

High Selectivity of Sulfided NiW/Al<sub>2</sub>O<sub>3</sub> Catalyst in Desulfurization of Dibenzothiophene in the Presence of Nitrogen-Containing Compounds

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The presence of nitrogen compounds greatly improved the selectivity of a sulfided NiW/Al<sub>2</sub>O<sub>3</sub> catalyst for the direct desulfurization of dibenzothiophene to biphenyl. Elemental sulfur precipitated after the reaction.

Nitrogen compounds are said to be poisons to catalysts for hydrodesulfurization. Several researchers have reported that the presence of nitrogen compounds greatly decreased the catalytic activity and did not improve the selectivity of a sulfided molybdena-alumina catalyst<sup>1,2)</sup> and single sulfide catalysts which did not contain a promoting metal such as MoS<sub>2</sub>, NiS, WS<sub>2</sub>, and CoS.<sup>3)</sup> However, the presence of acridine greatly enhanced the selectivity of a nickel-promoted molybdenum catalyst for desulfurization by increasing catalytic activity,<sup>4)</sup> yet provided little or no enhancement of activity of CoMo/Al<sub>2</sub>O<sub>3</sub> catalyst.<sup>5,6)</sup> We also found a sulfided NiW/Al<sub>2</sub>O<sub>3</sub> catalyst "poisoned" by adding nitrogen compounds to have high selectivity for desulfurization at low temperature during hydrodesulfurization.

The experiment was carried out in a continuous-flow microreactor at 260 to 360 °C and 10.1 MPa total pressure. Two grams of the NiW/Al<sub>2</sub>O<sub>3</sub> catalyst (6.5% NiO and 21% WO<sub>3</sub> supported on alumina, Ketjenfine, 14-20 mesh) were first preheated in air at 450 °C for 24 h. The catalyst was reduced in situ with hydrogen at 400 °C and 10.1 MPa for 4 h and then sulfided with 10% H<sub>2</sub>S/H<sub>2</sub> at atmospheric pressure and 400 °C for 3 h. A solution containing 5 wt% dibenzothiophene in xylene was then allowed to flow into the reactor. A solution containing 5 wt% dibenzothiophene and 0.25 wt% acridine was then introduced instead of the former solution after the reaction reached steady state.

In the hydrodesulfurization of dibenzothiophene on the sulfided NiW/Al<sub>2</sub>O<sub>3</sub> catalyst, the major product was biphenyl which was produced by fission of the C-S bond in dibenzothiophene. Also produced in the reaction were cyclohexylbenzene, small amounts of a number of hydrogenated and decomposed compounds as mentioned by Gates et al.,<sup>7)</sup> and methyl- and dimethyldibenzothiophene. The alkylidibenzothiophenes were produced by alkylation after cleavage of the saturated ring of hydrogenated compounds. These compounds were not formed in the reactions with the sulfided Mo/Al<sub>2</sub>O<sub>3</sub>,<sup>1)</sup> CoMo/Al<sub>2</sub>O<sub>3</sub>,<sup>8)</sup> and NiMo/Al<sub>2</sub>O<sub>3</sub><sup>4)</sup> catalysts in the presence of xylene, but with the HY<sup>9)</sup> and Co/HY<sup>10)</sup> zeolite catalysts, which had strong acid sites, in the absence of the solvent. Therefore, the sulfided NiW/Al<sub>2</sub>O<sub>3</sub> catalyst appears to have stronger acid sites than the sulfided CoMo/Al<sub>2</sub>O<sub>3</sub> and NiMo/Al<sub>2</sub>O<sub>3</sub>

catalysts.

Addition of acridine to the solution, however, markedly increased the concentration of biphenyl at all temperatures, while it decreased the concentrations of unconverted dibenzothiophene, cyclohexylbenzene, and small amounts of other products. This result shows that the "poisoned" sulfided NiW/Al<sub>2</sub>O<sub>3</sub> catalyst highly increased the selectivity for desulfurization while decreasing the concentration of decomposed and hydrogenated compounds. No alkyl dibenzothiophenes were formed at any reaction temperature; therefore, the strong acid sites on the catalyst surface were diminished after the addition of acridine. Moreover, the addition improved the material balance remarkably even at high temperature due to a decrease in the formation of compounds more volatile than the xylene used as a solvent.

The conversion of dibenzothiophene did not increase below 0.1 wt% addition of acridine, but a 0.25 wt% addition led to a great increase in the conversion of dibenzothiophene. Therefore, addition of a large amount of acridine improves the catalytic activity of the sulfided NiW/Al<sub>2</sub>O<sub>3</sub> catalyst for hydrodesulfurization of dibenzothiophene with the selective formation of biphenyl.

Sulfur precipitated from the solution after the reaction. This observation indicated that not all amounts of sulfur removed in the reaction desorbed as hydrogen sulfide from the catalyst surface but some desorbed as elemental sulfur. Amines such as hydrogenated acridines appeared to help the desorption of sulfur by forming an amine-sulfur complex.<sup>11)</sup> The addition of other nitrogen compounds such as pyridine, piperidine, and quinoline exhibited similar observations.

#### References

- 1) M. Nagai and T. Kabe, *J. Catal.*, **81**, 440 (1983).
- 2) S. W. Cowley and F. E. Massoth, *J. Catal.*, **51**, 291 (1978).
- 3) H. Urimoto and N. Sakikawa, *J. Jpn. Pet. Inst.*, **15**, 926 (1972).
- 4) M. Nagai, *Ind. Eng. Chem. Product Res. Dev.*, **24**, 489 (1985).
- 5) R. Ramachandran and F. E. Massoth, *Chem. Eng. Commun.*, **18**, 239 (1982).
- 6) C. N. Satterfield, M. Model, and J. F. Mayer, *AIChE J.*, **21**, 1100 (1975).
- 7) B. C. Gates, J. R. Katzer, and G. C. A. Schuit, "Chemistry of Catalytic Processes," McGraw-Hill Co., New York (1977), p. 426.
- 8) Unpublished data.
- 9) M. Nagai, H. Urimoto, and N. Sakikawa, *Nippon Kagaku Kaishi*, **1975**, 356 (1975).
- 10) M. Nagai, S. Obata, M. Yamada, and N. Sakikawa, *Nippon Kagaku Kaishi*, **1976**, 956 (1976).
- 11) S. Oae, "Yuki Iou Kagoubutsu No Kagaku," Kagakudojin, Kyoto (1968), Chap. 2.

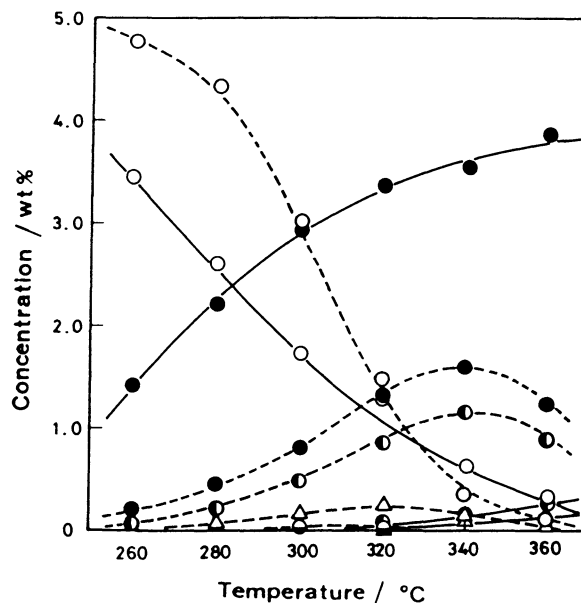


Fig. 1. Product distribution as a function of temperature over the sulfided NiW/Al<sub>2</sub>O<sub>3</sub> catalyst with (—) and without (---) acridine. ○ Dibenzothiophene, ● biphenyl, △ cyclohexylbenzene, ● methyl and dimethyl dibenzothiophenes, hydrogenated dibenzothiophenes, bicyclohexyl and hydrocarbons which have higher boiling point than bicyclohexyl.

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