

Clarification of the effects of chelate-added hydrodesulfurization catalyst by means of in-situ XAFS

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Introduction

Currently, Co-Mo sulfide catalysts are used for HDS treatment. It is well known that catalytic synergy generates between Co and Mo sulfides in the catalyst system. In the industrial catalysts, chelating agents are added to catalysts to improve HDS activity. However, the role for the catalysts properties in the addition of chelating agents are not clarified in detail.

In this study, the chemical state analysis of Co and Ni in Co-W and Ni-W sulfide catalysts are studied by means of an in situ fluorescence XAFS technique.

Experimental

Co(Ni)-W/Al₂O₃ catalyst were prepared by a double impregnation method in the presence or absence of nitrilotriacetic acid (NTA) as a chelating compound (NTA/Co(Ni) mole ratio = 1.0). The catalysts were dried at 373 K overnight. The W and Co or Ni contents were 16.7 and 2.7 wt.% for the all catalysts.

The Co and Ni K-edge XAFS spectra for Co-Mo, Ni-W and Co-W catalysts were measured at BL-9A or BL-7C of KEK-IMSS-PF in a fluorescence mode under in situ conditions [1].

Results and Discussion

It was found from Figure 1 that the Co species in a Co-W/Al₂O₃ catalyst prepared by a double impregnation method (uncalcined after Co addition) were sulfided even at room temperature. Sulfidation of Co rapidly proceeded with increasing temperature and almost completed at 473K. On the other hand, the Co species of a Co-W/Al₂O₃ catalyst with nitrilotriacetic acid (NTA) were scarcely sulfided at room temperature. Furthermore, the rate of sulfidation was very slow compared with the catalyst prepared without NTA addition even at a higher temperature [2]. With each catalyst, isosbestic points appeared in the series of XANES spectra, indicating that these XANES spectra consist of two components of the spectra due to oxide and sulfide species. We analyzed the spectra by assuming a linear combination of these Co species. The calculated spectra showed good agreement with the measured spectra. It is obvious from Figure 2 that the sulfidation of Co is significantly depressed by the addition of NTA. Comparison of the spectra for the both catalyst systems indicates that the formation of Co₉S₈ is also suppressed by the addition of NTA. It is clearly demonstrated that the addition of NTA hinders sulfidation of Co, leading to a selective formation of a Co-W-S phase.

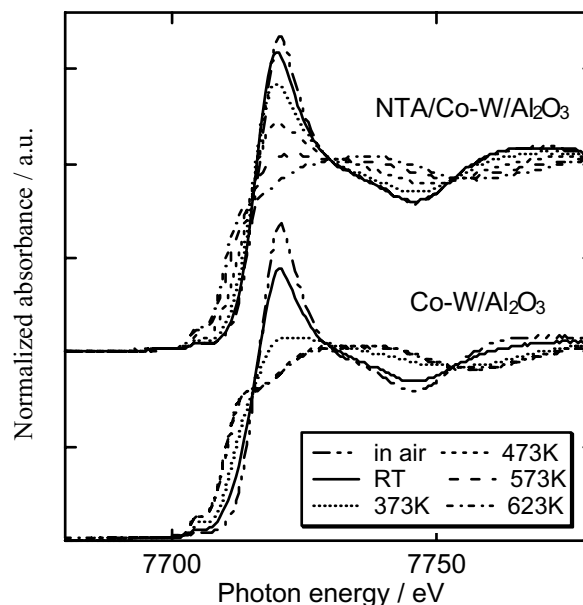


Figure 1 Co K-edge XANES spectra for Co-W/Al₂O₃ and NTA-Co-W/Al₂O₃ during the sulfidation treatment.

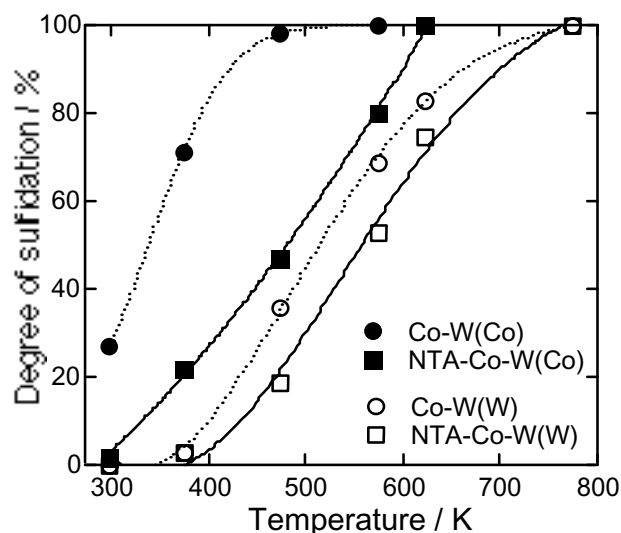


Figure 2. Degree of sulfidation of Co and W obtained by XANES analysis against the sulfidation temperature for Co-W/Al₂O₃ catalysts

References

- [1] K.K. Bando et al., Topics in Catal., 18, 59 (2002).
- [2] T. Kubota et al., J. Phys. Chem. Chem. Phys., 5, 4510 (2003).

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