

Selective decoration of sonochemically prepared MoS₂/Al₂O₃ with Co or Ni by impregnation with an acetylacetonate precursor

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Introduction

Development of the highly active hydrotreating catalyst is a key issue to complying with the further tightening environmental regulations. Previously, we developed highly active hydrodesulfurization (HDS) catalysts by combining sonochemical synthesis and chemical vapor deposition (CVD) methods. [1, 2] The sonochemically prepared MoS₂ catalysts exhibited significantly improved HDS activities due to the high dispersion of active sites. However, the MoS₂ dispersion was degraded when the catalyst was promoted with either Co or Ni, commonly by an impregnation method using nitrate, because the catalyst had to be treated at elevated temperatures, ca 400°C, to decompose the precursor. CVD was proposed as a method for effectively decorating the MoS₂ surface with Ni or Co, while maintaining the high dispersion of MoS₂ crystallites, compared with the case of a conventional impregnation method. In this study, we developed a new procedure to promote the MoS₂ by an impregnation method using Co or Ni acetylacetonate (acac) as a precursor, which allowed the effective decoration of MoS₂ with the promoter and the maintenance of the high dispersion. Newly developed catalysts showed activities comparable to those of Ni(Co)MoS₂/Al₂O₃ catalysts containing the promoter added by a CVD method.

Materials and Methods

Highly dispersed MoS₂/Al₂O₃, designated as Mo(s), was prepared by a sonochemical method using Mo(CO)₆ and S₈ as precursors dissolved in a hexadecane and mesitylene mixture. [3] Mo(s) was promoted with either Ni or Co by an incipient wetness impregnation method using various precursors such as Ni(NO₃)₂, Co(NO₃)₂, Ni(acac)₂ and Co(acac)₂. Prepared catalysts were designated as Ni(i)Mo(s)N, Co(i)Mo(s)N, Ni(i)Mo(s)A, and Co(i)Mo(s)A, according to the method of promoter addition, i.e., (i) for impregnation, and the types of precursors, i.e., N for nitrate and A for acetylacetonate. For comparison, Ni was also added to Mo(s) by CVD using Ni(CO)₄ as a Ni precursor, and the catalyst was designated as Ni(c)Mo(s). Prepared catalysts were characterized by infrared and X-ray photoelectron spectroscopy (XPS). The catalytic performance was evaluated in the HDS of dibenzothiophene (DBT) and 4,6-dimethyldibenzothiophene (4,6-DMDBT).

Results and Discussion

Figure 1 shows FTIR spectra of NO adsorbed on Mo(s) and Co(i)Mo(s). Peak I is due to NO adsorbed on sulfided Co and peak III due to one adsorbed on sulfided Mo. Peak II is originated from NO adsorbed on both Co and Mo. Compared to Mo(s), Co(i)Mo(s) samples show a lower intensity of peak III because a fraction of the surface Mo species was covered and combined with Co. Moreover, the intensity of peak III was lower in Co(i)Mo(s)A than in Co(i)Mo(s)N, indicating that a larger fraction of the Mo species was decorated with Co when

the latter was added using Co(acac)₂ instead of Co(NO₃)₂. Figure 2 compares catalytic activities of prepared catalysts for DBT HDS. Co(i)Mo(s)A and Ni(i)Mo(s)A show activities higher than those of the catalysts prepared using nitrate, which is in accordance with the IR results indicating an increase in the amount of the CoMoS or NiMoS phase in the catalysts prepared from acetylacetonate. The activity of Ni(i)Mo(s)A was nearly the same as that of Ni(c)Mo(s), indicating that both catalysts were superior to those prepared using nitrate.

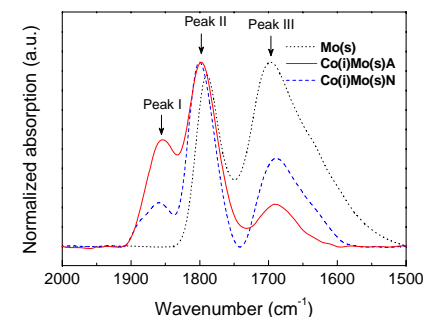


Figure 1. FTIR spectra of NO adsorbed on Mo(s), Co(i)Mo(s)A, and Co(i)Mo(s)N.

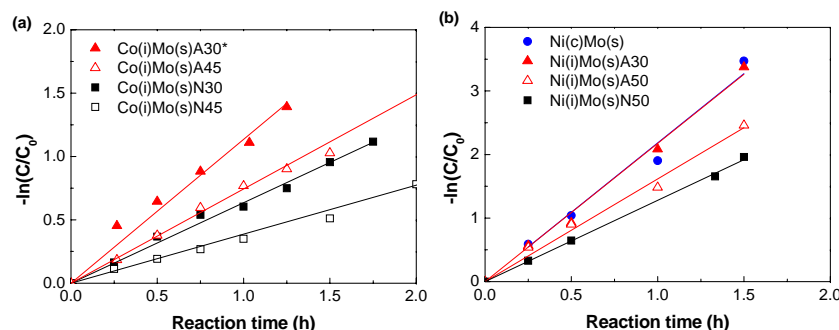


Figure 2. DBT conversions obtained using (a) CoMo and (b) NiMo catalysts. *Co(i)Mo(s)A30 indicates Co(i)Mo(s) containing 3.0 wt% of Co added using Co(acac)₂.

Significance

Sonochemically prepared MoS₂/Al₂O₃ was promoted by an impregnation method using Co(acac)₂ or Ni(acac)₂ as a precursor. The acetylacetonate compound was selectively deposited on the MoS₂ sites to form larger amounts of the CoMoS or NiMoS phase after sulfidation.

References

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