why the band looks like singlet is considered to be due to the molecular structure of dinitrosyl species.

The IR intensity of the Ni-site band in Ni–Mo/Al_2O_3 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 does not appear after sulfiding at the pressure of 3.1 MPa. As a result, 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 site even at lower pressure of sulfiding. This suggests that Ni interacts with Mo as well as Co.

5. Conclusion

The surface structures of Co–Mo/Al_2O_3 and Ni–Mo/Al_2O_3 sulfided at high pressure ($\leq$5.1 MPa) were investigated by means of both in situ DRIFT method of adsorbed NO and Mo K-edge EXAFS method. The former measurement indicated that CUS are selectively formed on the promoter site of Co–Mo/Al_2O_3 and Ni–Mo/Al_2O_3, especially by higher pressure of sulfiding. The latter indicated that Mo site of Co–Mo/Al_2O_3 is not sintered by higher pressure of sulfiding. Therefore, the present results suggest that the selective formation of CUS on the promoter site of Co–Mo/Al_2O_3 and Ni–Mo/Al_2O_3 is caused by Co–Mo or Ni–Mo interaction by higher pressure sulfiding, resulting in the selective capping of CUS of Mo site by the promoter.

Acknowledgements

This work was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture of Japan.

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