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Characterization of Active Sites in Sulfided Molybdenum/Alumina Hydrodesulfurization Catalysts

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The site configuration of Al_2O_3-supported molybdenum sulfides catalytically active for hydrodesulfurization (HDS) of thiophene has been investigated as a function of pretreatment conditions (H_2S/H_2=0—0.2) by using X-ray photoelectron, laser Raman and IR spectroscopies and temperature-programmed desorption of adsorbed NO. It has been found that when MoO_3/Al_2O_3 catalysts are presulfided with H_2S/H_2, MoS_2-like species are formed, whereas when prereduced and subsequently sulfided during the HDS reaction, molybdenum oxide sulfides or highly dispersed amorphous molybdenum sulfides are initially produced. The turnover frequency of the HDS reaction calculated on the basis of the NO adsorption was shown to increase with decreasing dispersion degree of sulfided molybdenum. It is proposed that two kinds of NO adsorption sites are present; triply and doubly coordinatively unsaturated (cus) molybdenum sites. It is considered that both sites are catalytically active, possibly, the triply cus species being more active. It is concluded that the HDS activity of sulfided MoO_3/Al_2O_3 catalysts is determined by the structure, dispersion and coordinative unsaturation of sulfided molybdenum.

Supported molybdenum catalysts are widely used in industry for hydrodesulfurization (HDS). Cobalt and/or nickel are employed to promote the molybdenum catalysts. The synergic effects of the promoters have been studied by many workers[1–6] and reviewed by several authors.[7–12] Recently, Topsøe et al. have shown by using Mössbauer emission spectroscopy that a Co–Mo–S phase on promoted sulfide catalysts is responsible for HDS reactions.[12–15] In this model, it is considered that molybdenum is described as a MoS_2-like structure. EXAFS studies indicated the presence of such structures on sulfided Mo/Al_2O_3 and $Co–Mo/Al_2O_3$ catalysts.[16–18] However, the configurations of active sites on these dispersed molybdenum sulfides have not been unveiled yet. They are functions of the degree of the molybdenum sulfidation[19] and support.[20]

In order to characterize the catalytically active Mo-sites, several molecules are used as a probe; NO,[21–27] O_2,[14,28–35] CO,[36,37] H_2S,[38,39] and pyridine.[19,40,41] The amount of NO,[15,42] O_2,[43] or H_2S[38] chemisorption is relatively well correlated to HDS activities. However, it has not been established yet which is the most appropriate probe molecule. Nitric oxide is considered to be one of the most convenient molecule for the IR studies due to its high extinction coefficient and for differentiating adsorption sites.[21–27] In addition, it is well-established that NO adsorbs on multiply cus (coordinatively unsaturated) molybdenum sites as a dinitrosyl[21] or dimeric[23] complex. Valyon and Hall[22] have suggested that cus Mo-sites in reduced catalysts are Mo^{2+} from the IR study of the coadsorption of NO and O_2.

In order to reveal the configuration of the active sites on molybdenum sulfides responsible for the thiophene HDS reaction, an NO adsorption study was carried out herein for MoO_3/Al_2O_3 catalysts sulfided under various conditions, coupled with X-ray photoelectron (XPS), laser Raman (LRS) and IR spectroscopies and temperature-programmed desorption techniques.

Experimental

γ-Al_2O_3 was supplied by the Catalysis Society of Japan as a reference catalyst (JRC-ALO-4).[39] The B.E.T. surface area of the support was 163 m^2g^{-1}.

Supported molybdenum catalysts were prepared by an incipient impregnation method.[39] The loading level of MoO_3 was adjusted to be 2.5—30 wt% with respect to the support. An aqueous solution of the appropriate concentration of ammonium heptamolybdate (Nakarai Chemicals) was added to the Al_2O_3 (1.2 cm^3g-$(Al_2O_3)^{-1}$) and kneaded for 10 min at room temperature. Subsequently, the catalyst slurry was dried at 383 K for 18 h, followed by calcination in air at 823 K for 5 h.

The presulfidation of the catalyst was carried out at 673 K for 1.5 h in a stream of an atmospheric pressure of H_2S/H_2 (H_2S/H_2; 0—0.20, 500 mL STP min^{-1}). Subsequently, the HDS reaction of thiophene was carried out at the same temperature in an atmospheric pressure of a thiophene/H_2 stream (1.6% thiophene, 1 L STP min^{-1}), followed by measurements of catalytic activity at the reaction time of 1—1.5 h. The reaction gas was analyzed by GLC. The catalyst was, then, treated with an atmospheric pressure of a deoxygenated and dehydrated H_2-stream at 673 K for 1 h and evacuated for 1 h at the same temperature. After being cooled to room temperature under a dynamic vacuum, the amount of NO chemisorption was measured at room temperature (exposed to NO for 0.5 h and evacuated for 1 h, accompanied by NO physisorption experiments). After that, the XP spectra of the catalyst was measured without exposing the catalyst to air. The XPS measurements were made on a Hitachi 507 photoelectron spectrometer using Al $K\alpha_{1,2}$ radiation (1486.6 eV). The anode was operated at 9 kV and 50 mA. Assuming linear backgrounds, the intensity ratios were determined by using the integrated areas of the Mo3d, S2p, S2s, and Al2p levels. The binding energies were referenced to the Al2p level at 74.5 eV.

The measurements of IR, temperature-programmed desorption (TPD) of NO and LR spectra were made in situ for the activated catalyst samples. The samples were exposed to NO and/or H_2S at room temperature for the IR and TPD studies. The IR spectra of the catalyst were recorded in a transmittance mode at room temperature on a Hitachi EP1-G double beam spectrophotometer by employing self-supporting wafers. The TPD study of NO adsorbed on the sulfided catalyst was conducted in a dynamic vacuum at a rate of 1.8 K min^{-1} from room temperature to ca. 570 K and evolved gases were continuously and repeatedly analyzed by a mass filter (ULVAC, MSQ-150A). The LR spectra were obtained by using an in situ cell at room temperature with a JASCO R-800 spectrometer equipped with a double monochromater. The 514.5 nm line of a NEC GLS-3200 Ar^+ laser was used for excitation at the intensity of 150—200 mW at the source. A spectral resolution was 5 cm^{-1}.

Results and Discussion

The HDS activities of the MoO_3/Al_2O_3 catalysts for thiophene are shown in Fig. 1 as a function of the H_2S/H_2 ratio in the presulfidation and the loading level of MoO_3. It is apparent that when the catalyst (5–30 wt% MoO_3) is presulfided at an increasing H_2S/H_2 ratio, the activity decreases steeply at a low H_2S/H_2 ratio (< 0.02) and then diminishes gradually at a futher increase in the ratio. At $H_2S/H_2=0$, the MoO_3/Al_2O_3 catalyst was reduced with H_2 and then sulfided with thiophene and/or resultant H_2S during the HDS reaction. At 2.5 wt% MoO_3 content, on the other hand, the HDS activity increases as the H_2S/H_2 ratio increases. It has been previously found that the activation mode of the catalyst affects the activity of the sulfided catalyst.[19]

In addition, the duration of the sulfiding treatment is an important factor determining the HDS activity when the H_2S/H_2 ratio is very low. On the sulfidation by thiophene/H_2 ($H_2S/H_2=0$ in Fig. 1), the catalytic activity of the 15 wt% MoO_3/Al_2O_3 catalyst decreased gradually to a conversion of 35% after a 12 h-treatment. During this treatment, the H_2S/H_2 ratio caused by the conversion of thiophene was calculated to be ca. 0.008. Therefore, the H_2S/H_2 ratio is considered to determine the rate of the sulfidation of molybdena under our experimental conditions. A direct sulfidation of the catalyst without the prereduction has been found to provide a sulfided catalyst similar to the one obtained at $H_2S/H_2=0$.[19] Accordingly, it is considered that the dependence of the HDS activity on both the sulfidation conditions and the loading level of MoO_3 is correlated to the differences in the structure (including a transient one) and dispersion degree of molybdenum sulfides formed on the catalyst surface.

As shown in Fig. 1 the HDS activity increases up to a loading level of 15 wt% MoO_3 and becomes independent of the MoO_3 loading level regardless of the sulfidation conditions. This is attributable to a formation of well-dispersed molybdenum species up to 15 wt% MoO_3 and in accord with the XRD and XPS results; no detection of crystalline MoS_2 by XRD and a linear correlation between the Mo3d/Al2p XPS intensity ratio and the surface concentration of molybdenum at <15 wt% MoO_3 as observed previously.[19] No significant change in the Mo3d/Al2p ratio was observed on the sulfidation of the catalyst with H_2S/H_2. The previous observations[19] of a considerable variation in the XPS intensity ratio on sulfidation may be attributed to the use of CS_2/H_2 for sulfiding instead of H_2S/H_2 and/or to different levels of impurities on Al_2O_3 surfaces which greatly modify the surface properties of Al_2O_3 as shown previously for the H_2S adsorption.[39]

The degree of sulfidation of molybdenum, S/Mo atomic ratio, is depicted in Fig. 2 as a function of the

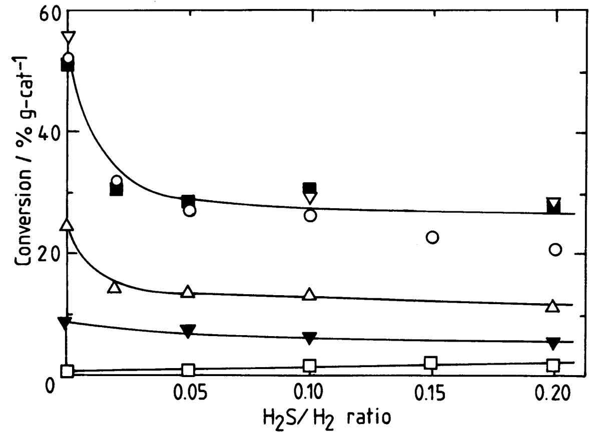

Fig. 1. Dependence of the thiophene HDS activity of sulfided MoO_3/Al_2O_3 catalyst on the H_2S/H_2 ratio in sulfiding.
□, 2.5 wt%; ▼, 5 wt%; △, 10 wt%; ○, 15 wt%; ▽, 20 wt%; ■, 30 wt%.

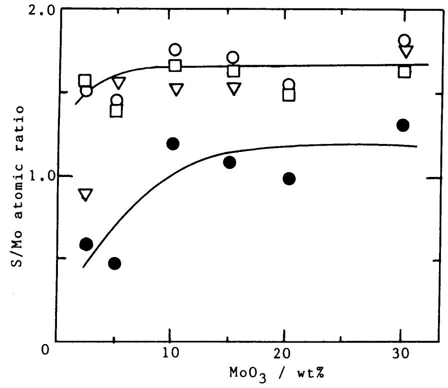

Fig. 2. S/Mo atomic ratio as a function of the MoO_3 content for the sulfided catalyst after the HDS of thiophene at 673 K.
●, $H_2S/H_2=0$; ▽, 0.05; ○, 0.1; □, 0.2.

MoO_3 content. The S/Mo ratio was calculated from the S2p/Mo3d XPS intensity ratio.[19] Apparently, the S/Mo ratio is increased by the H_2S/H_2-presulfidation and almost independent of the H_2S/H_2 ratio at$>$0.05. The S/Mo ratio gradually increases with the MoO_3 content up to 10 wt% (except a considerably low S/Mo ratio for the 2.5 wt% MoO_3 catalyst activated at 0.05) and becomes constant (S/Mo=1.6—1.7). It is evident that the S/Mo ratio is lower than two, this suggesting an incomplete transformation of supported molybdenum to MoS_2. As shown in Fig. 2, under the conditions of $H_2S/H_2=0$, however, the S/Mo atomic ratio increases with increasing the MoO_3 content up to 15 wt% and levels off at a lower S/Mo ratio (1.0—1.2) compared with that attained when presulfided. This suggests that the structures of sulfided molybdenum species formed on the catalyst surface are significantly different between the presulfidation and prereduction conditions. It is noted that the molybdenum sulfide species produced at a very low H_2S/H_2 ratio are gradually transformed to the stable molybdenum sulfide species produced at $H_2S/H_2> 0.1$ (vide infra).

These findings suggest that a considerable portion of molybdenum species which resists sulfiding exists in the low MoO_3 content catalysts, especially, at 2.5 wt% MoO_3. Zingg et al.[44] have reported with MoO_3/Al_2O_3 catalysts that the molybdenum occupies mainly tetrahedral sites at a low MoO_3 content and that two types of tetrahedral molybdenum species are present on the oxidic catalyst. These are monomeric and dimeric species. The monomeric species resists sulfiding, while the dimeric species are easily sulfided to MoS_2. Our results are in line with their model.

It is well-established that NO adsorbs on cus Mo-sites in a pair.[21] The amount of NO adsorption is relatively well correlated to the HDS activity.[15,42] Therefore, the dispersion degree of molybdenum was assessed by the amount of NO chemisorption. The fraction of cus Mo-sites thus obtained is shown in Fig. 3 against the MoO_3 content. The fraction varied with the H_2S/H_2 ratio, too. At H_2S/H_2 ratio of $>$0.1, the proportion of the adsorption site decreases as the MoO_3 content increases. As for the 2.5 wt% MoO_3 catalyst, 25–30% of molybdenum adsorb two NO molecules when properly activated. While, at the low H_2S/H_2 ratios, the fraction of NO-adsorption sites shows a maximum (at 10 and 20 wt% MoO_3 for H_2S/H_2=0.05 and 0, respectively). The proportion of cus Mo-sites in the low MoO_3 content catalysts (2.5 and 5 wt%) increases with increasing H_2S/H_2 ratio, while the fraction decreases for the catalysts containing 10—30 wt% MoO_3.

The turnover frequency (TOF) of the thiophene HDS reaction on the sulfided molybdenum catalyst was obtained on the basis of the amount of NO chemisorption. The TOF is shown in Fig. 4 as a function of the MoO_3 content. When the catalyst was presulfided with H_2S/H_2, the TOF increased with the MoO_3 content almost irrespective of the sulfidation conditions. At $H_2S/H_2=0$, however, a plateau is seen above 15 wt% MoO_3. It is considered that the dependence of TOF on the MoO_3 content results from the changes of the structure and dispersion of active molybdenum species.

In an analogy with the estimation of the dispersion degree of metal by using CO or H_2 adsorption for supported metal catalysts,it is proposed that the extent of dispersion of molybdenum sulfides ($D_{\text{Mo-S}}$) is evaluated from the amount of NO adsorption and the degree of sulfidation of molybdenum as in Eq. 1.

$$D_{\text{Mo-S}} = (\text{Fraction of Mo which adsorbs } (\text{NO})_2)/(\text{Fraction of molybdenum sulfides}) \qquad (1)$$

On the basis of the XPS results of Li and Hercules,[45] it is assumed here that the stoichiometry of sulfided

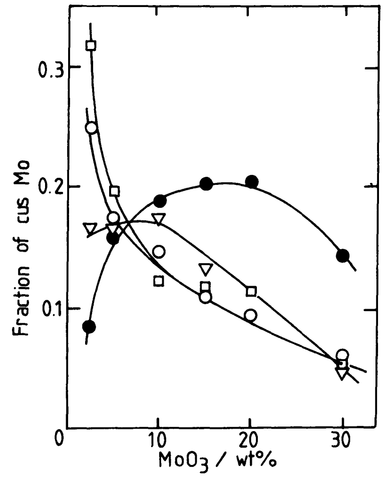

Fig. 3. Fraction of cus Mo (a half of the NO/Mo molecular ratio) vs. MoO_3 content measured after the HDS of thiophene at 673 K.
●, $H_2S/H_2=0$; ▽, 0.05; ○, 0.1; □, 0.2.

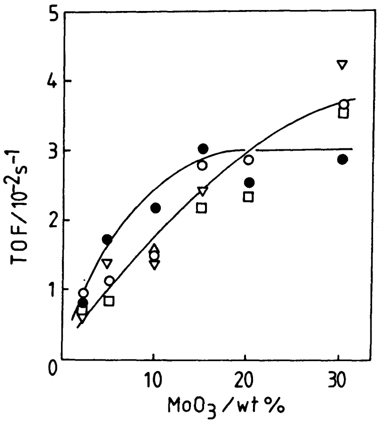

Fig. 4. Dependence of the TOF of thiophene HDS reaction over the sulfided catalyst upon the MoO_3 content.
●, $H_2S/H_2=0$; ▽, 0.05; ○, 0.1; □, 0.2.

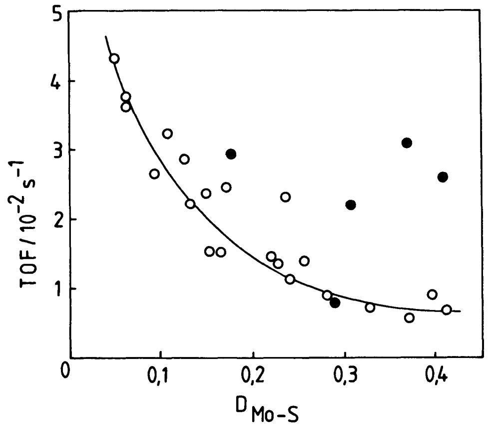

Fig. 5. Dependence of the TOF of thiophene HDS reaction on the dispersion degree of molybdenum sulfide.
●, H_2S/H_2=0; ○,>0.1.

molybdenum species is two. The incomplete sulfiding of Mo in Fig. 2 indicates a partial transformation of Mo oxides to the sulfide species. The TOF of the thiophene HDS reaction is depicted in Fig. 5 against the dispersion degree of molybdenum sulfides. When the catalyst was presulfided ($H_2S/H_2 > 0$),the TOF is evidently correlated to the dispersion degree of molybdenum sulfides; the TOF increases, as the degree of MoS_2 dispersion decreases. The decreased dispersion degree is considered to correspond to an increased size of molybdenum sulfides, although no crystalline MoS_2 was detected by XRD except the catalyst with the lowest dispersion (30 wt% MoO_3). However, the TOF at H_2S/H_2=0 is higher than that for the presulfided catalysts and seems independent of the dispersion degree of molybdenum sulfides. It is suggested that the structure of sulfided molybdenum species formed at H_2S/H_2=0 are different from those produced by presulfiding with H_2S/H_2.

In order to characterize the molybdenum sulfides, in situ LRS techniques were used. Typical spectra are shown in Fig. 6. Regardless of the H_2S/H_2 ratio and loading levels, the peak at ca. 960 cm^{-1} in the oxidic state, which is characteristic of well-dispersed polymolybdate phases,[46-48] completely disappeared after sulfidation. The LR spectra indicated that molybdenum oxides with Mo=O bonds were completely sulfided by H_2S/H_2 or the thiophene HDS reaction. When the catalyst was presulfided, a strong peak at 405 cm^{-1} accompanied by broad peaks at ca. 450 and 380 cm^{-1} was observed. These pair peaks are assigned to a MoS_2 phase.[49] The above findings indicate that the molybdenum sulfides formed on sulfided catalyst have a MoS_2-like structure. Clausen et al.[16,17] and Huntly et al.[18] recently observed the presence of microcrystalline MoS_2 in sulfided catalysts by using EXAFS. On the other hand, when the catalyst was prereduced and subsequently sulfided during the reaction, the peaks at 380 and 405 cm^{-1} were not observed and only broadened peaks at 450 and 350 cm^{-1} due to a Mo–S stretching bands[49] were detected as shown in Fig. 6. It is considered that the structure of the active molybdenum species is not a MoS_2-like structure, suggesting the formation of molybdenum oxide sulfides or highly dispersed amorphous molybdenum sulfides. However, after a prolonged sulfiding by the thiophene/H_2(12 h), the LR spectra showed a transformation of the above sulfides to MoS_2-like species. This is consistent with the variation in the catalytic activity.

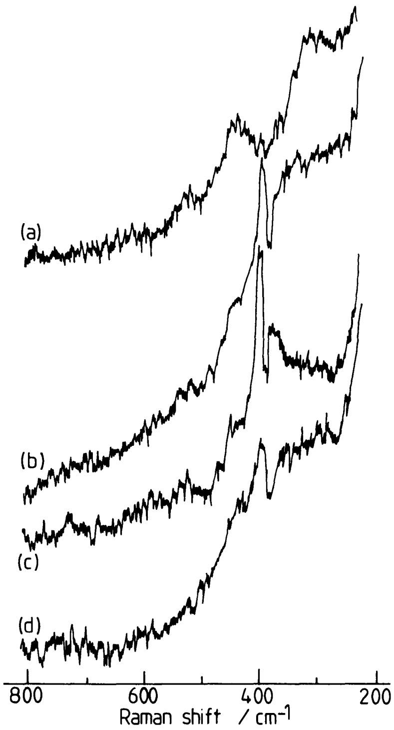

Fig. 6. In situ laser Raman spectra for MoO_3/Al_2O_3 catalysts sulfided at 673 K in an atmospheric H_2S/H_2 stream, followed by the HDS of thiophene at the same temperature.
(a) 15 wt%, H_2S/H_2=0; (b) 15 wt%, 0.02; (c) 15 wt%, 0.1; (d) 2.5 wt%, 0.1.

The IR spectra of NO adsorbed on the sulfided catalysts are illustrated in Fig. 7. Irrespective of the pretreatment conditions, the spectra consist of two adsorption peaks at 1795 and 1715—1690 cm^{-1}. They are assigned to symmetric and asymmetric stretching bands of dinitrosyl species, respectively.[50] The band positions indicate that two NO molecules adsorb on sulfided Mo-sites.[22,25] It is considered that even under the pretreatment conditions of H_2S/H_2=0, cus Mo-sites are actually sulfided during the HDS reaction of thiophene. However, the spectroscopic features at H_2S/H_2=0 and those at 0.1 are significantly different; the symmetric/asymmetric intensity ratios are 1.02 and 1.36 at H_2S/H_2=0 and 0.1, respectively. The ON–Mo–NO angle (θ) is suggested to be different in

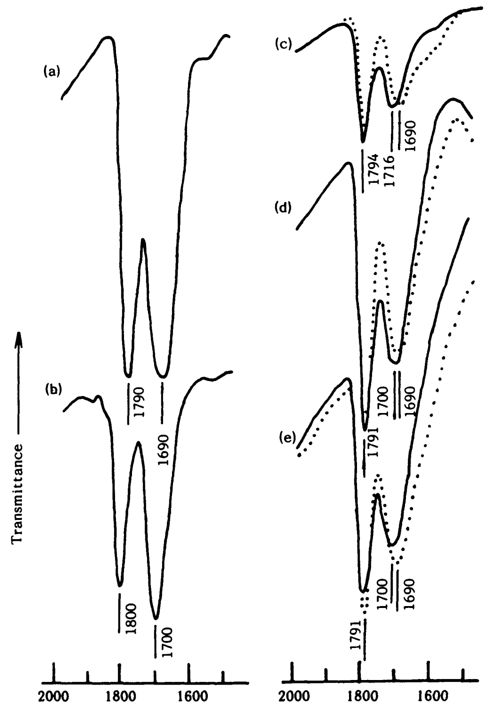

Fig. 7. IR spectra of NO adsorbed on the MoO_3/Al_2O_3 catalysts reduced or sulfided at 673 K in an atmospheric H_2 or H_2S/H_2 stream, followed by the HDS of thiophene at the same temperature.
(a) 10 wt%, only reduced; (b) 10 wt%, $H_2S/H_2=0$; (c) 2.5 wt%, 0.1; (d) 10 wt%, 0.1; (e) 20 wt%, 0.1. The dotted line shows the change of the IR spectrum of preadsorbed NO when the sample was exposed to H_2S (5.3 kPa) and evacuated at room temperature for 30 min.

these two sulfides and calculated to be 90 and 81°, when prereduced and presulfided, respectively, on the basis of a theoretical equation;[50] $I_{sym}/I_{asym}=\cot^2(\theta/2)$. In conjunction with the results of LRS measurements, the IR spectrum observed at $H_2S/H_2=0.1$ is assigned to NO molecules adsorb on a MoS_2-like structure, whereas the spectrum at $H_2S/H_2=0$ to dinitrosyls adsorbed on molybdenum oxide sulfides or highly dispersed amorphous molybdenum sulfides. The IR spectroscopic features for NO adsorbed on the catalyst at $H_2S/H_2=0$ is very close to those for NO held on a reduced MoO_3/Al_2O_3 catalyst as shown in Fig. 7. This suggests that the structure of the sulfides formed under mild sulfidation conditions is similar to the structure of molybdenum oxide precursor phase. Taking into consideration the observations[51] that part of polymolybdate species are reduced at a relatively low temperature such as 673 K employed here, it is considered that initial sulfidations occur with polymolybdate species irrespective of the prereduction and keep these original structures almost intact to produce molybdenum oxide sulfides or amorphous molybdenum sulfides. A formation of oxide sulfides from polymolybdates has been proposed by Schrader and Chang using LRS.[49]

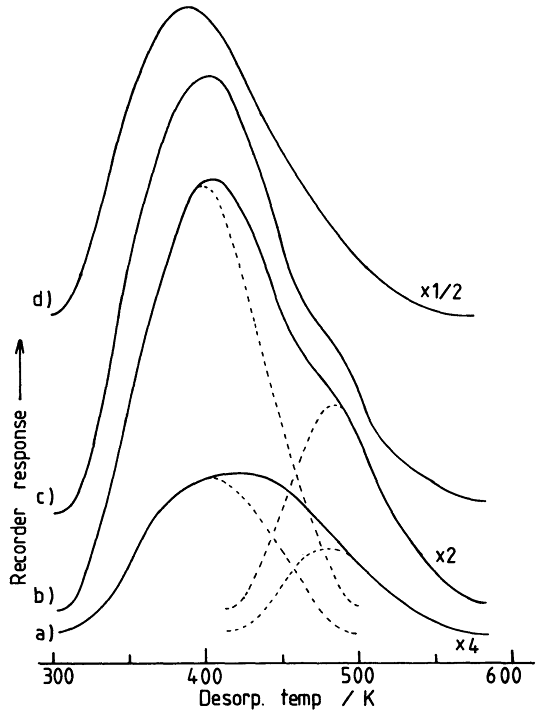

Fig. 8. TPD profiles ($m/z=30$) of NO adsorbed on the sulfided MoO_3/Al_2O_3 catalyst ($H_2S/H_2=0.1$).
(a) 2.5 wt%, (b) 5 wt%, (c) 10 wt%, (d) 20 wt%. The broken lines show the resolved peaks.

The dependence of the TOF of thiophene HDS reaction on the dispersion degree of sulfided molybdenum in Fig. 5 suggests the presence of several kinds of molybdenum sites. In order to characterize further the NO adsorption sites, the TPD study of NO adsorbed on sulfided catalyst was conducted. The TPD profiles of NO ($m/z=30$) are shown in Fig. 8. The main peak is observed at a desorption temperature of ca. 400 K, accompanying a weak shoulder at a higher temperature side (ca. 480 K). It seems that the relative intensity of the main peak at ca. 400 K increases with increasing MoO_3 content in the catalyst. It is revealed that two kinds of NO adsorption sites are differentiated by the TPD techniques. According to the IR measurements in Fig. 7, the TPD peaks are likely to be attributed to the signals due to distinct sulfided Mo-sites but not to composite peaks of sulfided and reduced Mo-sites. The presence of two desorption peaks in the TPD study was confirmed for molybdenum sulfides supported on TiO_2 in a more conclusive manner.[52] Segawa et al.[53] reported two NO desorption peaks for reduced MoO_3/TiO_2 systems. The thermal desorption of NO accompanied a production of N_2O; the desorption temperature of N_2O was ca. 400 K and the peak area intensity ratio of N_2O/NO did not vary significantly with MoO_3 content.

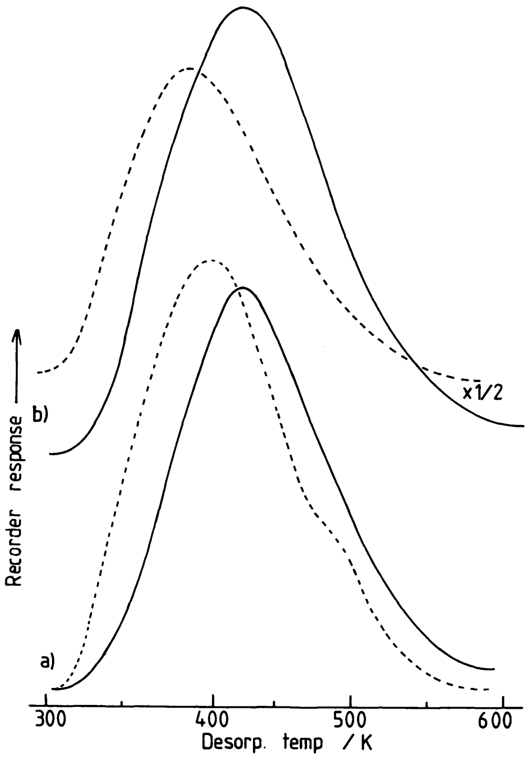

Fig. 9. TPD profiles (m/z=30) of NO on the sulfied MoO_3/Al_2O_3 catalyst (H_2S/H_2=0.1) coadsorbed with H_2S.
(a) 10 wt%, (b) 20 wt%. The broken lines show the TPD profile of adsorbed NO alone.

In order to determine the configuration of the sulfided Mo-sites, a coadsorption of NO and H_2S was examined. Figure 7 shows the changes in the IR spectra of NO when H_2S was introduced. No NO molecules were desorbed by the exposure of the sample to H_2S and by a subsequent evacuation at room temperature. On a contact of the NO-adsorption system with H_2S, the symmetric and asymmetric bands became considerably well separated, since the wavenumber of the latter peak was red-shifted by ca. 10 cm^{-1}. A pre-adsorption of H_2S considerably reduced the IR intensity of adsorbed NO. However, a similar red-shift of the lower-wavenumber peak of NO band was also observed. Accordingly, the spectral changes are considered to result from the interactions between adsorbed NO and H_2S molecules.

The TPD profiles of NO coadsorbed with H_2S are shown in Fig. 9. The desorption peak of H_2S (m/z=34) was observed at ca. 360 K. This is attributed to α-H_2S adsorbed on bare Al_2O_3 surface.[39] Hydrogen sulfide adsorbed on sulfided molybdenum sites is expected to desorb at higher temperature than 600 K.[39] It is noteworthy that the temperature of NO desorption at ca. 400 K is increased by 30 K on the exposure of the sample to H_2S. The peak area intensity ratio of N_2O/NO significantly decreased by the H_2S adsorption. These findings also suggest the presence of direct interactions between adsorbed NO and H_2S molecules. On the basis of the IR and TPD results, we propose here that sulfided Mo-sites for NO adsorption consist of triply and doubly cus molybdenum species and that NO molecules adsorbed on the triply cus sites desorb at ca. 400 K, while those on the doubly cus sites at ca. 480 K. Both NO species adsorb to form dinitrosyl or dimeric complex. Hydrogen sulfide molecule adsorbs on the triply cus Mo-sites preadsorbed with two NO molecules, affecting the IR and TPD of NO. The TPD peak at 430 K is assigned to the desorption of NO adsorbed on the triply cus Mo-sites coadsorbed with H_2S or SH. With increasing MoO_3 content in the MoO_3/Al_2O_3 catalyst, the size of MoS_2 particles increases as deduced from the decrease in the NO/Mo ratio, accompanying an increase in the fraction of the triply cus Mo-sites. This may be rationalized by a stabilization of multiply cus Mo-sites by electronically compensating properties of bulky semiconducting MoS_2 phases.

Combining the results on the TOF of sulfided MoO_3/Al_2O_3 catalysts for the HDS reaction with the configuration of the NO adsorption sites, it is suggested that both the triply and doubly cus molybdenum species are active for the HDS of thiophene, probably the triply cus Mo-sites showing higher activity. The activity of the sulfided MoO_3/Al_2O_3 catalyst is determined by two adverse factors; the number of active sites (NO adsorption sites) and the relative proportion of the triply and doubly cus Mo-sites. These adverse factors are considered to cause a volcano type correlation between the intrinsic activity (activity/unit weight of Mo) and sulfidation degree of molybdenum (S/Mo) as observed previously.[19]

Conclusion

On the basis of the results of XPS, LRS, and IR of NO absorbed on the catalyst, it is revealed that the structure of molybdenum sulfides formed on MoO_3/Al_2O_3 catalysts varies with the H_2S/H_2 ratio in the presulfiding atmosphere. It is demonstrated that MoS_2-like structure is formed when presulfided ($H_2S/H_2>0.02$), while molybdenum oxide sulfides or highly dispersed amorphous molybdenum sulfides are initially formed when prereduced ($H_2S/H_2=0$). The difference in the structure causes the difference in the thiophene HDS activity.

From the results of IR and TPD of NO adsorbed on sulfided catalysts, it is suggested that the NO adsorption sites consist of multiply cus molybdenum species, triply and doubly cus Mo-sites. The fraction of the triply cus Mo-sites increases with increasing molybdenum content or with increasing size of molybdenum sulfide clusters. Taking into account the thiophene HDS activity, it is considered that both sites are active for the reaction, the triply cus sulfided molybdenum species being more active than the doubly cus sulfided molybdenum species.

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