

Hydrodesulfurization of 4,6-dimethyldibenzothiophene over Rhodium Phosphide Catalyst

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In the near future, regulation of sulfur oxide emissions from ships will be strict, because the fuels for ships contain larger quantities of sulfur compounds compared to gasoline and diesel fuel. Thus, the petroleum industry claims that the development of highly active hydrodesulfurization (HDS) catalysts, which exhibit higher activity than commercial CoMo catalysts, will prevent air pollution and acid rain. In particular, nickel phosphide (Ni₂P) catalyst has high potential for the HDS reaction [1]. On the other hand, we have reported that noble metal phosphides (NiM_xP_y) [2, 3], especially rhodium phosphide (Rh₂P) [2-4], showed high and stable HDS activity. In this study, activity of Rh₂P for HDS of 4,6-dimethyldibenzothiophene (4,6-DMDBT) was studied to examine its catalytic performance for HDS of heavy oil.

The P-added Rh/SiO₂ catalyst was prepared by a co-impregnation method using rhodium (III) chloride trihydrate (RhCl₃·3H₂O) and ammonium dihydrogen phosphate (NH₄H₂PO₄) aqueous solution. After drying at 110 °C, the catalyst was calcined at 500 °C for 4 h, followed by reduction in hydrogen (H₂) at 550 °C for 1 h. This catalyst was labeled as Rh-P. The HDS of 4,6-DMDBT was performed at 250-310 °C under 3.0-5.0 MPa using a fixed-bed flow reactor. The reduced catalyst (0.2 g) was charged into the stainless steel reactor and heated (10 °C min⁻¹) in a H₂ stream (30 ml min⁻¹) at 500 °C for 1 h. The reaction products were analyzed using a gas chromatograph equipped with a flame ionization detector (FID).

Effect of reaction temperature on HDS activities of Rh-P and sulfided NiMo catalysts were examined. For NiMo catalyst, the maximum HDS activity was observed at 270 °C. It is well known that 4,6-DMDBT has higher steric hindrance, which can be reduced by hydrogenation of aromatic ring. Over NiMo catalyst, selectivity of

hydrogenated products, such as 3,3-methylcyclohexylfluenes (3,3-MCHTs) and 3,3'-dimethylbicyclohexyls (3,3'-DMBCHs), decreased with increasing reaction temperature. This indicates that higher reaction temperature, which is thermodynamically unfavorable condition for hydrogenation reaction, would cause decreasing catalytic activity of NiMo catalyst. On the other hand, HDS activity of Rh-P catalyst increased with increasing reaction temperature. Furthermore, selectivity of hydrogenated products, especially 3,3'-DMBCHs, over Rh-P catalyst also increased. These results indicate that Rh-P catalyst would show higher hydrogenation activity than NiMo catalyst.

Fig. 1 shows the effect of reaction pressure on HDS activities of Rh-P and NiMo catalysts. For NiMo catalyst, HDS activity slightly increased with increasing reaction pressure. On the other hand, HDS activity of Rh-P catalyst significantly increased with increasing reaction pressure. At the same time, selectivities for hydrogenated products also increased. At 5.0 MPa, HDS activity of the Rh-P catalyst was higher than that of NiMo catalyst. Thus, Rh-P catalyst would show higher HDS activity for heavy oil than commercial NiMo catalyst.

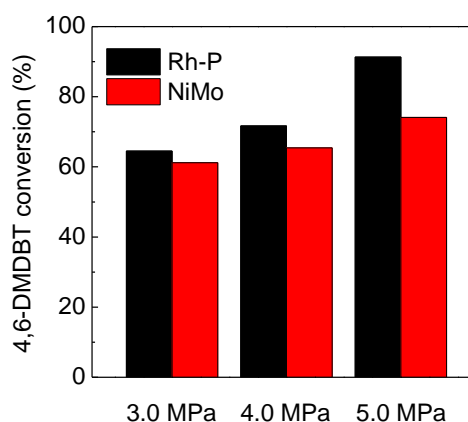


Fig.1 Effect of reaction pressure on activities of Rh-P and NiMo catalysts for HDS of 4,6-DMDBT at 310 °C.

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