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Effects of Solvents in Deep Desulfurization of Benzothiophene and Dibenzothiophene

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Solvent effects on hydrodesulfurization of benzothiophene (BT) and dibenzothiophene (DBT) catalyzed by Co-Mo/Al_2O_3 were investigated under deep desulfurization conditions by using Langmuir-Hinshelwood (L-H) rate law. Solvents affected heats of adsorption of thiophenes rather than activation energy of HDS. Activation energies of HDS and heats of adsorption of thiophenes and solvents were estimated from the kinetic data.

In recent years, much attention has been focused on deep desulfurization of light oil. Under deep desulfurization conditions, effects of components in light oil on catalytic activity and selectivity of hydrodesulfurization (HDS) will be nonnegligible and become very important to control catalysis of HDS. So far, a number of attempts have been made to elucidate the mechanism of HDS by studying kinetics of HDS of benzothiophene (BT) and dibenzothiophene (DBT) which are among the key compounds in HDS of light oil.[1-6] Further, retarding effects of nitrogen-containing compounds on HDS have been often studied and well-known. However, the retarding effects of solvents on HDS have been scarcely reported nor estimated quantitatively by kinetic parameters. This led us to the investigation of the solvents effects on HDS under the deep HDS condition, since solvents can be regarded as a model of components of light oil.

In this study, we found the significant effects of solvents on the catalytic activity of HDS. We now report the kinetic study and the quantitative estimation of the effects of solvents on deep desulfurization of BT and DBT catalyzed by Co-Mo/Al_2O_3.

Solvents of the commercial GR grade (n-heptane, toluene, xylene, decalin, tetralin, 1-methylnaphthalene) were used without further purification. The commercial Co-Mo/Al_2O_3 catalyst (CoO: 5.0 wt%; MoO_3: 12.5 wt%) was used. The reactor was a 10 mm-i.d. stainless steel tube packed with 0.2 g of catalyst particles diluted with quartz sand to 3 cm^3. After the catalyst bed was heated for 24 h at 450 ^oC 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 ^oC for 3 h. After these treatment, the hydrodesulfurization reaction was carried out under the following conditions: temperature 140-310 ^oC; flow rate of solution: 14 g/h (WHSV 70 h^{-1}); concentration of BT and DBT: 0.1-3.0 wt%. Reaction products were analyzed by gas chromatography with FID detector.

Effects of solvents on HDS of BT and DBT catalyzed by Co-Mo/Al_2O_3 were investigated at 140-310 ^oC, 50 atm, 0.1 wt% of BT HDS and biphenyl (BP), cyclohexylbenzene (CHB) and a trace amount of hexahydrodibenzothiophene in DBT HDS. Figure 1 shows the effect of temperature on the conversion of BT and DBT.

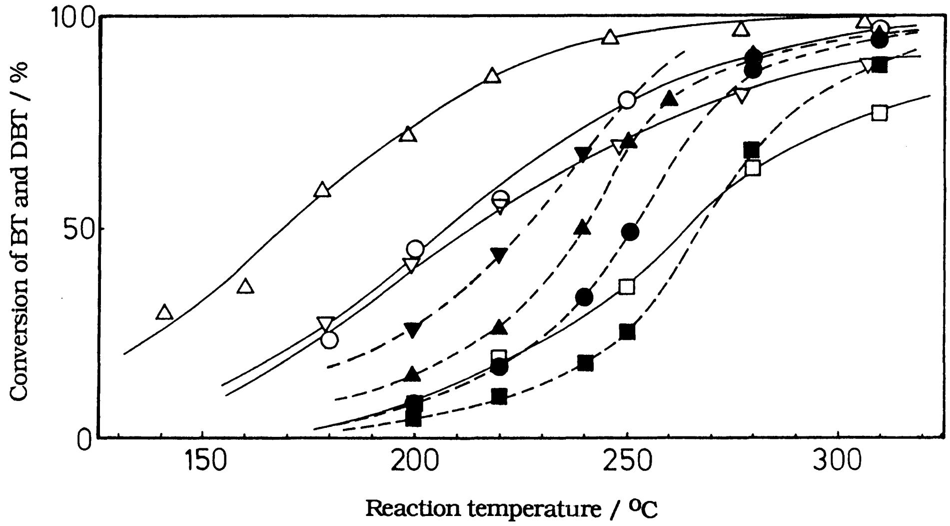

Fig. 1. Effect of temperature on the conversion of BT and DBT.
BT 0.1 wt%: △: toluene; ○: decalin; ▽: n-pentadecan; □: 1-methylnaphthalene.
DBT 0.1 wt%; ▼: n-heptane; ▲: xylene; ●: decalin; ■: tetralin.

The orders of catalytic activity were toluene>decalin>n-pentadecane>1-methylnaphthalene in HDS of BT and n-heptane>xylene>decalin>tetralin in HDS of DBT, respectively. In order to estimate the these data quantitatively, the kinetic experiments were performed at 180-220 °C in HDS of BT and at 200-240 °C in HDS of DBT. The dependence of HDS rates on the concentration of BT and DBT and hydrogen partial pressure indicated that HDS of BT and DBT under deep desulfurization conditions proceeds along with equation 1, which represents the mechanism that thiophenes and hydrogen adsorb on the separate active sites of catalysts:

$$r_{HDS} = kK_TP_T \,/\, (1 + K_TP_T + K_SP_S) \times K_HP_H \,/\, (1 + K_HP_H), \qquad (1)$$

where r_{HDS}=rate of HDS; k=rate constant of HDS; K_T, K_S, and K_H=adsorption equilibrium constants of BT or DBT, hydrogen sulfide and hydrogen; P_T, P_S, and P_H=partial pressure of BT or DBT, hydrogen sulfide and hydrogen. Kilakowski and Gates,[2)] and Vrinat and de Mourgues[5)] recommended similar equations to Eq. 1 in HDS of BT and DBT, respectively. In our present study, since the amount of hydrogen sulfide formed were very small, and near to 100 ppm, K_SP_S could be neglected. Further, since the amounts of converted BT and DBT were kept constant with an increase in partial pressure of hydrogen, HDS reactions of BT and DBT could be regarded as zero order against the partial pressure of hydrogen. Therefore, all data obtained here were treated by Eq. 2 which gave a good fit to all temperature examined:

$$r_{HDS} = k'K_TP_T \,/\, (1 + K_TP_T). \qquad (2)$$

Arrhenius plots of k' in HDS of BT and DBT using various solvents are shown in Fig. 2. Activation energies of HDS of BT and DBT were 22±1 and 24±2 kcal/mol, respectively, and did not affected by solvents. On the

Table 1. Heat of Adsorption of Solvents in Deep Desulfurization of Benzothiophene and Dibenzothiophene[a)]

Solvent	Xylene	Decalin	n-Pentadecane	Tetralin	1-Methylnaphthalene
Heat of Adsorption	15±3	16±2	17±1	18±2	24±2

a) Q / kcal mol^{-1}; Calculated on the basis of Eq. 3.

contrary, heats of adsorption of BT and DBT were strongly affected by solvents. In cases of toluene in BT HDS and n-heptane in DBT HDS which are considered to have the least retarding effect, heats of adsorption of BT and DBT are 22±1 and 22±1 kcal/mol, respectively. When a solvent with larger retarding effect was used, heat of adsorption of BT and DBT became smaller. These results indicated that the HDS reaction is retarded by competitive adsorption between BT or DBT and solvents to active catalytic sites. Therefore, the retarding effects of solvents were estimated by using Eq. 3 where k' and K_T in HDS of BT with toluene and DBT with n-heptane were applied:

$$r_{HDS} = k'K_TP_T \,/\, (1 + K_TP_T + K_{sol}P_{sol}), \qquad (3)$$

where K_{sol}=adsorption equilibrium constant of solvent; P_{sol}=partial pressure of solvent. Van't Hoff plots of K_{sol} revealed the linear relationship and heat of adsorption of solvents calculated by the slopes are shown in Table 1. The values of decalin, a common solvent in HDS of BT and DBT, were about same. The results in Table 1 indicate that the retarding effects of solvent increase in the order xylene<decalin<n-pentadecane<tetralin<1-methylnaphthalene and that solvents such as 1-methylnaphthalene, which has the high aromaticity, adsorbs competitively with thiophenes such as BT and DBT on Co-Mo/Al_2O_3 by more than 1:1 ratio.

Evidence regarding the relative ease with which BT and DBT desulfurize is contradictory.[1)] One reported the equivalent reactivities between BT and DBT[9)] and the other found DBT less reactive than BT.[10)] Concerning experiments in representative industrial conditions, Nag et al.[11)] reported that rate constant ratios of HDS of BT to that of DBT catalyzed by Co-Mo/Al_2O_3 were 13 at 573 K and 71 atm and 20 at 523 K and 40 atm, respectively. In the present study, the rate constant ratios were 10 at 200 and 220 °C and 50 atm in the case of decalin and 13 at 200 and 220 °C and 50 atm in the cases of toluene (BT) and n-heptane (DBT), respectively. It appears in industrial pressurized system catalyzed by Co-Mo/Al_2O_3 that

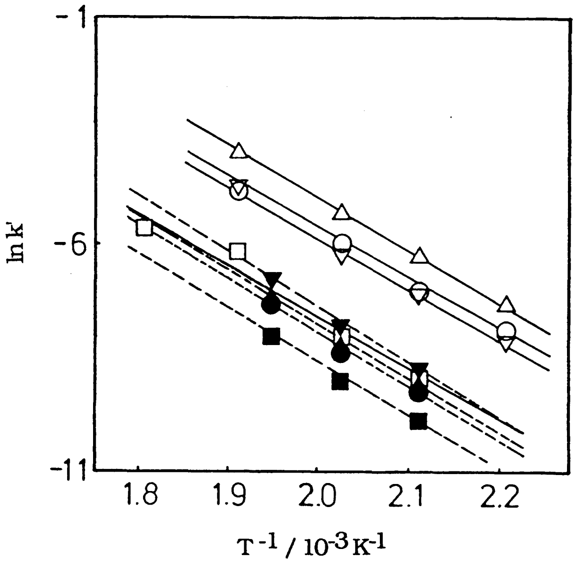

Fig. 2. Arrhenius plots of k'.
Symbols are the same as in Fig. 1.

dibenzothiophene is one order of magnitude less reactive than benzothiophene.

Kilakowski and Gates2) reported in HDS of BT without solvent that activation energy and heat of adsorption of BT were 20±3 and 15±10 kcal/mol when the rate equation derived from the mechanism on the basis of competitive adsorption of BT and hydrogen onto active sites was applied while heat of adsorption of BT was 19 kcal/mol on the basis of Eq. 1. On the other hand, Broderick and Gates,3) Vrinat and de Mourgue4) and Singhal et al.5) reported in the kinetic studies of dibenzothiophene HDS over a wide range of temperature and pressures that activation energies of DBT were 30, 23 and 39 kcal/mol, respectively. The differences of these seem to be due to reaction temperature performed since the higher range of reaction temperature made it larger. The temperature range where we performed (200-240 °C) are very similar to that of Vrinat and de Mourgues (473-520 K) and the value of activation energy of HDS is very similar each other. Broderick and Gates also reported that heat of adsorption of DBT was 4.5 kcal/mol.3) This value was much smaller than that we obtained. This is due to the lack of consideration of the solvent effect. Although they performed the experiment using DBT dissolved in n-hexadecane, the retarding effect of n-hexadecane was not considered. As shown in Table 1, heat of adsorption of n-pentadecane was 17±1 kcal/mol in this study. Taking into account the effect of solvent in study of Broderick and Gates, heat of adsorption of DBT could become larger.

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