XAFS study on the sulfidation mechanisms of Co-Mo catalysts supported on activated carbon and alumina: effect of complexing agent

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The effect of nitrilotriacetic acid (NTA) as a complexing agent on the sulfidation mechanisms of Co-Mo catalysts supported on activated carbon and alumina was examined by the XAFS technique. The XAFS results revealed that NTA interacted with Co atoms and formed the Co-NTA interaction, while it showed almost no influence on the local structures around Mo atoms. The Co-NTA interaction suppressed the aggregation of cobalt atoms and the interaction between cobalt and alumina during sulfiding, and consequently promoted the formation of the Co-Mo-S phase.

Keywords: XAFS, HDS catalyst, Co-Mo, complexing agent, nitrilotriacetic acid.

1. Introduction

Co-Mo/Al_2O_3 catalysts are extensively used as commercial hydrodesulfurization (HDS) catalysts. The structures of active species in Co-Mo catalysts are widely recognized to be the so-called “Co-Mo-S” phase in which Co atoms are coordinated at the edge sites of small MoS_2 slabs proposed by Topsøe et al. (1981). Bouwens et al. (1991) reported that the Co-Mo-S phase was selectively generated on activated carbon with a large surface area by the addition of nitrilotriacetic acid (NTA). But the physical properties of the carbon support were much different from alumina and there are few reports about the NTA effect on alumina supported Co-Mo catalysts.

In this report, we describe the effect of NTA on the formation of the Co-Mo-S phase when employing alumina as a support.

2. Experimental

2.1 *Catalyst preparation*

The Co-Mo/Al_2O_3 catalysts with 3.1 wt% of CoO and 12.2 wt% of MoO_3 were prepared by coimpregnation of γ-Al_2O_3 (SA=211 m^2g^{-1}, PV = 0.91 cm^3g^{-1}) with an aqueous solution of $Co(NO_3)_2$ and $(NH_4)_6Mo_7O_{24}$, followed by drying at 383 K for 12 h and calcining at 773 K for 3 h.

The carbon supported Co and Co-Mo catalysts were prepared using a carbon support with a similar surface area (SA=225 m^2g^{-1}, PV=0.85 cm^3g^{-1}) to the alumina support. The loading of Co(3.3 wt%) and Mo(13.0 wt%) were adjusted to have the same number of atoms per unit surface area as that of the alumina support (Co; 1.2 atoms nm^{-2} Mo; 2.4 atoms nm^{-2}). Calcination was not applied to the carbon supported catalysts to prevent the change in the properties of the carbon support.

NTA-added catalysts (Co-Mo(NTA)/Al_2O_3, Co(NTA)/carbon and Co-Mo(NTA)/carbon) were prepared by adding NTA to the aqueous solution of $Co(NO_3)_2$ and $(NH_4)_6Mo_7O_{24}$ with a NTA/Co molar ratio of two.

2.2 *XAFS measurement*

The catalyst after drying or calcining was pressed into a pellet, with a proper thickness for the transmission measurement and introduced into the in-situ transfer cell, which enable the XAFS measurement without an exposure of the catalyst to the air. The catalysts were sulfided in a stream of 5% H_2S/N_2 (100cm^3/min) for 4 h at 673 K (rate; 100 K/h). The XAFS spectra were recorded at the room temperature using BL-7C (Si (111) DXM) and BL-10B (channel-cut Si (311) DXM).

Fourier transformation of k/f(k) weighted EXAFS oscillations was performed in the range of Δk=8.5 for Co K-edge and Δk = 11.0 for Mo K-edge. Phase shifts and back scattering amplitudes were corrected using theoretical values for CoO and MoO by Teo and Lee (1979).

3. Results and Discussion

3.1 *Mo K-egde XAFS*

Fourier transforms of the Mo K-edge EXAFS spectra of the Co-Mo catalysts show two peaks assigned to Mo-S and Mo-Mo shell which are almost same peak position as those of reference MoS_2 (Fig. 1), indicating the existence of MoS_2-like structure in the catalysts. Table 1 summarizes the coordination numbers of S($N_{Mo\text{-}S}$) and

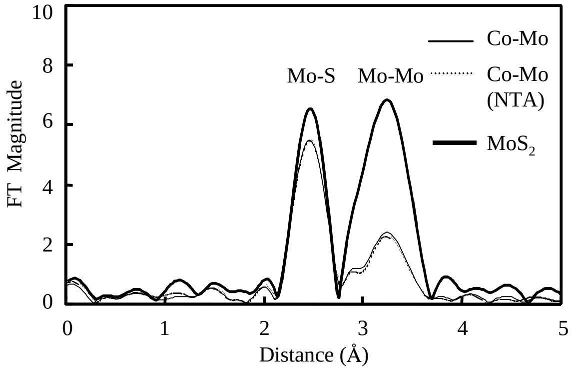

Figure 1
Fourier transforms of the Mo K-edge EXAFS spectra for Co-Mo/Al_2O_3 catalysts.

Table 1
The effect of NTA on the local structures around Mo atoms in Co-Mo catalysts from the Mo K-edge EXAFS measurement.

Catalysts	N(Mo-S)	N(Mo-Mo)	N(Mo-Mo) /N(Mo-S)
Co-Mo/C	4.7	2.0	0.43
Co-Mo(NTA)/C	4.9	2.1	0.43
Co-Mo/Al_2O_3	5.0	2.1	0.42
Co-Mo(NTA)/Al_2O_3	5.0	2.0	0.40
MoS_2	6	6	1

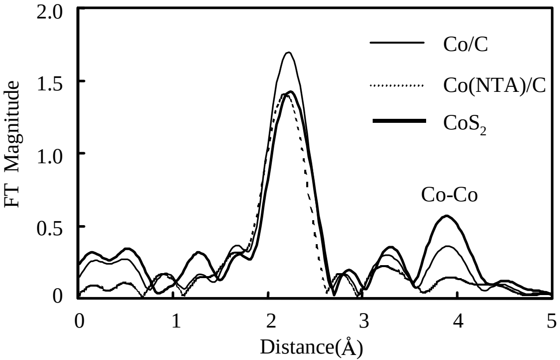

Figure 2
Fourier transforms of the Co K-edge EXAFS spectra for Co/carbon catalysts.

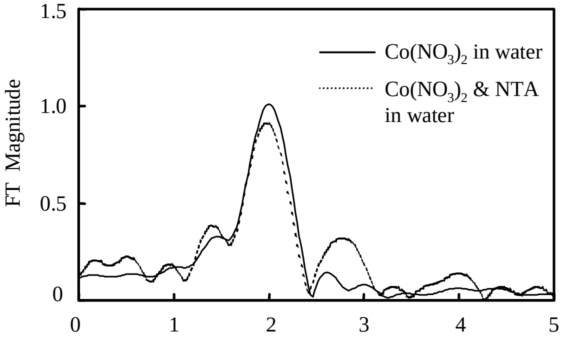

Figure 3
Fourier transforms of the Co K-edge EXAFS spectra for the Co aqueous solutions.

Mo ($N_{Mo\text{-}Mo}$) around Mo atoms calculated from the peak intensities of MoS_2. There is almost no difference in the degree of the sulfidation and the aggregation of Mo atoms by the addition of NTA. Therefore, the addition of NTA hardly changes the local structures around Mo atoms during sulfiding.

3.2 *Co K-edge XAFS*

Fig. 2 shows the Co K-edge EXAFS Fourier transforms of Co/carbon, Co(NTA)/carbon catalysts. The addition of NTA shortens the distance of the first shell coordination from 2.22 Å which is similar to one of the Co sulfide (2.24 Å) to 2.18 Å. Also, the peak intensity of the second shell at around 3.9 Å, attributed to the Co-Co bond of the Co sulfide, decreases by the addition of NTA. Furthermore, as shown in Fig. 3, the peak features changes by the addition of NTA even in the Co aqueous solution, indicating the interaction between NTA molecule and Co atom. These results suggest that the Co-NTA interaction is formed in the Co aqueous solution and still remains after sulfiding. Thus, the Co-Co interaction which will lead to the bulky Co sulfide is suppressed due to the Co-NTA interaction.

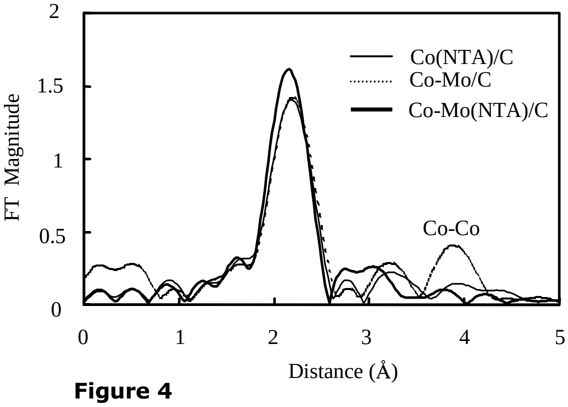

Figure 4
Fourier transforms of the Co K-edge EXAFS spectra for Co/carbon and Co-Mo/carbon catalysts.

Fig. 4 shows the Co K-edge EXAFS Fourier transforms of Co/carbon, Co-Mo/carbon catalysts. The addition of NTA into Co-Mo/carbon preparation shortens the distance of the first shell from 2.19 Å to 2.15 Å and the peak due to the Co-Co bond of the Co sulfide decreases. This tendency is consistent with the results by Bouwens et al. (1991) in which the Co-Mo-S phase increased instead of the Co_9S_8 –like species by the addition of NTA. The distance of Co(NTA)/carbon (2.18 Å) is shifted to 2.15 Å by the addition of Mo. Therefore, Mo atoms can interact with Co atoms in the replacement of NTA molecules during sulfiding, while the Co-NTA interaction can remain even in the sulfiding condition and consequently suppress the formation of the bulky Co sulfide. Thus, the effect of NTA is to keep Co atoms highly dispersed and increased the number of Co atoms which can interact with Mo atoms, that is, the number of Co atoms in the Co-Mo-S phase.

The Co K-edge XANES spectra of Co-Mo/Al_2O_3,Co-Mo(NTA) /Al_2O_3 catalysts and Co reference compounds are shown in Fig. 5. For Co-Mo/Al_2O_3 catalyst, The spectral features around 7725 and 7740 eV derived from remaining the $CoAl_2O_4$-like species are observed. The addition of NTA almost erases these features.

Fig. 6 shows the Co K-edge EXAFS Fourier transforms of Co-Mo/Al_2O_3, Co-Mo(NTA)/Al_2O_3 catalysts. The distance of the first shell for Co-Mo/Al_2O_3 catalyst is 2.13 Å, which is shorter than Co-Mo/carbon (2.19 Å) and Co-Mo(NTA)/carbon (2.15 Å). This results is due to the remaining $CoAl_2O_4$-like species, considering the XANES results. The peak is shifted to 2.16 Å by the addition of NTA, which is almost same as one of Co-Mo(NTA)/ carbon (2.15 Å). It is unlikely that NTA affects the formation of Co-Mo-S during sulfiding, because NTA is eliminated during the calcination. NTA presumably suppresses the migration of Co into the alumina support during calcination due to the formation of Co chelated structure. Probably, mild calcination conditions such as those applied in the present study (773 K, 3 h) are essential, if any calcination procedure is employed, to enhance the role of NTA in the formation of the Co-Mo-S phase

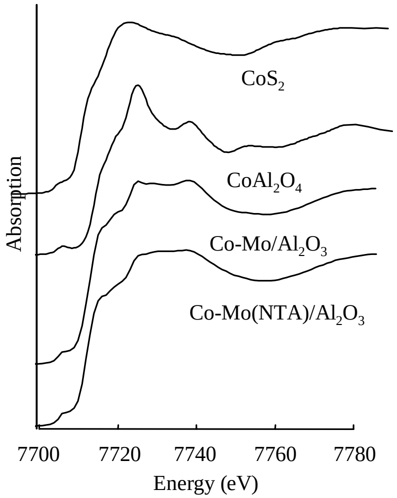

Figure 5
Co K-edge XANES spectra of Co-Mo/Al$_2$O$_3$ catalysts and Co reference compounds.

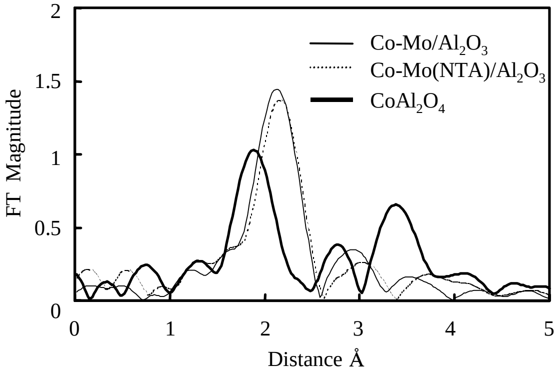

Figure 6
Fourier transforms of the Co K-edge EXAFS spectra for Co-Mo/Al$_2$O$_3$ catalysts.

4. Conclusions

The present study has elucidated two different effects of NTA on the formation of the Co-Mo-S phase; one is the suppression of the formation of Co_9S_8-like species during presulfiding, the other prevention of the migration of Co into the alumina support.

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References

Topsøe, H et al., (1981). J. Catalysis. 68, 433-452.
Bouwens, S. M. A. M.., van Veen, J. A. R., Koningsberger, D. C., Beer, V. H. J. de ., Prins, R.., (1991). J. Phys. Chem. 95, 123-134.
Teo, B. K., & Lee, P. A., (1979). J. Am. Chem. Soc. 101, 2815-2832.

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