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Deep Hydrodesulfurization of Alkyl-Substituted Dibenzothiophenes in Light Oil

Atsushi ISHIHARA, Haruhiko TAJIMA,+ and Toshiaki KABE*
Department of Chemical Engineering, Tokyo University of Agriculture
and Technology, Nakamachi, Koganei, Tokyo 184
+Chemicals Inspection & Testing Institute, 4-1-1, Higashimukojima, Sumida-ku, Tokyo 131

Hydrodesulfurization of polyaromatic sulfur-containing compounds in light oil was carried out by using Co-Mo/Al_2O_3 under experimental conditions representative of industrial practice. Alkyl-substituted dibenzothiophenes in light oil, especially 4, 6-dimethyldibenzothiophene, were difficult to desulfurize even under deep desulfurization conditions.

Recently, deep hydrodesulfurization of light oil has been one of the most important problems which must be solved for reduction of air pollution. Polyaromatic sulfur-containing compounds (PASC) such as benzothiphene (BT) and dibenzothiophene (DBT) are key compounds in hydrodesulfurization reactions.1-7) Under deep desulfurization conditions where those compounds must be desulfurized up to ppm orders of concentration, however, it has not been well-known what kind of sulfur compounds exists in light oil and which of those is still not desulfurized at the final stage of the reaction.

In this study, the light oil is analyzed and desulfurized by Co-Mo/Al_2O_3. It was found that alkyl-substituted dibenzothiophenes are most difficult to desulfurize in deep desulfurization of light oil.

Light oil used in this study was the middle distillate of Arabianlight. The commercial Co-Mo/Al_2O_3 catalyst (CoO: 4.5 wt%; MoO_3: 17.0 wt%) was used. The reactor was a 20 mm-i.d. stainless steel tube packed with 5.9 g of catalyst particles diluted with quartz sand. After the catalyst bed was heated for 24 h at 450 ^{o}C in air, it was presulfided with a mixture of 3% H_2S in H_2 flowing at 30 l/h at atmospheric pressure and 400 ^{o}C for 3 h. After these pretreatments, HDS reaction was carried out under the following conditions: temperature: 350-390 ^{o}C; LHSV: 4 h^{-1}; Gas/Oil: 120 Nl/l.

Polyaromatic sulfur-containing compounds (PASC) in light oil were desulfurized by Co-Mo/Al_2O_3 and determined by gas chromatography-atomic emission detector and gas chromatography-mass spectroscopy. When the original oil was hydrodesulfurized at 390 ^{o}C, 1.46 wt% of sulfur content in original oil decreased to 0.04 wt%. Figure 1 shows the change in the residual amount of sulfur in thiophenes with reaction temperature. Although alkylbenzothiophenes were completely desulfurized at 350 ^{o}C, alkyldibenzothiophenes were difficult to desulfurize and 2% of C1-DBT, 12% of C2-DBT and 10% of C3-DBT did not convert even at 390 ^{o}C.8) Specifically, 6% of 4-methyldibenzothiophene (4-MDBT) and 52% of 4, 6-dimethyldibenzothiophene (4,6-DMDBT) remained until the final stage. This indicates that a substituent attached to the carbon adjacent to carbon bonded by sulfur remarkably retards HDS by inhibiting the access of sulfur in thiophenes to the catalyst surface.

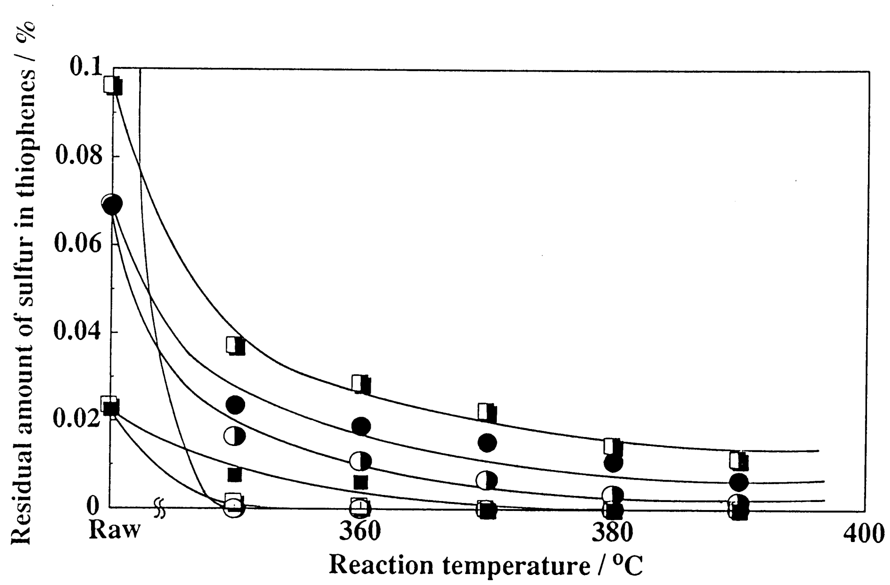

Fig. 1. Change in residual amount of sulfur in thiophenes with reaction temperature.
○: BT; ❑: DBT; ◑: C1-DBT; ◨: C2-DBT; ●: C3-DBT; ■: Others

When DBT, 4-MDBT and 4, 6-DMDBT were separately desulfurized in decalin, the conversion decreased in the order DBT>4-MDBT>4, 6-DMDBT. Similar results were reported by Kilakowski et al.9) and Houalla et al.10) In light oil, however, about 50 °C higher temperature is required to obtain the same conversions as those of DBTs in decalin. Thus, the rate of HDS of thiophenes in light oil decreases to about 1/10 of that in decalin. This clearly shows the extent of the retarding effects of components in light oil. We have already reported the retarding effect of solvent on the catalytic activity of HDS.2) In development of deep desulfurization processes, it is important to take into account such effects of various components contained in light oil.

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8) C1, C2, and C3 represent the number of carbon contained in total alkyl substituents attached to dibenzothiophene.
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