Poisoning Effect of Nitrogen Compounds on Dibenzothiophene Hydrodesulfurization on Sulfided NiMo/Al$_2$O$_3$ Catalysts and Relation to Gas-Phase Basicity

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The nature of hydrodesulfurization sites of sulfided NiMo/Al$_2$O$_3$ catalysts has been examined by selective poisoning studies using various nitrogen compounds. The reactions were carried out with a flow microreactor at 220–340°C and 10.1 MPa total pressure. Major products were biphenyl and cyclohexylbenzene. The hydrogenation of biphenyl to cyclohexylbenzene rarely occurred at 260°C in the presence of dibenzothiophene. Nitrogen compounds were effective poisons for dibenzothiophene hydrogenation but not for the desulfurization reaction at lower temperatures. The poisoning effect of nitrogen compounds was not correlated with their solution basicities but with their gas-phase basicities. These results indicated that hydrogenation occurred on Brønsted sites that appeared on sulfided NiMo/Al$_2$O$_3$ catalysts. © 1986 Academic Press, Inc.

INTRODUCTION

In the petroleum industry, the long-term trend will be toward processing heavier feedstocks containing large percentages of sulfur and nitrogen. The heavier feedstocks require more stringent processing conditions to reduce the troublesome compounds. Nickel (cobalt)-promoted molybdenum catalysts are most commonly employed for hydrodesulfurization. The nature of the active sites on the surface of the catalyst has been the subject of considerable investigation. Particular attention has been focused on the selective poisoning studies of surface sites that are active in hydrodesulfurization. Poisoning studies on the hydrodesulfurization of thiophene have been reported by Cowley and Massoth (*1*), Satterfield *et al.* (*2*), and Desikan and Amberg (*3*). It is unclear, however, what types of sites on the surface are poisoned by nitrogen compounds during the reaction, because thiophene may be easily decomposed even when thiophene is not adsorbed on particular active sites.

We (*4, 5*) have recently studied the selectivity of Mo/Al$_2$O$_3$ catalysts in the hydrodesulfurization of dibenzothiophene. Nitrogen compounds were strong, effective poisons for the hydrogenation of dibenzothiophene but not for its desulfurization. The observation indicated that hydrogenation and desulfurization occurred on different surface sites of the sulfided molybdenum catalysts. The literature supports the proposal of two different kinds of sites for hydrogenation and desulfurization (*3, 6, 7*).

The acidity of a solid acid has been determined conventionally by a nitrogen compound titration method in solution. Aqueous basicity (pK_a) differs from intrinsic basicity because it includes solvation. Recently, however, the gas-phase basicity of nitrogen compounds was determined by ion cyclotron resonance techniques and high-pressure mass spectrometry (*8–11*). Gas-phase basicities can assess intrinsic molecular properties in the absence of complex interactions with solvent molecules. These basicities must provide an understanding of the acidic characteristics of a molybdenum catalyst, since a sulfided molybdenum catalyst plays the part of a solid acid. Very re-

cently, Stair (*12*) reported the concept of Lewis acids and bases applied to the understanding of surface chemistry. Experiments were, therefore, designed to evaluate the poisoning effect of nitrogen compounds with various gas-phase basicities.

In the present paper, we report the poisoning effect of nitrogen compounds on dibenzothiophene hydrodesulfurization catalyzed with sulfided $NiMo/Al_2O_3$ and determine the correlation between the poisoning effects and the gas-phase basicities. We will also discuss what type of acidic site (Brønsted and/or Lewis site) is effective for the hydrodesulfurization of dibenzothiophene.

EXPERIMENTAL

The catalyst used was 15% MoO_3 and 3% NiO supported on γ-Al_2O_3 (Ketjenfine 153s); surface area, 255 m^2/g and pore volume, 0.56 cm^3/g. Catalyst particles of 0.84- to 1.19-mm-sized granules were used in this work.

Dibenzothiophene was synthesized according to the Gilman and Jacoby method (*13*). The composition has been described in previous studies (*4, 5*). Hydrogen was predried by passing through 13X molecular sieves. H_2S was used from a prepared mixture containing 10 vol% H_2S in H_2.

Poisoning studies were carried out in a microreactor under continuous flow conditions at high pressure. Two grams of the catalyst in the reactor were reduced with hydrogen at 10 liters/h, 400°C and 10.1 MPa pressure for 4 h, and then were presulfided *in situ* with H_2S at 30 liters/h at atmospheric pressure and 400°C for 3 h. After sulfiding, the reactor was allowed to cool to 260°C, and the solution containing 5 wt% of dibenzothiophene in xylene was placed in the reactor at 260°C. After a steady state was attained, the solution containing both dibenzothiophene and a poisoning compound in xylene was introduced into the reactor. The next feed contained both dibenzothiophene and a more concentrated poisoning compound. Analysis of the reaction prod-

ucts was accomplished by gas chromatography using 1% Silicone OV-17 on a Uniport B column from 80 to 200°C. More thorough analyses were done by obtaining the mp, mass spectra, and IR spectra of the individual products as described in previous papers (*5, 14*).

As shown in Fig. 5, the concentration of the compounds (wt%) was converted to partial pressure (Pa) since the compounds were transformed into vapor at 260°C.

RESULTS

Temperature Dependence

Figure 1 shows the product distribution in dibenzothiophene hydrodesulfurization on a sulfided $NiMo/Al_2O_3$ catalyst without the addition of nitrogen compounds at 10.1 MPa total pressure in the range 240 to 330°C. The major products were biphenyl and cyclohexylbenzene from the desulfurization of dibenzothiophene at all temperatures. These two compounds were present in almost equimolecular amounts, although biphenyl exceeded cyclohexylbenzene in the case of the sulfided $CoMo/Al_2O_3$ catalyst (*15*). Above 260°C bicyclohexyl and ethylbicyclo[4.4.0]decane were produced from the desulfurization of perhydrodibenzothiophene and from the isomerization of bicyclohexyl, respectively. Hydrogenated dibenzothiophene compounds such as tetrahydro- and hexahydrodibenzothiophene were produced at about 0.10 wt% maximum at 260°C and then decreased with increasing temperature. Perhydrodibenzothiophene was also observed in negligible amounts. The solvent, xylene, was nearly unreacted up to 260°C but became hydrogenated with rising temperature. The material balances became poor above 280°C because the hydrocarbon products decomposed to yield more volatile material. No sign of deactivation of the catalyst was observed during the run for 12 h in the absence of nitrogen compounds.

The apparent activation energies for the disappearance of dibenzothiophene and for
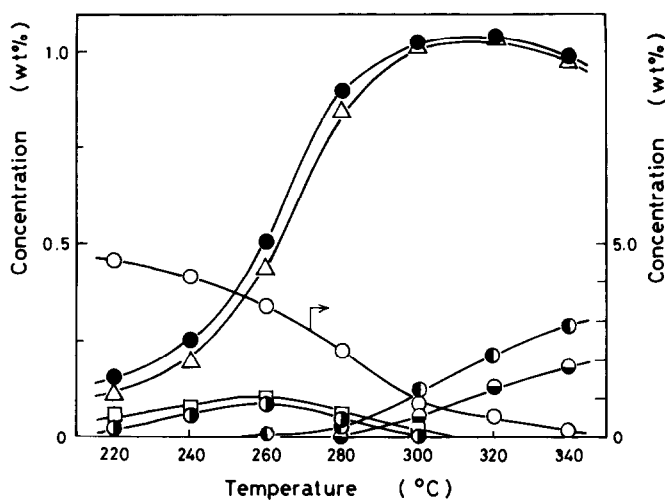
FIG. 1. Hydrodesulfurization of dibenzothiophene on a sulfided NiMo/Al₂O₃ catalyst at 10.1 MPa of total pressure. ●, Biphenyl; △, cyclohexylbenzene; ○, dibenzothiophene; □, tetrahydrodibenzothiophene; ◑, hexahydrodibenzothiophene; ◐, bicyclohexyl; ◓, cyclohexylhexane and ethylbicyclo[4.4.0]decane.

the formation of biphenyl and cyclohexylbenzene were 102 (220–240°C), 76.1 (220–280°C), and 86.1 (220–280°C) kJ/mol, respectively.

The equilibrium in the hydrogenation of dibenzothiophene was estimated on the basis of the molar ratios of the reaction products shown in Fig. 1. Standard free energy of hydrogenation steps in dibenzothiophene hydrodesulfurization could not be estimated by the van Krevelen group contribution technique because the values were less accurate. The molar ratios are given in Table 1. The ratio of tetrahydrodibenzothiophene (4H) to dibenzothiophene (D)

increased up to 260°C and then decreased with increasing temperature. The ratio of hexahydrodibenzothiophene (6H) to tetrahydrodibenzothiophene increased gradually up to 300°C. It was difficult to determine the ratio of perhydrodibenzothiophene to hexahydrodibenzothiophene because of the negligible amount of perhydrodibenzothiophene. Apparently, the hydrogenation of dibenzothiophene to tetrahydrodibenzothiophene enters quasi-equilibrium at 260°C, but subsequent hydrogenations did not attain equilibria. The hydrogenation of dibenzothiophene on a NiMo/Al₂O₃ catalyst proceeds more easily than on a Mo/Al₂O₃ catalyst (4, 5) and a CoMo/Al₂O₃ catalyst (15).

Formation of Cyclohexylbenzene from Biphenyl

The addition of biphenyl to a xylene solution containing dibenzothiophene was examined at 260°C to make sure that the hydrogenation proceeds on the sulfided NiMo/Al₂O₃ catalyst. Figure 2 illustrates that the concentration of cyclohexylbenzene increased slightly at 0.01 wt% after the addition of 1.0 wt% biphenyl. Since this increased concentration was negligible com-

TABLE 1

Experimentally Determined Molar Ratios of
Tetrahydrodibenzothiophene to Dibenzothiophene
and Hexahydrodibenzothiophene to
Tetrahydrodibenzothiophene

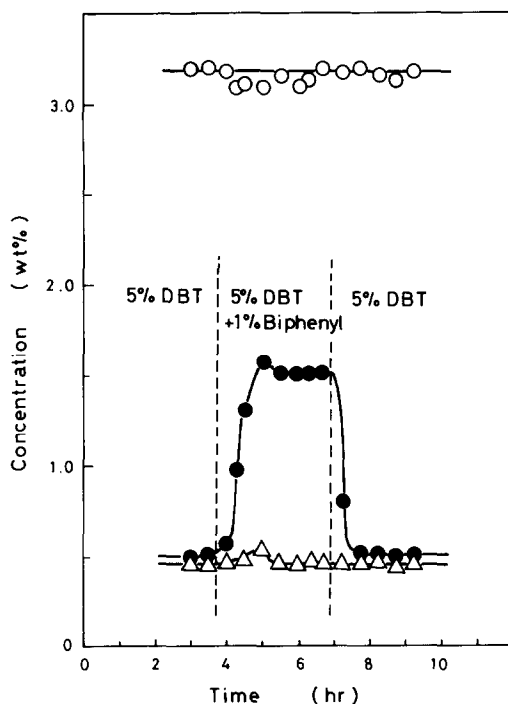| Temperature (°C)	[4H]/[D]	[6H]/[4H]
220	1.75×10^{-2}	1.68×10^{-1}
240	2.70×10^{-2}	2.47×10^{-1}
260	3.37×10^{-2}	4.15×10^{-1}
280	2.56×10^{-2}	5.74×10^{-1}
300	1.75×10^{-2}	7.02×10^{-1}

FIG. 2. Effect of added biphenyl on the formation of cyclohexylbenzene at 260°C. See Fig. 1 for symbols. DBT, dibenzothiophene.

pared with 0.5 wt% cyclohexylbenzene, the hydrogenation of biphenyl to cyclohexylbenzene rarely occurred in the presence of large amounts of dibenzothiophene at 260°C, analogous with that on the sulfided Mo/Al$_2$O$_3$ catalyst. This indicated that dibenzothiophene adsorbed more strongly than biphenyl and was hydrogenated preferentially on the hydrogenation sites of the NiMo/Al$_2$O$_3$ catalyst. As shown in Fig. 3, the scheme for the hydrodesulfurization of dibenzothiophene on the sulfided NiMo/Al$_2$O$_3$ catalyst is consistent with that on the sulfided Mo/Al$_2$O$_3$ catalyst (5).

Poisoning Effect of Nitrogen Compounds on Dibenzothiophene Hydrodesulfurization

The changes in the products of dibenzothiophene hydrodesulfurization upon the addition of acridine at 260°C and 10.1 MPa total pressure are shown in Fig. 4. The concentration of biphenyl increased extraordinarily with an increase in acridine up to 0.1 wt%, then increased more gradually. On the other hand, the concentrations of cyclohexylbenzene, subsequent decomposed compounds, and hydrogenated compounds decreased with the increase in added acridine. The changes were not caused by inhibition of the hydrogenation of biphenyl to cyclohexylbenzene, since Fig. 2 showed that biphenyl was scarcely hydrogenated to yield cyclohexylbenzene on a sulfided NiMo/Al$_2$O$_3$ catalyst. These changes are similar to those of the sulfided Mo/Al$_2$O$_3$ catalyst in the previous paper (4). This observation is very interesting because one of the desulfurization products increases while the others decrease upon the addition of acridine.

The addition of acridine decreased the concentration of unreacted dibenzothiophene slightly. This increase in the conversion was not observed for the sulfided Mo/Al$_2$O$_3$ catalyst (5). It seemed that nitrogen compound enhanced the desulfurization on the NiMo/Al$_2$O$_3$ catalyst (16).
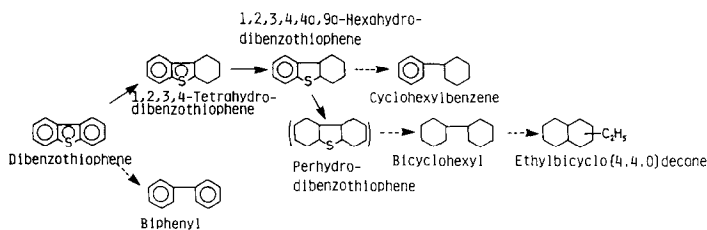

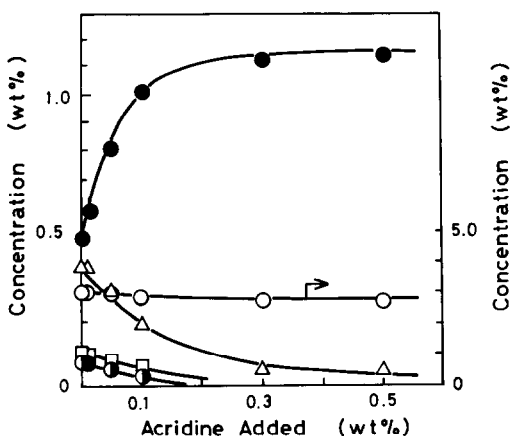FIG. 3. Reaction scheme for the hydrodesulfurization of dibenzothiophene (5).

FIG. 4. Effect of added acridine on the products of dibenzothiophene hydrodesulfurization. See Fig. 1 for symbols.

The addition of other nitrogen compounds showed the same characteristics as acridine. The concentrations (mole) of cyclohexylbenzene and hexahydrodibenzothiophene decreased in the following order: acridine > quinoline > pyridine > piperidine > cyclohexylamine > γ-picoline > dicyclohexylamine > aniline. The increasing amount of biphenyl was also of the same order.

Kinetics of Poisoning of Nitrogen Compounds in the Hydrogenation of Dibenzothiophene

The poisoning effect is consistent with the result in our previous paper (4) that nitrogen compounds are selective poisons for dibenzothiophene hydrogenation, but not for desulfurization. The equation was derived by assuming that the desulfurization and the hydrogenation occur on different sites. All of the dibenzothiophene, hexahydro-, perhydrodibenzothiophene, and hydrogen adsorbed competitively on the desulfurization sites, whereas dibenzothiophene, tetrahydro-, and hexahydrodibenzothiophene adsorbed on the hydrogenation sites. The nitrogen compounds adsorbed strongly on the hydrogenation sites.

Since the hydrogenation of dibenzothiophene to tetrahydrodibenzothiophene was

quasiequilibrium, we determined the poisoning effect of nitrogen compounds on the hydrogenation of tetrahydrodibenzothiophene to hexahydrodibenzothiophene which was not in equilibrium at 260°C and 10.1 MPa total pressure. We assumed the same equation obtained for dibenzothiophene hydrodesulfurization on the sulfided Mo/Al_2O_3 catalyst (5). The formation of hexahydrodibenzothiophene (6H) on the hydrogenation sites of the catalyst is represented by

$$r_{6H} = kK_DP_DK_HP_H/(1 + K_DP_D + \Sigma K_{N_j}P_{N_j} + K_{4H}P_{4H} + K_{6H}P_{6H}), \quad (1)$$

where P_i is the partial pressure; K_i and k are constants; D, H, 4H, and N_j are dibenzothiophene, hydrogen, tetrahydrodibenzothiophene, and nitrogen compounds containing hydrogenated compounds, respectively. If the nitrogen compound was found to adsorb more strongly on the hydrogenation sites than both dibenzothiophene and the hydrogenated compounds, the denominator of Eq. (1) was adequately approximated by $1 + K_NP_N$.

$$r_{6H} = kK_DP_DK_HP_H/(1 + K_NP_N). \quad (2)$$

Figure 5 depicted plots of (P_D/r_{6H}) vs P_N. This relationship showed good linearity at low pressures (<ca. 2 kPa). The assumption was validated at low pressures of the nitrogen compounds; however, the addition of large amounts of the nitrogen compounds might have altered the nature of a $NiMo/Al_2O_3$ catalyst (16). The K_N values of acridine, quinoline, pyridine, piperidine, cyclohexylamine, γ-picoline, dicyclohexylamine, and aniline were 200, 131, 107, 85, 77, 63, 45, and 19, respectively. The poisoning effect indicated that a high-molecular-weight nitrogen compound has strong inhibition characteristics.

DISCUSSION

Aqueous basicity (pK_a) has been determined for many years in liquid solution and is directly related to the acidity of the catalysts. Aliphatic cyclic compounds such as

piperidine and cyclohexylamine had lower adsorption constants than the heterocyclic aromatic compounds such as pyridine, quinoline, and acridine, although the aqueous basicities of the heterocyclic aromatic compounds (pK_a = 5–6) were much lower than those of the aliphatic cyclic amines (pK_a = 11–12) (17). The adsorption constant of acridine was higher than those of pyridine and quinoline despite similar pK_a values (17). Furthermore, γ-picoline, withdrawing the methyl group into a *para* position in pyridine, had a lower adsorption constant than pyridine, in spite of being a stronger base than pyridine. Thus, there is a great gap between the adsorption constants of the various added nitrogen compounds and their solution basicities.

A gas-phase basicity reveals intrinsic basicity because it does not include solvation. This basicity will solve the problem of the acidic property of the molybdenum catalyst in a gas–solid reaction. Gas-phase basicities of the nitrogen compounds used in the
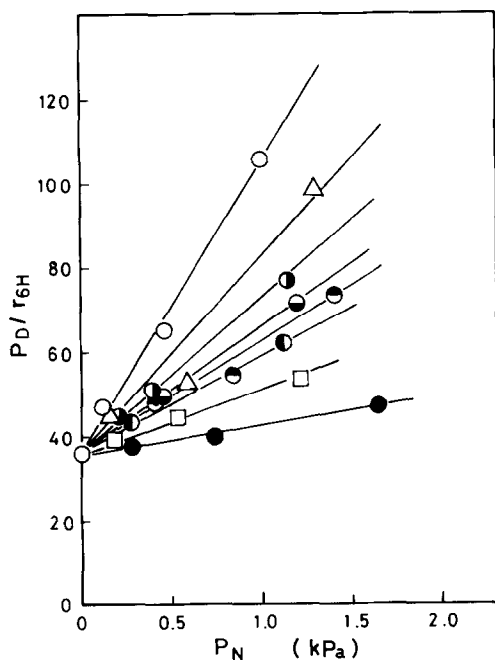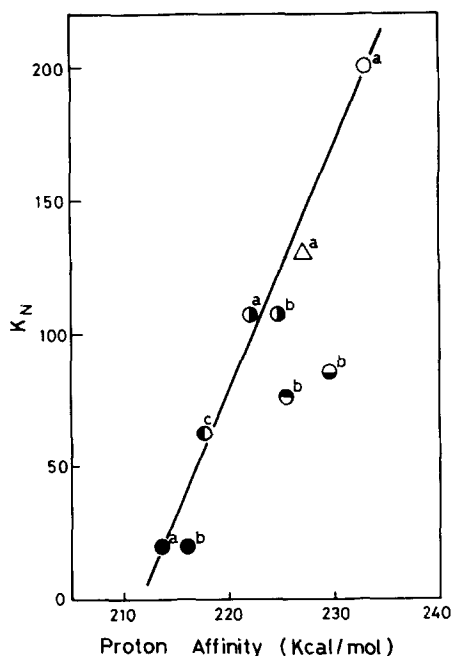

FIG. 6. Correlation between K_N and gas-phase basicity of the nitrogen compounds. All symbols are the same as in Fig. 5. (a) From Ref. (11). (b) Gas-phase basicity data from Ref. (18). (c) Proton affinity value derived from Refs. (11) and (19).

FIG. 5. Plot of P_D/r_{6H} vs P_N. O, Acridine; △, quinoline; ◑, pyridine; ○, piperidine; ◓, cyclohexylamine; ◐, γ-pycoline; □, dicyclohexylamine; ●, aniline.

present work were determined by Aue et al. (18), Brown and Tse (19), and Meot-Ner (11), except for dicyclohexylamine. Figure 6 shows the correlation between the gas-phase basicities of added nitrogen compounds and their adsorption constants, K_N. A good linear correlation is displayed for all the nitrogen compounds except cyclohexylamine and piperidine. The two compounds show lower K_N values than expected at the straight line. This is apparently because two perhydrogenated nitrogen compounds were adsorbed on the desulfurization sites and were decomposed as well as adsorbed on hydrogenation sites. The adsorption constant, K_N, increased uniformly with increasing basicities of the nitrogen compounds in the gas phase. The degree of inhibition of the nitrogen compounds is due to the strength of their basicities which reveal intrinsic basicity; therefore, the poisoning effects of nitrogen compounds are correlated with the acidity of the surface of the

catalyst. This leads to the determination of what type of acidic site (Brønsted or Lewis site) is effective for hydrodesulfurization.

Since gas-phase basicity is obtained by measuring the equilibrium constants for the proton transfer reactions, it is in accord with the proton affinity, which is a direct measure of the Brønsted base strength of the molecule. Hence, it is apparent that a nitrogen compound adsorbs strongly on Brønsted acid sites rather than Lewis acid sites or coordinatively unsaturated sites. The Brønsted acid sites appear as OH groups or SH groups adjacent to the anion vacancy on the surface of the sulfided catalyst (20). Thus, the hydrogenation of dibenzothiophene apparently occurs on Brønsted acid sites of the sulfided NiMo/Al$_2$O$_3$ catalyst surface. The nature of desulfurization sites will be understood through the poisoning studies of the effect of sulfur and oxygen compounds on the hydrodenitrogenation of acridine (or carbazole).

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