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Selectivity of Molybdenum Catalyst in Hydrodesulfurization, Hydrodenitrogenation, and Hydrodeoxygenation: Effect of Additives on Dibenzothiophene Hydrodesulfurization

MASATOSHI NAGAI AND TOSHIAKI KABE

Department of Chemical Engineering, Tokyo University of Agriculture and Technology, Koganei-shi, Tokyo 184 Japan

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Kinetic studies of the hydrodesulfurization of dibenzothiophene on a presulfided molybdena–alumina catalyst were carried out in a high-pressure-flow microreactor. The mechanism discussed is based on selective poisoning studies, using various nitrogen, polyaromatic, sulfur, and oxygen compounds. The nitrogen compounds inhibited the hydrogenation of dibenzothiophene because they adsorbed more strongly than did dibenzothiophene at lower temperatures. At higher temperatures, the nitrogen compounds also hinder the desulfurization together with the hydrogenation of dibenzothiophene. The sulfur and the oxygen compounds retarded all reactions of the desulfurization of dibenzothiophene. The reactions of the desulfurization, the denitrogenation, and the deoxygenation proceed on one type of site and the hydrogenation reactions on another site.

INTRODUCTION

Crude petroleum and synthetic fuels from both oil shale and coal will be extensive in the future. Unfortunately, however, crude oils also contain sulfur, nitrogen, and oxygen compounds as impurities.

Much work (*1–3*) has been performed on the hydrodesulfurization process. One group favors a preliminary hydrogenation of the thiophene ring (*4*) and another supports initial C–S bond cleavage leading to hydrocarbons and H_2S (*5–7*). The same kind of duality, hydrogenation and hydrogenolysis, exists for benzothiophene and dibenzothiophene found in the heavy feedstocks. We have, therefore, chosen the hydrodesulfurization of dibenzothiophene on a presulfided molybdena–alumina catalyst proceeded via two different reaction pathways, as shown in Fig. 1 (*8*).

Although in the hydrotreatment, a commonly used catalyst is known to be poisoned by nitrogen compounds and hydrogen sulfide formed during the treatment, the basic mechanism of the poisoning is poorly understood. The effects of pyridine on the hydrodesulfurization activity of $CoMo/Al_2O_3$ catalyst were only by Desikan and Amberg (*1*), Cowley and Massoth (*9*), and Satterfield *et al.* (*10*). These studies show that there were two catalytic sites, and pyridine apparently poisoned these sites in different degrees. It is not obvious that pyridine inhibits either hydrogenation of thiophene or the breaking of the C–S bond. Hydrogen sulfide inhibits the hydrogenation of 1-butene (*11*) and of biphenyl (*12*) catalyzed by a sulfided $CoMo/Al_2O_3$ catalyst in the absence of thiophene. However, Ramachandran and Massoth (*13*) reported no effect of hydrogen sulfide on hexene hydrogenation over a $CoMo/Al_2O_3$ catalyst, and Broderick *et al.* (*12*) found dibenzothiophene hydrogenation was not inhibited by H_2S. There is practically no study on the effect of oxygen compounds on the hydrodesulfurization.

During the course of the poisoning study, we noticed selective poisoning patterns for the hydrodesulfurization of dibenzothiophene on a molybdena–alumina catalyst. Because the selectivity pattern is characteristic of the correlation between hydrogenation and hydrogenolysis and the nature of active site, we now have deter-

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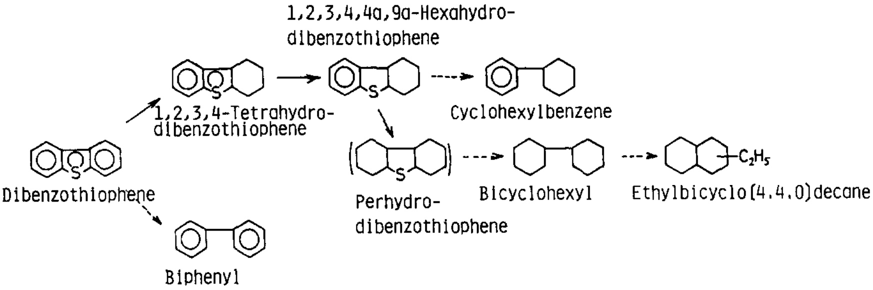


FIG. 1. Reaction scheme for hydrodesulfurization of dibenzothiophene. Solid arrows indicate hydrogenation sites poisoned by nitrogen compounds, and dashed arrows desulfurization sites poisoned by hydrogen sulfide.

mined the changes in the product composition in the hydrodesulfurization of dibenzothiophene in the presence of various nitrogen compounds, a low-molecular-weight sulfur compound, oxygen compounds, and a polyaromatic compound. These compounds added are given in Table 1.

Selectivities of a molybdena–alumina catalyst in hydrogenation and hydrogenolysis discussed are based on the kinetics of the poisoning effect on these reactions.

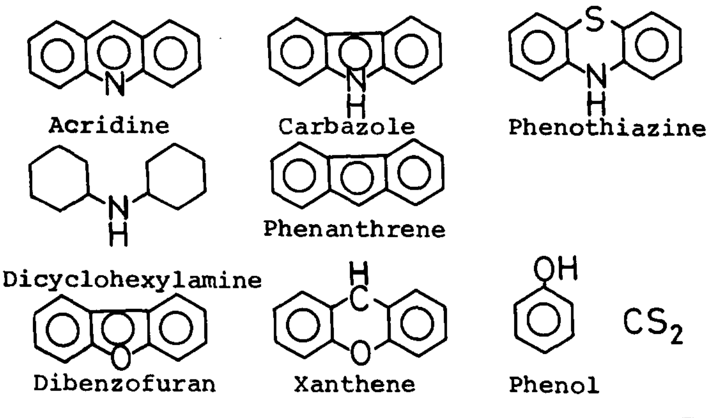
EXPERIMENTAL

Catalyst and reagents. A 12.5% MoO_3/Al_2O_3 catalyst was prepared by impregnating the γ-alumina support with a solution of ammonium paramolybdate. The solution was evaporated to dryness at 90°C with stirring, followed by drying at 100°C and then calcining at 550°C for 5 h in air. Although the catalyst was supplied as a 1/32-in. extrudate, it was crushed and screened to provide 0.84- to 1.19-mm granules used in this work. The surface area of the catalyst is 188 m^2/g.

Dibenzothiophene was synthesized according to the method of Gilman and Jacoby (*14*): mp 100.5–101°C (Ref. (*14*), 99°C); elementary analysis C 78.29, H 4.40, S 17.31; Calcd., C 78.22, H 4.38, S 17.40. The other chemicals used were commercial reagent grade. The hydrogen was dried over molecular sieves (Type 13X) prior to use.

Apparatus and procedure. The reactor

TABLE 1
The Compounds Added



was an 11-mm-i.d. stainless-steel tube packed with 2.0 g of catalyst particles. A single charge was used throughout the entire series of experiments. After the catalyst bed was heated for more than 24 h at 450°C in air, the catalyst was reduced *in situ* with hydrogen at 400°C and at 100 atm pressure for 4 h. The catalyst was then presulfided with a mixture of 10% H_2S in H_2 flowing at 30 liters/h at atmospheric pressure and 400°C for 3 h. After sulfiding, the reactor was cooled to 300°C in a H_2S/H_2 stream, and then the solution containing 5 wt% of dibenzothiophene in xylene was supplied to the feed pump. A typical reaction was carried out under the following conditions; temperature, 300°C; total pressure, 100 atm; flow rate of hydrogen, 28 liters/h; flow rate of solution, 15 ml/h. After steady state was reached in about 3 h, the solution containing both 5 wt% of dibenzothiophene and a poisoning compound was then injected instead of the former solution. After 2 h, samples of the products were collected 3 times every 15 min. The next feed then contained dibenzothiophene and a more concentrated compound than the previous one. No sign of deactivation of the catalyst was observed during the run for 12 h.

Analytical. Reaction products were analyzed by gas chromatography using 1% Silicone OV-17 on 60 to 80 mesh Uniport B. The column was heated from 80 to 200°C at a rate of 10°C/min. More thorough analyses were done by obtaining mp, mass spectra, and ir of the individual products as described in a previous paper (*15*). The initial concentration (wt%) of the added compounds was converted to a partial pressure (atm), in Figs. 8, 9, and 10, since the compounds were completely transformed into vapor at 300°C.

RESULTS

Hydrodesulfurization of Dibenzothiophene

In the hydrodesulfurization of dibenzothiophene (5 wt%) on a presulfided molybdena–alumina catalyst at 300°C and a total pressure of 100 atm, the products, except for gaseous products, were cyclohexylbenzene (0.63 wt%), biphenyl (0.27 wt%), *cis-* and *trans-*1,2,3,4,4*a*,9*a*-hexahydrodibenzothiophene (0.11 wt%), 1,2,3,4-tetrahydrodibenzothiophene, bicyclohexyl (0.03 wt%), ethylbicyclo[4.4.0]decane (0.02 wt%). The conversion was 75%. This observation showed that cyclohexylbenzene was produced greater than biphenyl, in contrast to the results showing much production of biphenyl under the similar conditions for a sulfided $CoMo/Al_2O_3$ catalyst (*12, 16–18*). This is probably due to the presence of cobalt. We studied previously a kinetics of dibenzothiophene hydrodesulfurization (*8*) and reported that the reaction proceeded in the two different reaction pathways: one in which cyclohexylbenzene was produced through hexahydrodibenzothiophene, and the other in which biphenyl was produced by fission of the C–S bond in dibenzothiophene, as shown in Fig. 1. We described also that biphenyl was not hydrogenated to yield cyclohexylbenzene in the presence of a small amount of dibenzothiophene. This mechanism is consistent with that of dibenzothiophene hydrodesulfurization over a MoS_2 catalyst reported by Urimoto and Sakikawa (*19*).

Effect of Nitrogen Compounds and a Polyaromatic Compound

The changes in the product composition in the hydrodesulfurization of dibenzothiophene at 300°C and a total pressure of 100 atm in the presence of acridine are shown in Fig. 2. The amount of cyclohexylbenzene dropped from 0.62 wt% initially to 0.12 wt% at 0.05 wt% acridine and then became 0.04 wt% at 0.5 wt% acridine. All of the hydrogenated dibenzothiophene, bicyclohexyl, ethylbicyclo[4.4.0]decane, and cyclohexylbenzene decreased remarkably with an increase in acridine, while biphenyl increased. There were similar tendencies in the case of carbazole, dicyclohexylamine, phenothiazine, and phenanthrene. The

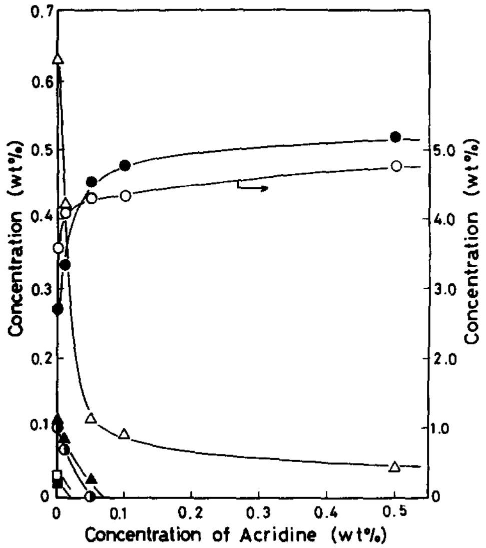


FIG. 2. Effect of acridine on the products of the hydrodesulfurization of dibenzothiophene. ○, dibenzothiophene; ◑, 1,2,3,4-tetrahydrodibenzothiophene; ▲, 1,2,3,4,4a,9a-hexahydrodibenzothiophene; ●, biphenyl; △, cyclohexylbenzene; □, bicyclohexyl; ■, ethylbicyclo[4.4.0]decane. Conditions: dibenzothiophene, 5 wt%; temperature, 300°C; total pressure, 100 atm; weight hourly space velocity, 7.

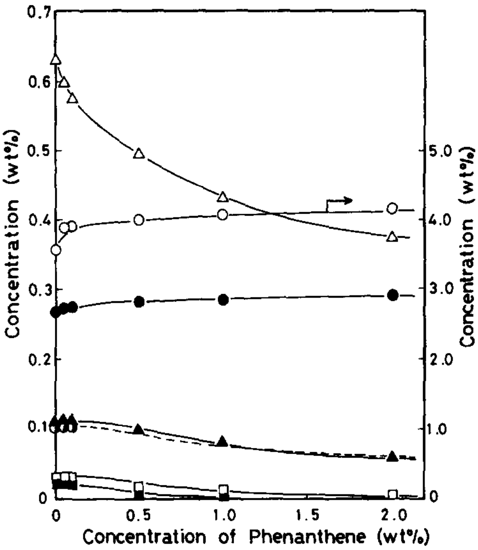


FIG. 3. Effect of phenanthrene on the products of the hydrodesulfurization of dibenzothiophene. Dotted line: concentration of tetrahydrodibenzothiophene estimated because it has the same retention time as a product of phenanthrene hydrogenolysis. The symbols and the reaction conditions are the same as those in Fig. 2.

changes in the product composition for the addition of phenanthrene is shown in Fig. 3. The amount of cyclohexylbenzene decreased gradually with an increase in phenanthrene and was 0.37 wt% at 2.0 wt% phenanthrene. The degree of decrease in cyclohexylbenzene was in the order of acridine > carbazole > phenothiazine > dicyclohexylamine > phenanthrene. The degree of increase in biphenyl was in the same

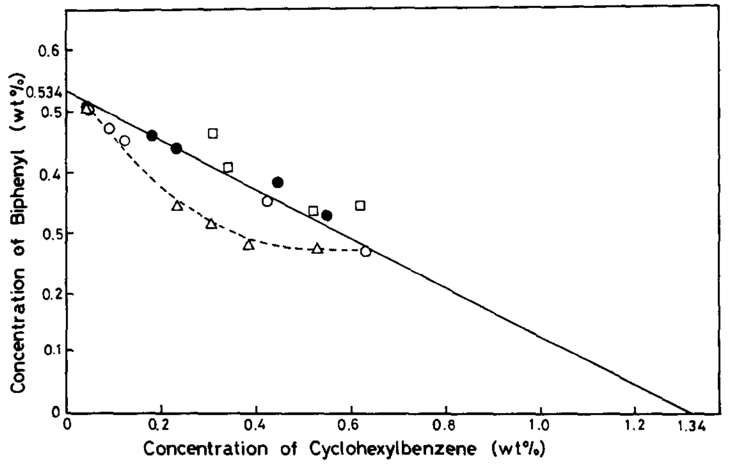


FIG. 4. Relationships between biphenyl and cyclohexylbenzene in the presence of the nitrogen compounds and phenanthrene. ○, acridine; △, carbazole; □, phenothiazine; ●, dicyclohexylamine; ◒, phenanthrene.

order. The amount of cyclohexylbenzene is plotted vs the amount of biphenyl in Fig. 4. The amount of cyclohexylbenzene showed a linear relation to the amount of biphenyl, except for the case of carbazole. The deviation from the relation is probably due to the denitrogenation of perhydrocarbazole to bicyclohexyl as well as the hydrogenation even at 300°C. In the case of acridine, dicyclohexylmethane produced from the hydrodenitrogenation of acridine was observed above 310°C. The nitrogen compound was found to depress also the desulfurization of dibenzothiophene at higher temperatures. However, the competitive reactions of nitrogen compounds and dibenzothiophene were not resolved due to more complex problems involving the inhibition of both hydrogenation and desulfurization.

Effect of Sulfur and Oxygen Compounds

The changes in the product composition in the hydrodesulfurization of dibenzothiophene at 300°C and a total pressure of 100 atm in the presence of carbon disulfide and xanthene are shown in Figs. 5 and 6. the amounts of cyclohexylbenzene and biphenyl decreased with an increase in carbon disulfide. All amounts of the desulfurization products diminished by the addition of these compounds, while dibenzothiophene and the hydrogenated dibenzothiophene compounds raised slightly. We also observed similar changes in the product composition in the presence of phenol and dibenzofuran. This tendency differs from that with the addition of nitrogen compounds and phenanthrene. A plot of the amount of cyclohexylbenzene vs the amount of biphenyl gives a straight line in Fig. 7.

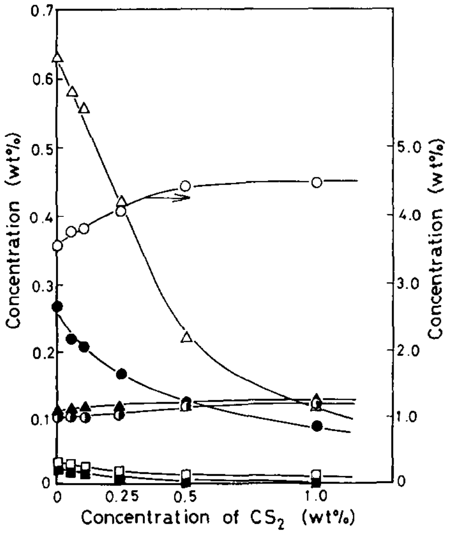


FIG. 5. Effect of carbon disulfide on the products of the hydrodesulfurization of dibenzothiophene. The symbols and the reaction conditions are the same as those in Fig. 2.

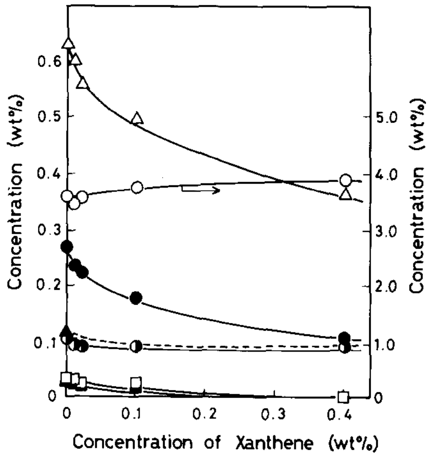


FIG. 6. Effect of xanthene on the products of the hydrodesulfurization of dibenzothiophene. Dotted line: concentration of tetrahydrodibenzothiophene estimated because it has the same retention time as xanthene. The symbols and the reaction conditions are the same those in Fig. 2.

DISCUSSION

Relationship between the Formation of Biphenyl and the Formation of Cyclohexylbenzene

The main desulfurization products in the hydrodesulfurization of dibenzothiophene were biphenyl and cyclohexylbenzene as described above. When nitrogen compounds were added, the amount of the desulfurization product increased but the others decreased. If the increasing amount of the product was directly proportional to the rate of the desulfurization, nitrogen

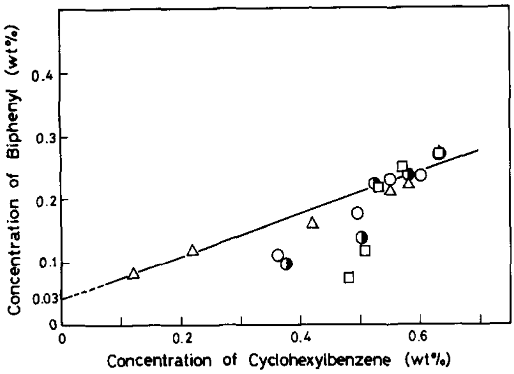


FIG. 7. Relationships between biphenyl and cyclohexylbenzene in the presence of sulfur and oxygen compounds. △, carbon disulfide; ○, xanthene; ◑, dibenzofuran; □, phenol.

compounds might be expected to accelerate the desulfurization of dibenzothiophene to biphenyl. However, there is no information on a direct promotion of hydrodesulfurization in the presence of nitrogen compounds, much less both the promotion of desulfurization and the simultaneous inhibition of other reactions. Furthermore, if cyclohexylbenzene is produced from the hydrogenation of biphenyl, the changes will be caused by inhibiting the hydrogenation of biphenyl to cyclohexylbenzene in the presence of the nitrogen compounds. However, this explanation is disproved on the basis of the previous study (*8*) which showed that hydrogenation does not take place during the hydrodesulfurization of dibenzothiophene. Hence, the phenomenon must be interpreted in another way.

A kinetics of dibenzothiophene hydrodesulfurization on a molybdena–alumina catalyst has been studied at temperatures of 270–340°C and at total pressures of 25–145 atm (*8*). It was shown that the best kinetic equations for the formation of biphenyl and cyclohexylbenzene were

$$r_{BP} = kK_DK_HP_DP_H/(1 + K_{6H}P_{6H} + K_DP_D + K_HP_H)^2 \quad (1)$$

$$r_{CHB} = kK_{6H}K_HP_{6H}P_H/(1 + K_{6H}P_{6H} + K_DP_D + K_HP_H)^2, \quad (2)$$

where r is the reaction rate; P_i is the partial pressure; K_i and k_i are constants; BP, CHB, 6H, D and H are biphenyl, cyclohexylbenzene, hexahydrodibenzothiophene, dibenzothiophene, and hydrogen. These equations were derived by assuming that the desulfurization and the hydrogenation occur on different sites. All of the dibenzothiophene, hydrogen, hexahydro-, and perhydrodibenzothiophene adsorbed competitively on the desulfurization site, while dibenzothiophene, tetrahydro-, and hexahydrodibenzothiophene on the hydrogenation site. The adsorption of perhydrodibenzothiophene is negligible because of small amount of bicyclohexyl.

The relationship between the increase in biphenyl and the decrease in cyclohexylbenzene can be explained in terms of the two rate equations. Acridine was successively hydrogenated to perhydroacridine but was not denitrogenated to yield dicyclohexylmethane at 300°C (*20*), which was not observed in the present study also. This indicates that acridine adsorbs only on the hydrogenation site. The other nitrogen compounds are found to adsorb almost on the hydrogenation site. Since the presence of nitrogen compounds does not influence adsorption on the desulfurization site, the sum of the adsorption of the compounds on the desulfurization site is approximately constant before and after the addition of the nitrogen compounds, *i.e.*, the denominator in Eq. (1) remains almost unchangeable. Hence, r_{BP} increases with the increase in dibenzothiophene on the addition of the nitrogen compounds. The decrease in r_{CHB} is interpreted from Eq. (2) in the same way. Furthermore, since dibenzothiophene and hexahydrodibenzothiophene adsorbed competitively on the desulfurization site, the increase in the formation of biphenyl from dibenzothiophene is correlated with the decrease in that of cyclohexylbenzene from hexahydrodibenzothiophene. The linear relationship in Fig. 4 added strong support for the suggestion that the desulfurization and the hydrogenation occur on different sites on a sulfided molybdena–alumina catalyst.

When the sulfur and the oxygen compounds were added, the amounts of both biphenyl and cyclohexylbenzene decreased in Figs. 5 and 6. If these added compounds adsorbed competitively with dibenzothiophene and hexahydrodibenzothiophene on the desulfurization site, the added compounds would retard the desulfurization of both biphenyl and cyclohexylbenzene. Then the decrease in biphenyl must be in agreement with the decrease in cyclohexylbenzene. The decreasing amount of cyclohexylbenzene is proportional to the decreasing amount of biphenyl from Fig. 7. Thus these compounds adsorbed competitively with dibenzothiophene and hexahydrodibenzothiophene on the desulfurization site. This relation will be explained also on the basis of the poisoning kinetics using Eqs. (1) and (2). Therefore, the relation between biphenyl and cyclohexylbenzene supported the idea that hydrogenation occurs on one site and desulfurization occurs on another site.

Kinetics of Selective Poisoning

Many investigators proposed that the hydrodesulfurization of thiophene was expressed by a Langmuir-type equation. Satterfield and Roberts (*7*) and Moro-oka and Hamrin (*21*) proposed a similar equation based on a study of the hydrodesulfurization of thiophene over a CoMo/Al_2O_3 catalyst at atmospheric pressure;

$$r_T = k_T P_T P_H/(1 + K_T P_T + K_S P_S)^2 \quad (3)$$

where T, H, and S are thiophene, hydrogen, and hydrogen sulfide. This equation was on the basis of a single mechanism in which thiophene, hydrogen sulfide, and hydrogen adsorbed competitively on the same site. At higher pressure of hydrogen and a small amount of hydrogen sulfide, Eq. (3) was in agreement with our Eqs. (1) and (2).

Very recently Singhal *et al.* (*22*) and Broderick *et al.* (*12, 18*) have reported on kinetics of hydrogenation and desulfurization of dibenzothiophene on a sulfided CoMo/Al_2O_3 catalyst, and they proposed Langmuir-type rate equations. Singhal *et al.* postulated that two types of sites are involved in the hydrodesulfurization, on one of which dibenzothiophene and the reaction products and H_2S competitively adsorb and a second site on which hydrogen adsorbs. Broderick *et al.* (*12*) proposed that the reactant to be hydrogenated is π-bonded at exposed Mo cations, where H_2S undergoes weak competitive adsorption and bases undergo strong competitive adsorption. However, their assumption differs from that in our studies; hydrogenation occurs on one site, and desulfurization occurs with competitive adsorption of hydrogen on another site.

We then studied the kinetics of the hydrodesulfurization of dibenzothiophene poisoned by nitrogen compounds on the basis of our assumption described above. Since the nitrogen compounds inhibited strongly the hydrogenation of dibenzothiophene because of a preferential hydrogenation of the nitrogen compounds, we determined the poisoning effect of nitrogen compounds on the hydrogenation of dibenzothiophene to tetrahydrodibenzothiophene. Dibenzothiophene, tetrahydro-, and hexahydrodibenzothiophene and the nitrogen compounds are assumed to adsorb competitively on one site, while dibenzothiophene, hexahydro-, and perhydrodibenzothiophene and hydrogen adsorb on another site. Therefore, the formation of tetrahydrodibenzothiophene from dibenzothiophene was represented by

$$r_{4H} = kK_D K_H P_D P_H/(1 + K_D P_D + K_{4H} P_{4H} + K_{6H} P_{6H} + K_{A_i} P_{A_i}), \quad (4)$$

where 4H and A_i are tetrahydrodibenzothiophene and the added compound. This equation is similar to that reported by Broderick and Gates (*18*). If the nitrogen compound is found to adsorb more strongly than the other compounds on the hydrogenation site, $K_D P_D + K_{4H} P_{4H} + K_{6H} P_{6H}$ can be neglected compared with $K_{A_i}P_{A_i}$. Then $K_{A_i}P_{A_i}$ is approximated by K_AP_A and Eq. (4) can be simplified as

$$r_{4H} = k'K_DP_DK_HP_H/(1 + K_AP_A), \quad (5)$$

(P_D/r_{4H}) was plotted against P_A at a constant pressure of hydrogen in Fig. 8. Figure 8 showed that the relation had good linearity. The values of K_A of acridine, carbazole, phenothiazine, dicyclohexylamine, and phenanthrene were 690, 650, 62, 41, and 10. Since this order depends on the strength of adsorption on the active site on which hydrogenation takes place, acridine and carbazole adsorb more strongly than dicyclohexylamine and phenanthrene. In the case of phenothiazine, the plot at high pressure deviates from a straight line because of the sulfur atom in the molecule. Since the basic pK_a of acridine, carbazole, and dicyclohexylamine are 5.6 (*23*), feeble (*23*), and about 11 (presumably), the relationship between K_A and pK_a does not exist. This may be because a solution basicity pK_a does not represent an intrinsic basicity and because the hydrogenated nitrogen compounds had a more greater pK_a of the original compounds. At higher temperatures, the nitrogen compounds were found to depress the desulfurization as well as the hydrogenation of dibenzothiophene. The relationship between desulfurization and denitrogenation will be discussed in detail at a next paper.

Next, we will discuss also the kinetics of the hydrodesulfurization of dibenzothiophene retarded by the sulfur and oxygen compounds. The rate Eqs. (1) and (2) were applied to this poisoning study. Both desulfurization and deoxygenation are sulfurization of dibenzothiophene retarded by the sulfur and oxygen compounds. Both desulfurization and deoxygenation are also assumed to proceed on one type of site and hydrogenation on another site. The sulfur and oxygen compounds retard the formation of biphenyl and cyclohexylbenzene instead of increasing the hydrogenated dibenzothiophene compounds in Figs. 5 and 6. Therefore, an additional substance inhibition term "K_AP_A" was introduced in the denominator of the rate expressions (1) and (2). If the added oxygen and sulfur compounds absorb strongly rather than dibenzothiophene and the hydrogenated compounds on the desulfurization site, "$K_{6H}P_{6H} + K_DP_D + K_HP_H$" in the denominator of the above expressions is assumed to be negligible, and the rate expressions become

$$r_{BP} = kK_DK_HP_DP_H/(1 + K_AP_A)^2 \quad (6)$$

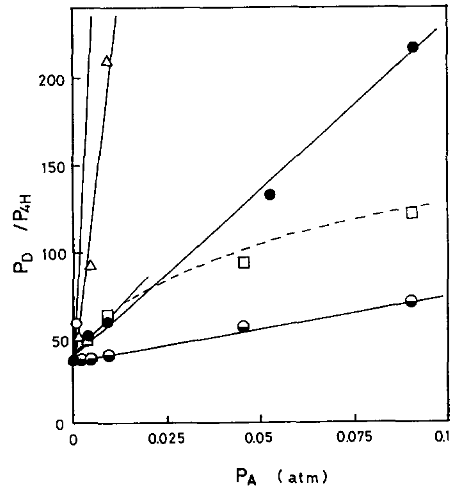


FIG. 8. Plot of P_D/P_{4H} vs P_A. The symbols are the same as those in Fig. 4.

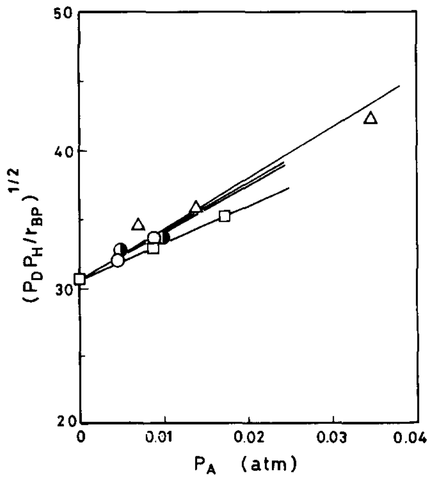


FIG. 9. Plot of $(P_DP_H/r_{BP})^{1/2}$ vs P_A. The symbols are the same as those in Fig. 7.

$$r_{\mathrm{CHB}} = kK_{6\mathrm{H}}K_{\mathrm{H}}P_{6\mathrm{H}}P_{\mathrm{H}}/(1 + K_{\mathrm{A}}P_{\mathrm{A}})^2. \quad (7)$$

Plots of $(P_{\mathrm{D}}P_{\mathrm{H}}/r_{\mathrm{BP}})^{1/2}$ vs P_{A} and $(P_{6\mathrm{H}}P_{\mathrm{H}}/r_{\mathrm{CHB}})^{1/2}$ vs P_{A} at a lower partial pressure of the added compound are shown in Figs. 9 and 10, respectively. For Eq. (6), K_{A} for CS_2 was 12.3, dibenzofuran 11.7, xanthene 11.2, phenol 9.2. For Eq. (7), K_{A} for CS_2 is 7.9, dibenzofuran 6.9, xanthene 4.7, phenol 4.7. K_{A} for Eq. (6) was approximately one-half K_{A} for Eq. (7), but the degrees for the two equations were similar. No relation held at higher pressures of the oxygen compound despite the sulfur compound. This seems to be negligible in the "$K_{6\mathrm{H}}P_{6\mathrm{H}} + K_{\mathrm{D}}P_{\mathrm{D}} + K_{\mathrm{H}}P_{\mathrm{H}}$" in the denominator of the expressions. Even more, when higher concentrations of the oxygen compounds are added, the values deviate from a straight line from Fig. 7. This is probably due to a variation in the surface structure of the catalyst oxidized by the oxygen compound or water formed in the hydrogenolysis of the oxygen compound added. However, the linear correlation as a first approximation supports the assumption that both the sulfur compound and the oxygen compounds adsorb competitively on the desulfurization site and then retard the desulfurization of dibenzothiophene and the hydrogenated compounds. Since the K_{A} of carbon disulfide, which was easily to form hydrogen sulfide at this temperature, was greater than that of the oxygen compounds, the hydrodesulfurization was more inhibited by a sulfur compound formed during hydrotreatment than by oxygen compounds.

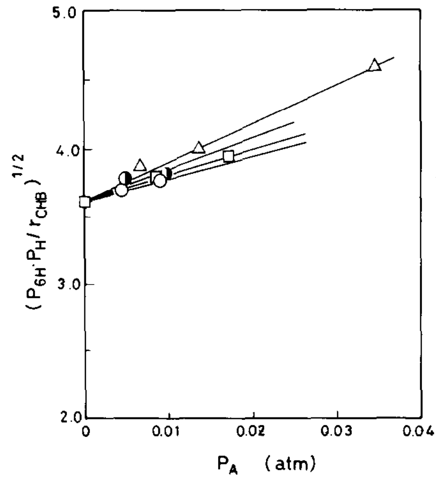


FIG. 10. Plot of $(P_{6\mathrm{H}}P_{\mathrm{H}}/r_{\mathrm{CHB}})^{1/2}$ vs P_{A}. The symbols are the same as those in Fig. 7.

In summary, the hydrodesulfurization of dibenzothiophene on a molybdena–alumina catalyst proceeds on two different types of site, namely the hydrogenation site and the desulfurization site. Nitrogen compounds adsorb much more strongly than dibenzothiophene and inhibit the hydrogenation of dibenzothiophene on the hydrogenation site. Desulfurization involves competitive reactions of deoxygenation and denitrogenation. The hydrodesulfurization on a molybdena–alumina catalyst includes a dual mechanism, in which hydrogenation and hydrogenolysis occur.

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