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Effects of Solvents on Deep Hydrodesulfurization of Benzothiophene and Dibenzothiophene

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Solvent effects on hydrodesulfurization (HDS) of benzothiophene (BT) and dibenzothiophene (DBT) catalyzed by Co–Mo/Al_2O_3 were investigated under deep hydrodesulfurization conditions. Data for BT and DBT are arranged by the Langmuir–Hinshelwood equation. Activation energies of HDS of BT and DBT were approximately 21 and 24 kcal/mol respectively, in every solvent. Heats of adsorption of BT and DBT are both estimated to be 22 kcal/mol. Significant solvent effects were found under deep desulfurization conditions, and the values of heat of adsorption for various solvents were estimated from the K_{sol} obtained. © 1993 Academic Press, Inc.

INTRODUCTION

Under deep desulfurization conditions, effects of other components in light oil cannot be disregarded. However, studies to date of hydrodesulfurization (HDS) have not shed light on the retarding effects of solvents, particularly in the cases of benzothiophene and dibenzothiophene, which are sulfur-containing key compounds in light oil.

Although a number of kinetic studies (*1–14*) have been performed on the HDS of BT and DBT in the presence of Co–Mo/Al_2O_3, there are only a few examples which cover a wide range of temperatures and pressures and take into account effects of reactants and products on the rate of reaction. Further, a mechanism of deep desulfurization of BT and DBT and retarding effects of components in feedstock, e.g., solvents, remains unknown.

In this paper, we report retarding effects of solvents in the kinetic study of deep HDS of BT and DBT catalyzed by Co–Mo/Al_2O_3. Adsorption equilibrium constants and heat of adsorption of solvents were estimated by an equation derived from the kinetic data.

EXPERIMENTAL

Materials. Solvents, *n*-heptane, toluene, xylene, decalin, *n*-pentadecane, tetralin, 1-methylnaphthalene (Kishida Chemicals), *n*-hexadecane, and dibenzothiophene (Tokyo Kasei Chemicals), were the commercial GR grade and were further purified by passage through a column (I.D. 20 mm; 30 cm) containing activated alumina (0.063–0.200 mm). Benzothiophene (Wako Chemicals) was distillated under vacuum before use. Dibenzothiophene (Tokyo Kasei Chemicals) was recrystallized from ethanol. Hydrogen (99.99%) was obtained from Tohei Chemicals. Hydrogen sulfide in hydrogen (H_2S:H_2 = 3:97) was obtained from Takachio Chemicals. The commercial Co–Mo/Al_2O_3 (CoO, 3.8 wt%; MoO_3, 12.5 wt%) was supplied as a 1/32 extrudate which was crushed and screened to provide 0.84- to 1.19-mm granules used in this work.

Apparatus and procedure. 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 cc. The single charge was used throughout the entire se-

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ries of experiments. After the catalyst bed was heated for more than 24 h at 450°C in air, it was presulfided with a mixture of 3% H_2S in H_2 flowing at 30 liter/h at atmospheric pressure and 400°C for 3 h. After these pretreatments, the reactor was cooled in a H_2S/H_2 stream to the expected temperature and was pressurized by hydrogen. Then, the solution containing benzothiophene or dibenzothiophene was supplied to the feed pump (Kyowa Seimitsu KHD-16). A typical reaction was carried out under the following conditions: temperature, 180–310°C; total pressure, 25–100 atm; flow rate of hydrogen, H_2 18 liter/h; flow rate of solution, 14 g/h (WHSV 70 h^{-1}); concentration of dibenzothiophene, 0.1–3.0 wt%. Conversion of DBT reached a steady state within about 3 h. Then, samples of products were collected from a gas–liquid separator four times every 15 min. In the sampling period, hydrogen sulfide was trapped through an aqueous solution of $Pb(CH_3COO)_2 \cdot 3H_2O$. PbS formed was filtered, dried at 120°C for 2 h, and weighed. Sulfur removed by the conversion of DBT was quantitatively recovered by the transformation of hydrogen sulfide into PbS in that period. Subsequently, reaction temperature was changed and after 1 h sampling was carried out in a similar manner. No sign of deactivation of the catalyst was observed during the run for 16 h.

Analytical. Reaction products were analyzed by gas chromatography with FID detector (Hitachi 163) using a OV-1 capillary column (I.D. 0.25 mm × 50 m).

Kinetic calculations. For hydrodesulfurization of BT and DBT, Langmuir–Hinshelwood kinetics have widely been reported (*1–14*),

$$r_{HDS} = k_{HDS}K_TP_T/(1 + K_TP_T + K_{H_2S}P_{H_2S}) \times K_HP_H/(1 + K_HP_H), \quad (1)$$

where r_{HDS} = rate of HDS; k_{HDS} = rate constant of HDS; K_T, K_{H_2S}, and K_H = adsorption equilibrium constants of thiophenes, hydrogen sulfide, and hydrogen; P_T, P_{H_2S}, and P_H = partial pressure of thiophenes, hydrogen sulfide, and hydrogen. Under our experimental conditions, the kinetic equation can be simplified for the following reasons: (1) Because the amount of converted BT or DBT was zero order with respect to partial pressure, the hydrogen pressure term can be included in the rate constant. (2) Under deep desulfurization conditions, the inhibition due to H_2S is not significant because of the low concentration of H_2S in the reactor and the constant hydrogen sweeping. Based on the above assumptions, Eq. (1) can be simplified to

$$r_{HDS} = k_{HDS}K_TP_T/(1 + K_TP_T). \quad (2)$$

RESULTS

Effects of solvents on hydrodesulfurization of benzothiophene and dibenzothiophene were investigated and the results in the case of 0.1 wt% of benzothiophene (BT) and (DBT) are shown in Fig. 1. At each temperature, the conversion of BT decreased in the order toluene > decalin > *n*-pentadecane > 1-methylnaphthalene. The conversion of DBT also decreased in the order *n*-heptane > xylene > decalin > tetralin. Figure 2 shows the effects of initial concentration of DBT on the conversion. The differences between *n*-heptane, xylene, decalin, and tetralin at 0.1 wt% of DBT were

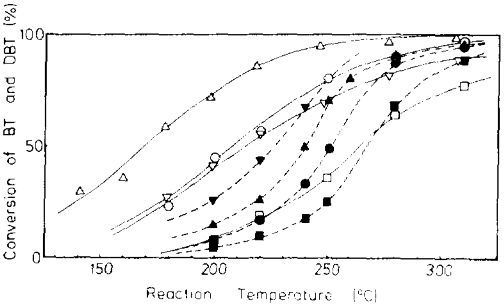

FIG. 1. Effects of solvents on conversion of benzothiophene and dibenzothiophene. 50 kg/cm^2; WHSH, 70 h^{-1}; catalyst, 0.2 g; H_2 18 liter/h; initial concentration of BT, 0.1 wt%. Solvent: △, toluene; ○, decalin; ▽, *n*-pentadecane; and □, 1-methylnaphthalene. Initial concentration of DBT, 0.1 wt%; solvent: ▼, *n*-heptane; ▲, xylene; ●, decalin; and ■, tetralin.

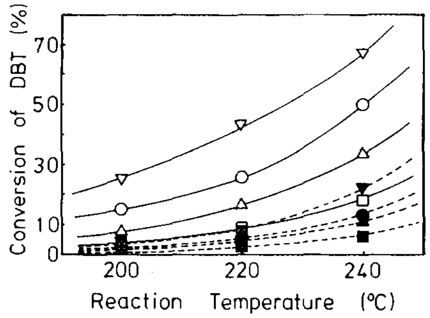

FIG. 2. Effect of initial concentration of dibenzothiophene on conversion of dibenzothiophene. 50 kg/cm^2; WHSH, 70 h^{-1}; catalyst, 0.2 g; H_2 18, liter/h; DBT, 0.1 wt%: ▽, *n*-heptane; ○, xylene; △, decalin; and □, tetralin. DBT 1.0 wt%: ▼, *n*-heptane; ●, xylene; ▲, decalin; and ■, tetralin.

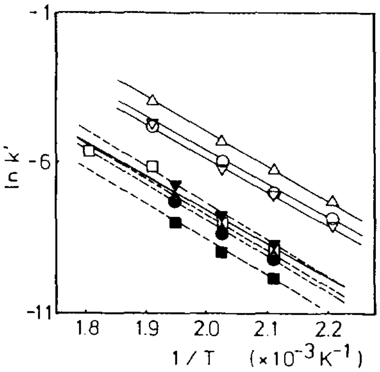

FIG. 3. Arrhenius Plots of *k'*. Solvents in BT HDS: △, toluene; ○, decalin; ▽, *n*-pentadecane; and □, 1-methylnaphthalene. Solvents in DBT HDS: ▼, *n*-heptane; ▲, xylene; ●, decalin; and ■, tetralin.

larger than those at 1.0 wt% of DBT, which shows that the effects of solvents at 0.1 wt% of DBT are larger than those at 1.0 wt%, especially at lower temperature. Therefore, the effects of solvents become large under deep desulfurization conditions. In deep desulfurization of light oil, its components will have a large influence on the catalytic activity and selectivity.

Kinetic parameters were estimated by Eq. (2). Arrhenius plots of *k'* in the use of each solvent were drawn in Fig. 3. Every slope of BT in Fig. 3 was approximately equal and the activation energy in the case of every solvent was calculated to be 21 kcal/mol. A similar result was also obtained in the case of DBT, and the activation energy was calculated to be 24 kcal/mol. These results show that the activation energy is not affected by solvent. Heats of adsorption of BT and DBT were estimated from the van't Hoff plots of K_{BT} and K_{DBT} and are summarized in Tables 1 and 2. When toluene in HDS of BT or *n*-heptane in HDS or DBT, which can be regarded to have the least retarding effect on HDS among the four solvents, was used, heats of adsorption of BT and DBT were both 22 kcal/mol. In contrast to the activation energy, the heat of adsorption seems to be affected by solvents and showed a small value when a solvent which adsorbed on the catalyst more strongly to retard the HDS rate was used. It is suggested that the competitive adsorption between benzothiophene and a solvent on the catalyst surface would retard the HDS reaction.

For better understanding of these results, the retarding effects of solvents were esti-

TABLE 1

Effects of Solvent on Heat of Adsorption of BT[a]

Solvent	Toluene	Decalin	*n*-Pentadecane	1-Methylnaphthalene
Q_{BT} (kcal/mol)	22	16	16	10

[a] Obtained on the basis of Eq. (2).

TABLE 2

Effects of Solvent on Heat of Adsorption of DBT[a]

Solvent	*n*-Heptane	Xylene	Decalin	Tetralin
Q_{DBT} (kcal/mol)	22	16	12	10

[a] Obtained on the basis of Eq. (2).

mated by Eq. (3) where the retarding term, $K_{sol}\ P_{sol}$, was introduced into Eq. (2):

$$r_{HDS} = k_{HDS}K_TP_T/(1 + K_TP_T + K_{sol}P_{sol}). \tag{3}$$

Here K_{sol} is the equilibrium adsorption constant, and P_{sol} is the partial pressure of solvent. In the determination of K_{sol}, the values of k' and K_T obtained from Eq. (2) in the case of toluene and n-heptane are used in HDS of BT and DBT, respectively. It was assumed that adsorption of toluene or *n*-heptane onto active sites of HDS of the catalyst would be much weaker than that of BT or DBT, that is, $K_{toluene}P_{toluene}$ or $K_{n\text{-heptane}}P_{n\text{-heptane}}$ could be ignored at every temperature in comparison with $K_{BT}P_{BT}$ or $K_{DBT}P_{DBT}$. Van't Hoff plots of K_{sol} revealed the linear relationship, and the heats of adsorption of solvents calculated by the slopes are shown in Table 3. Heats of adsorption of solvents increased in the order xylene < decalin < *n*-pentadecane < tetralin < 1-methylnaphthalene, indicating solvents such as 1-methylnaphthalene, which has the high aromaticity, adsorbs competitively with thiophenes such as BT or DBT on Co–Mo/Al_2O_3 by more than 1:1 ratio.

DISCUSSION

The kinetic study of HDS of DBT over a wide range of temperatures and pressures was reported by Broderick and Gates (*6*). They performed the reaction of DBT with hydrogen in the range 548–598 K and 34–160 atm on Co–Mo/Al_2O_3. For hydrogenolysis of DBT, they recommended the rate equation

$$r_{HDS} = kK_{DBT}P_{DBT}/(1 + K_{DBT}P_{DBT} + K_sP_s)^2 \times K_{H_2}P_{H_2}/(1 + K_{H_2}P_{H_2}), \tag{4}$$

where K_s and P_s are the adsorption equilibrium constant and partial pressure of hydrogen sulfide. For DBT hydrogenolysis in this study, the activation energy and the heats of adsorption of DBT, H_2S, and hydrogen were 30, 4.5, 5.3, and −8.4 kcal/mol, respectively. Although the important result in this study is the firmly established dependence of the hydrogenolysis rate on the H_2 concentration, the heat of hydrogen adsorption was the negative value. Further, the power of two in denominator term for DBT and H_2 adsorption was not justified in relation to a reaction mechanism.

Vrinat and de Mourgues (*7*) reported a vapor-phase kinetic study of DBT on Co–

TABLE 3

Heat of Adsorption of Solvents[a]

Solvent	Xylene	Decalin	*n*-Pentadecane	Tetralin	1-Methylnaphthalene
Q_{sol} (kcal/mol)	15	16	17	18	24

[a] Obtained on the basis of Eq. (4).

Mo/Al_2O_3 industrial catalyst at 473–520 K and 5–50 atm. The rate raw consistent with a Langmuir-Hinshelwood mechanism without the competitive adsorptions between DBT and hydrogen, and the inhibition by H_2S, and is best expressed as

$$r_{HDS} = kK_{DBT}P_{DBT}/(1 + K_{DBT}P_{DBT} + K_sP_s) \times K_{H_2}P_{H_2}/(1 + K_{H_2}P_{H_2}). \quad (5)$$

In this study, the activation energy of HDS and the heat of adsorption of hydrogen were 23 and 4.5 kcal/mol, respectively.

Singhal *et al.* (*8*) reported another kinetic study of DBT HDS over a wide range of reaction conditions (558–623 K, 7–26 atm, Co–Mo/Al_2O_3). They proposed Eq. (6), similar to Eq. (5),

$$r_{HDS} = kK_{DBT}P_{DBT}/(1 + K_{DBT}P_{DBT} + K_{prod}P_{prod}) \times K_{H_2}P_{H_2}/(1 + K_{H_2}P_{H_2}), \quad (6)$$

where K_{prod} and P_{prod} mean the adsorption equilibrium constant and partial pressure of products. In this study, the activation energy of HDS and heat of adsorption of hydrogen were 39 and 25 kcal/mol, respectively.

All these equations are similar to Eq. (1), which we used. However, there are some differences in the results. In our result, activation energy of HDS was about 24 kcal/mol in each solvent. The result of Vrinat and de Mourgues is closest to our results. Because solvents does not affect the activation energy, as shown in the present study, the differences in activation energy between the above results and ours are probably due to the reaction temperature. When the range of temperature is relatively high, the activation energy of HDS tends to be a high value. Since our experiments and Vrinat's were performed at the similar lowest temperature range, similar results seemed to be obtained.

Heat of adsorption of hyrogen also appears to depend on the range of hydrogen pressure. When the range of hydrogen pressure is small and relatively low, heat of adsorption of hydrogen reveal a high values as shown by Singhal's result. When the range of hydrogen pressure was extended to 50 atm by Vrinat or 160 atm by Broderick, heat of adsorption of hydrogen remarkably decreased and the result by Broderick showed negative value. In the present our result, hydrogen reached the saturation of adsorption over 25 atm at every temperature, and the rate of HDS did not change with respect to hydrogen pressure. Although these results show the mechanism that DBT and hydrogen adsorb the separate adsorption sites on the catalyst, we cannot obtain K_{H_2} and heat of adsorption of hydrogen from these data. In the range of hydrogen where Broderick performed his experiments, because the rate of HDS is near zero order reaction with respect to hydrogen pressure and the increase of rate with an increase of hydrogen pressure was extremely small, it seems that they could not obtain the meaningful value of heat of adsorption of hydrogen.

Heat of adsorption of DBT are affected by solvent as shown in Table 1. When a solvent which adsorbs strongly on a catalyst in used, Q_{DBT} is estimated to be smaller than that without solvent. The value of Q_{DBT} obtained by Broderick and Gates were smaller than those obtained by us. This would be due to the lack of consideration of a solvent in the data of Broderick. As shown in Table 2, heat of adsorption of *n*-hexadecane which was used by Broderick and Gates was 20 kcal/mol, largest among the four. Therefore, it may be difficult to obtain the sure value of Q_{DBT} in the reaction with heaviest solvents such as *n*-hexadecane.

The kinetic study of benzothiophene HDS over a wide range of temperature and pressure was reported by Kilanowski and Gates (*13*). They performed the reaction of benzothiophene with hydrogen at temperatures 525, 575 and 605 K below 2 atm on Co–Mo/Al_2O_3. They showed that Eq. (7) below, where benzothiophene, hydrogen sulfide, and hydrogen competitively adsorbed on same adsorption sites and the retarding term, $K_{H_2}P_{H_2}$, in the denominator was neglected, roughly fits the data at all three temperature and that Eq. (8) below, where benzothiophene and hydrogen adsorbed on separate adsorption sites and benzothiophene and hydrogen sulfide competitively adsorbed on same adsorption sites, reasonably fits the data at the two higher temperatures:

$$r_{HDS} = kK_{BT}P_{BT}K_{H_2}P_{H_2}/(1 + K_{BT}P_{BT} + K_SP_S)^2 \quad (7)$$

$$r_{HDS} = kK_{DBT}P_{DBT}/(1 + K_{DBT}P_{DBT} + K_SP_S) \times K_{H_2}P_{H_2}/(1 + K_{H_2}P_{H_2}). \quad (8)$$

When Eq. (7) was used in their no-solvent system, the activation energy was 20 ± 3 kcal/mol and heats of adsorption were 15 ± 10 and 6 ± 6 kcal/mol, respectively. It was described that the uncertainty in these latter values reflects the poorness of fit of the data to Eq. (7) at 525°C. When Eq. (8) was used, the values for BT and H_2S, were 19 and 13 kcal/mol, respectively. Our results in the case of toluene showed very close values to the results of Kilanowski in both activation energy and heat of adsorption of BT.

CONCLUSION

Under deep desulfurization conditions, the effects of solvents were investigated. Activation energies and heats of adsorption of BT and DBT were estimated by a Langmuir–Hinshelwood rate equation. Although activation energies were not affected by solvents and were 21 and 24 kcal/mol, respectively, heats of adsorption of BT and DBT were different depending on solvents. When heats of adsorption of solvents were estimated from the retarding term $K_{sol}P_{sol}$ introduced into the denominator of the rate equation, they increased in the order xylene < decalin ≤ *n*-pentadecane < tetralin < 1-methylnaphthalene.

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