CHARACTERIZATION OF SULFIDED SPECIES USING TEMPERATURE-PROGRAMMED REDUCTION OF SULFIDED MOLYBDENUM CATALYSTS

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Abstract - Temperature-programmed reduction of sulfided catalyst (TPR-S) was conducted for characterization of sulfided species produced by sulfurization. This method can provide quantitative information by monitoring H_2 consumption and H_2S production due to different kinds of sulfided species. In this study, the sulfided species in Mo/Al_2O_3 catalyst were characterized using this method. These results indicated the presence of adsorbed H_2S species on Al_2O_3 and sulfur- Al_2O_3 interaction species.

Key words TPR-S, Molybdenum, Sulfurization

INTRODUCTION

Hydrodesulfurization (HDS) catalysts such as $Co-Mo/Al_2O_3$ are usually sulfided before HDS reaction. Sulfurization as an activation process significantly influences on the sulfided states of catalysts and their HDS activities. TPR-S method proposed by Moulijn and co-workers [1] is one of useful techniques for characterization of sulfided species. TPR-S patterns for sulfided catalysts usually show several peaks which are attributed to different types of sulfided species.

TPR-S has the following advantages.

- Ultraviolet-spectrometer (UV, set at 202nm) is used for the detection of H_2S . In comparison with gas chromatography, UV is more sensitive and convenient for monitoring H_2S on-line system.
- H_2 consumption and H_2S production can be quantitatively monitored.
- All sulfided species can be reduced at high temperature up to 1350K.
- In situ measurement of sulfided catalyst is possible.

In this study, a similar instrument as reported one [1] was used for the characterization of sulfided species in the sulfided Mo/Al_2O_3 catalyst.

EXPERIMENTAL

Materials MoS_2 powder (Wako Pure Chemical) and Al_2O_3 support (Surface area, $190m^2/g$; Amount of impurity (SO_4^{2-}) is 0.01 as S/Al_2O_3 molar ratio) were used as references. Mo/Al_2O_3 catalyst (10wt% as MoO_3) was prepared by vacuum impregnation of Al_2O_3 support with a $(NH_4)_6Mo_7O_{24}$ solution.

TPR-S The catalyst was packed in a quartz reactor in an oven. Mo/Al_2O_3 catalyst was calcined at 650K for 2hr, and then cooled to room temperature. This was exposed to the sulfiding gas (3% H_2S , 23% H_2 , 74% Ar) at room temperature for 2hr. The catalyst was sulfided with a sulfiding gas flow at a constant heating rate of 10K/min from 300K to 650K, and kept at 650K for 30min. Sulfiding gas was purged by Ar gas after the sample was cooled to room temperature. After replacement by the reducing gas (65% H_2 , 35% Ar), the catalyst was reduced at a constant heating rate of 10K/min from 300K to 1350K, and kept at 1350K for 30min. On reduction of the sulfided catalyst (TPR-S measurement), H_2S was monitored by UV detector. Sequentially, H_2 through a trap of molecular sieves for H_2O and H_2S was detected by thermal conductivity detector (TCD).

RESULTS AND DISCUSSION

MoS₂ Fig.1 shows TPR-S patterns of MoS₂ powder. Peaks of H₂ consumption and H₂S production can be observed at more than ca. 1000K. Intensities of these peaks increase with increasing reduction temperature up to 1350K. Reduction of Mo species continues in the isothermal range and then decreases gradually. Molar ratios of H₂ consumption and H₂S production to Mo are of 2.12 ± 0.06 and of 1.94 ± 0.06 , respectively. These values are in good agreement with the estimated value of 2.0 by assuming reduction of MoS₂ to Mo metal. This result indicates that reduction of MoS₂ can be quantitatively analyzed by TPR-S measurement.

Al₂O₃ support Fig.2 shows TPR-S patterns of Al₂O₃ support. Patterns for H₂S show four peaks centered at 387, 489, 729, and 939K. H₂S production peaks at 387 and 489K are not accompanied with H₂ consumption peaks. The amount of H₂S adsorbed on Al₂O₃ support is 0.02 as S/Al₂O₃ molar ratio. Okamoto et al. reported that H₂S desorption on Al₂O₃ occurred at 400 and 560K in their temperature-programmed desorption study[2]. Therefore, the peaks at 387 and 489K are also attributed to adsorbed H₂S on Al₂O₃ support.

Broad peaks of H₂S production and H₂ consumption are observed at 729K. Molar ratio of sulfur estimated from H₂S production (S/Al₂O₃=0.01) is similar to that of sulfur impurity in Al₂O₃ support. However, peaks for hydrogenation of sulfur impurity are apparently observed at 939K. Furthermore, H₂S/H₂ ratio 1.1 indicates that H₂ is consumed for hydrogenation of sulfur. Thus, these results suggest that sulfur-Al₂O₃ interaction species are formed on sulfurization.

Mo/Al₂O₃ catalyst TPR-S patterns of Mo/Al₂O₃ catalyst are shown in Fig.3. Patterns of H₂ consumption and H₂S production show four peaks centered at 465, 729, 909, and 1350K. Three sets of these peaks are attributed to the following sulfided species, as reported previously[1];

Peaks at 465K: Chemisorbed sulfur produced from H₂S decomposition on Mo-sulfided species.

Peaks at 909K: Mo-oxysulfided species.

Peaks at 1350K: MoS₂-like species.

Peaks at 729K are similar to those of Al₂O₃ support. The result indicates sulfur-Al₂O₃ interaction species are also formed in sulfided Mo/Al₂O₃ catalyst. However, H₂S desorption peaks are not clearly observed in H₂S patterns of sulfided Mo/Al₂O₃ catalyst. A decrease in H₂S adsorption might be due to a decrease in Al₂O₃ surface caused by Mo loading. Furthermore, no peaks for hydrogenation of sulfur impurity are observed. State of sulfur impurity in Mo/Al₂O₃ catalyst may be different from that in Al₂O₃ support.

Molar ratios of H₂S production and H₂ consumption to Mo are 2.20 and 2.81, respectively. These values are larger than the stoichiometric ratio of 2.0 for MoS₂. The presence of excess sulfur indicates the existence of adsorbed H₂S, chemisorbed sulfur, and sulfur-Al₂O₃ interaction species.

In conclusion, two sulfided species such as H₂S adsorption onto Al₂O₃ support and sulfur-Al₂O₃ interaction species were also observed in TPR-S measurement of Mo/Al₂O₃ catalyst, in addition to sulfided species reported previously[1].

Fig.1 TPR-S patterns of MoS₂ powder.

Fig.2 TPR-S patterns of Al₂O₃ support.

Fig.3 TPR-S patterns of Mo/Al₂O₃ catalyst.

REFERENCES

1. B.Scheffer, N.J.J.Dekker, P.J.Magnus, and J.A.Moulijn, *J.Catal.*, **121**, 31(1990).
2. Y.Okamoto, M.Oh-hara, A.Maezawa, T.Imanaka, and S.Teranishi, *J.Phys.Chem.*, **90**, 2396(1986).