Catalytic performance of rhodium phosphide for hydrodesulfurization of 4,6-dimethyldibenzotiophene

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Abstract: 4,6-dimethyldibenzothiophene (4,6-DMDBT) can be removed from heavy oil by hydrogenation of aromatic ring to decrease steric hindrance. The hydrogenating ability of Rh-P catalyst was the highest among those of NM-P catalysts and this ability was higher than that of commercial NiMoS catalyst. In HDS of DBT, the order of catalytic activities for DBT HDS was as follows; NiMoS ≈ Rh-P > Pd-P > Ru-P. On the other hand, Rh-P catalyst showed higher activity for HDS of 4,6-DMDBT than NiMoS catalyst. The high activity of Rh-P catalyst for HDS of 4,6-DMDBT can be explained by its high hydrogenating ability.

Keywords: Rhodium phosphide, Hydrodesulfurization, 4,6-dimethyldibenzothiophene.

1. Introduction

Since fuels for ships contain larger quantities of sulfur compounds compared to gasoline and diesel fuel, regulation of sulfur oxide emissions from ships will be strict in the near future. Thus, the petroleum industry claims development of highly active hydrodesulfurization (HDS) catalysts, which exhibit higher activity than commercial CoMo catalysts, to prevent air pollution and acid rain. Hydrogenation is an important method for the desulfurization of refractory organic sulfur compounds, such as 4,6-dimethyldibenzothiophene (4,6-DMDBT)[1,2]. Therefore, high hydrogenation activity is one of the important characteristics of highly active HDS catalyst[3].

Transition metal phosphides, especially nickel phosphide (Ni_2P), catalysts have high potential for the HDS reaction[4]. On the other hand, we have reported that noble metal phosphides (NM_XP_Y)[3,5,6], especially rhodium phosphide (Rh_2P), showed high and stable HDS activity. In general, it is well known that noble metal has higher hydrogenating ability than transition metals. Thus, NM_XP_Y catalysts also would have high hydrogenating abilities, and these catalysts would also show high activities for HDS of refractory organic sulfur compound. In this study, activities of NM_XP_Y for hydrogenation of biphenyl and HDS of dibenzothiophene (DBT) and 4,6-DMDBT were studied to examine its catalytic performance for HDS of heavy oil.

2. Experimental

The SiO_2-supported noble metal-phosphorus (NM-P) catalyst was prepared by a co-impregnation method using noble metal (NM) chlorides ($RhCl_3{\cdot}3H_2O$, $PdCl_2$, and $RuCl_3{\cdot}3H_2O$) and ammonium dihydrogen phosphate ($NH_4H_2PO_4$) aqueous solutions. After drying at 110 °C, the catalyst was calcined at 500 °C for 4 h, followed by reduction in hydrogen (H_2) at optimal temperatures (Rh-P: 550 °C, Pd-P: 500 °C, Ru-P 650 °C) for 1 h. These catalysts were labeled as NM-P. The HDS of 4,6-DMDBT was performed using a fixed-bed flow reactor at 250-310 °C under 3.0-5.0 MPa. The reduced catalyst (0.2 g) was charged into the stainless steel reactor and heated (10 °C min^{-1}) from room temperature to reaction temperature in a H_2 stream (30 ml min^{-1}). 4,6-DMDBT xylene solution (0.024mol/L) was fed using high pressure pomp (PU-2080, JASCO) with 0.07 ml/min. The reaction products were analyzed using a gas chromatograph equipped with a flame ionization detector (FID). Hydrogenation of biphenyl and HDS of DBT were also performed using a fixed-bed flow reactor at 270 °C under 2.5 MPa. Presulfided NiMo/Al_2O_3 (NiMoS) catalyst was used as a reference to evaluate the activity of Rh-P catalyst.

3. Results and discussion

We examined the hydrogenation activities of NM-P and NiMoS catalysts. The order of biphenyl conversion was Rh-P >> NiMoS > Pd-P > Ru-P. Furthermore, bicyclohexyl, which is fully hydrogenated product, was yielded over Rh-P catalyst, indicating that Rh-P catalyst have superior hydrogenating activity. The order of catalytic activities for DBT HDS was NiMoS ≈ Rh-P > Pd-P > Ru-P. Rh-P catalyst showed the same HDS activities as NiMoS catalyst. There are large difference between product selectivities of these catalysts, hydrogenated products, such as cyclohxylbenzene (CHB) and bicyclohexyl (BCH), were mainly obtained over Rh-P catalyst. On the other hand, NiMoS catalyst mainly yields biphenyl (BP). On the basis of these results, the high selectivity of hydrogenated products over Rh-P catalyst can be explained by high hydrogenation activity. It is well known that 4,6-DMDBT has higher steric hindrance, which can be reduced by hydrogenation of aromatic ring. Thus, Rh-P catalyst would show higher activity for HDS of 4,6-DMDBT than NiMoS catalyst.

Effect of reaction temperature on HDS activities of Rh-P and sulfided NiMo catalysts were examined. The maximum HDS activity for NiMo catalyst was observed at 270 °C. The selectivity of hydrogenated products (3,3-methylcyclohexyltluenes and 3,3’-dimethylbicyclohexyls) over NiMoS catalyst decreased with increasing reaction temperature. This result indicates that higher reaction temperature, which is thermodynamically unfavorable condition for hydrogenation reaction, would cause decreasing HDS activity of NiMoS catalyst. For Rh-P catalyst, the HDS activity increased with increasing reaction temperature. Furthermore, selectivity of hydrogenated products, especially 3,3’-dimethylbicyclohexyls, over Rh-P catalyst also increased. These results imply that Rh-P catalyst would show higher hydrogenation activity than NiMoS catalyst. **Table 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 NiMoS catalyst.

Table 1. Catalytic activities of Rh-P and NiMoS catalysts for HDS of 4,6-DMDBT at different pressures.

Catalyst	4,6-DMDBT conversion (%)		
	3.0 MPa	4.0 MPa	5.0 MPa
Rh-P	64.5	71.7	91.3
NiMoS	61.2	65.4	74.1

4. Conclusions

The Rh-P catalyst showed the highest hydrogenating ability among NM-P catalysts. In HDS of DBT, catalytic activity of Rh-P was the same as that of NiMoS. Furthermore, Rh-P catalyst had higher activity for HDS of 4,6-DMDBT than NiMoS catalyst. Thus, Rh-P catalyst with higher hydrogenating ability would show higher activity for HDS of heavy oil than commercial NiMoS catalyst.

References

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