# Effect of Solvents and Acridine on Dibenzothiophene Hydrodesulfurization

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**Synopsis.** A selective poisoning pattern was observed for the hydrodesulfurization of dibenzothiophene on the sulfided $Mo/Al_2O_3$ catalyst in the presence of acridine and the solvents xylene and tetralin, using a microreactor at 270—340 °C and 10.1 MPa total pressure.

The selective poisoning pattern is characteristic of the correlation between hydrogenation and C–S hydrogenolysis during the hydrodesulfurization (HDS) of dibenzothiophene on a sulfided $Mo/Al_2O_3$ catalyst.[1] When nitrogen and aromatic heterocyclic compounds were added to the feed, the compounds depressed the hydrogenation of dibenzothiophene, but not the C–S hydrogenolysis reactions during the HDS of dibenzothiophene. On the other hand, the addition of sulfur and oxygen compounds depressed the C–S hydrogenolysis of dibenzothiophene to biphenyl and of hexahydrodibenzothiophene to cyclohexylbenzene. This selective poisoning study provided a good perspective for an understanding of the nature of active sites for HDS; hydrogenation and C–S hydrogenolysis occurred on different surface sites of the sulfided molybdenum catalysts.[2]

Although the solvents are used primarily to dissolve a feed such as polynuclear aromatic sulfur compounds, there is little understanding of the effect of solvents on hydrogenation and C–S hydrogenolysis reactions during the HDS reaction. In this study, tetralin and xylene were chosen as the solvents in order to determine which type of site is inhibited by the solvent during the reaction. The present study focused on the selectivity of the sulfided $Mo/Al_2O_3$ catalyst for the hydrogenation and the C–S hydrogenolysis in the presence of the solvent and a poison compound, acridine, at high hydrogen pressure.

## Experimental

The apparatus was a high-pressure system with an 11 mm i.d. microreactor which has been described elsewhere.[3] Hydrogen was dried by passage through a Linde 13X molecular sieve trap prior to use. Dibenzothiophene was synthesized via the same procedure as described in a previous paper.[1] Acridine and all other reagents obtained commercially were used without further purification. The 12.5% $MoO_3/Al_2O_3$ catalyst (0.84—1.19 mm granules) was packed in the reactor and oxidized for more than 24 h at 450 °C in air. Sulfiding was carried out with a 10% $H_2S/H_2$ mixture flowing at 30 L $h^{-1}$ at atmospheric pressure and 400 °C for 3 h after reduction of the oxidized catalyst in 10 L $h^{-1}$ hydrogen at 400 °C and 10.1 MPa pressure for 4 h. After sulfiding, the reactor was cooled to 300 °C in the $H_2S/H_2$ stream, and then a solution containing 5 wt% (3.53 mmol $L^{-1}$) of dibenzothiophene in xylene (or tetralin) was allowed to flow into the reactor. A typical reaction was carried out at 300 °C and at 28 L $h^{-1}$ hydrogen flow and at 10.1 MPa total pressure. After the reaction had reached a steady state (in about 3 h), acridine was added to the feed at the concentration required to produce 0 to 3.1 kPa. Xylene was barely hydrogenated at 300 °C in the presence of dibenzothiophene or acridine. The liquid product samples were analyzed by FID gas chromatography.

## Results and Discussion

The major products were biphenyl and cyclohexylbenzene in the dibenzothiophene HDS: the former product was formed by the direct C–S bond breakage of dibenzothiophene and the latter by the C–S hydrogenolysis of hexahydrodibenzothiophene after successive hydrogenation. The effect of acridine on dibenzothiophene HDS in xylene solvent is shown in Fig. 1. When acridine was added to the xylene solution containing dibenzothiophene, the amount of biphenyl increased in inverse proportion to the amount of cyclohexylbenzene. The addition of 0.1 wt% acridine brought about the maximum amount of 0.42 wt% biphenyl. Acridine was preferentially hydrogenated to perhydroacridine without the direct C–N hydrogenolysis of acridine on a sulfided $Mo/Al_2O_3$ catalyst at 300 °C, since no hydrocarbon products were observed from the acridine hydrodenitrogenation either in this reaction or in the hydrodenitrogenation of acridine alone.[4] Moreover,

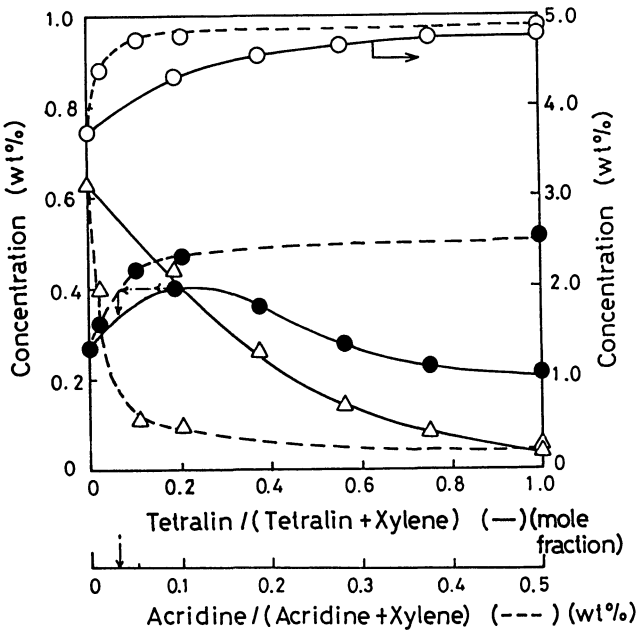


Fig. 1. Effect of xylene/(tetralin+xylene) solvent fraction (——) and of acridine (----)[1] on the major products of the HDS of dibenzothiophene at 300 °C. ○, dibenzothiophene; ●, biphenyl; △, cyclohexylbenzene.

the hydrogenation of biphenyl to cyclohexylbenzene did not occur in the presence of dibenzothiophene even on the sulfided $NiMo/Al_2O_3$ catalyst at 300 °C.[5] Therefore, the preferential hydrogenation of acridine depressed the hydrogenation of dibenzothiophene. Thus, acridine inhibited the hydrogenation sites, but not the C–S hydrogenolysis sites. The addition of acridine to the feed expelled dibenzothiophene from the hydrogenation sites. The dibenzothiophene was in turn adsorbed on the C–S hydrogenolysis sites to be desulfurized to form biphenyl. Therefore, it appeared that the decrease in cyclohexylbenzene resulted in enhanced biphenyl formation in the xylene solvent.

Changes in the ratio of xylene and tetralin in dibenzothiophene HDS are shown in Fig. 1. The amount of biphenyl was increased by increasing the tetralin-fraction and was maximized to 0.405 wt% at a 22% tetralin-fraction and was minimized to 0.2 wt% biphenyl. The amount of cyclohexylbenzene was gradually decreased to 0.035 wt% from 0.63 wt% when the tetralin-fraction was increased to 100% tetralin. The selective poisoning pattern in the presence of less than a 22% tetralin-fraction was observed for the results obtained in the presence of acridine in xylene. This suggested that less than 22% tetralin in xylene did not inhibit the C–S hydrogenolysis sites but did affect the hydrogenation sites at 300 °C. Furthermore, more than 22% tetralin inhibited both the C–S hydrogenolysis and hydrogenation sites.

The amount of a mixture of 78% xylene and 22% tetralin corresponded to the amounts of cyclohexylbenzene and biphenyl in the presence of 0.03 wt% acridine, as shown in Fig. 1. A 22% fraction of tetralin corresponded to 11.9 $mmol\,h^{-1}\,g\text{-}cat^{-1}$ of tetralin which was adsorbed on the hydrogenation sites only. The corresponding amount of acridine was $3.98\times10^{-3}$ $mmol\,h^{-1}\,g\text{-}cat.^{-1}$. This amount was 1/3000 th the value obtained from the mixture of xylene and tetralin. These results showed that acridine was adsorbed on the hydrogenation sites 3000-fold stronger than tetralin. In a previous paper,[1] the poisoning effect of the nitrogen and aromatic compounds on the HDS of dibenzothiophene over the sulfided $Mo/Al_2O_3$ catalyst was studied. The strength of the adsorption constant of acridine was 67 times as great as that of phenanthrene, although tetralin was not tested in the dibenzothiophene HDS. The result suggested that tetralin was adsorbed on the hydrogenation sites 45 times less than phenanthrene.

The formation of biphenyl and cyclohexylbenzene in the HDS of dibenzothiophene in either xylene or tetralin solvent in the range of 270 to 340 °C is shown in Fig. 2. The concentrations of biphenyl and cyclohexylbenzene in the dibenzothiophene HDS in xylene solvent were 1.2 and 18 times that in tetralin at 300 °C, respectively. Tetralin inhibited both hydrogenation and C–S hydrogenolysis more than did xylene. The apparent activation energies for the formation of biphenyl were 84.9 $kJ\,mol^{-1}$ in tetralin and 76.5 $kJ\,mol^{-1}$ in xylene. The formation of cyclohexylbenzene in tetralin was much less than that in xylene. The apparent activation energies for the formation of cyclohexylbenzene were 186 in tetralin, and 157 (270—300 °C) and 58.9 (300—340 °C) $kJ\,mol^{-1}$ in xylene.[6]

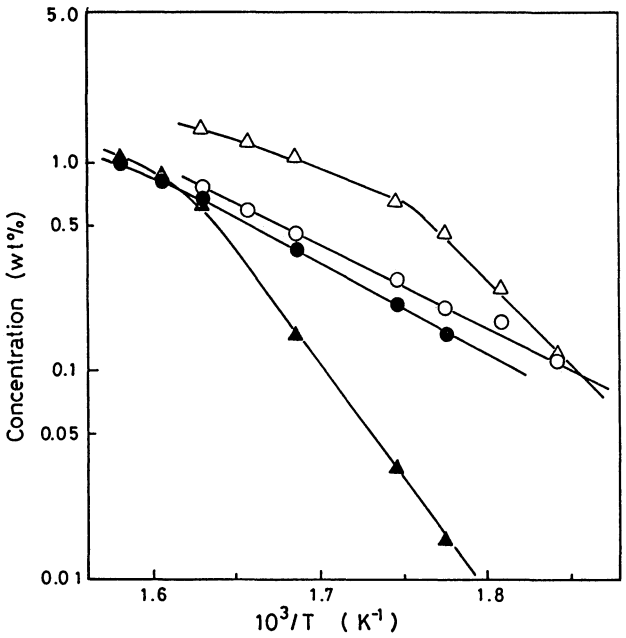


Fig. 2. Arrhenius plots of the formation of biphenyl and cyclohexylbenzene in xylene (open symbol)[6] and tetralin (closed symbol). ○●, biphenyl; △▲, cyclohexylbenzene.

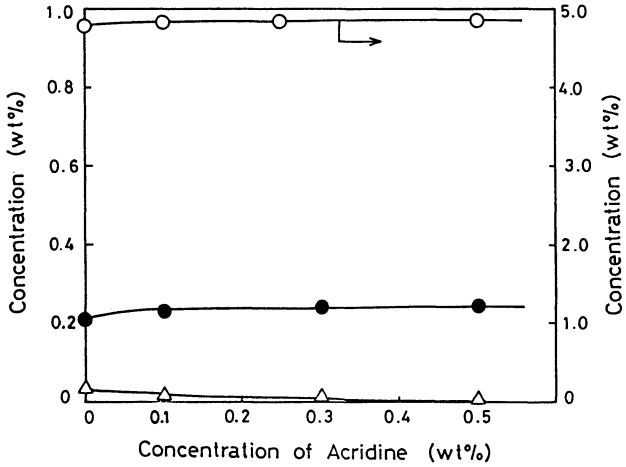


Fig. 3. Effect of acridine on the major products of the HDS of dibenzothiophene in tetralin solvent at 300 °C. The symbols are the same as those in Fig. 1.

The presence of acridine on dibenzothiophene HDS in the tetralin solvent is shown in Fig. 3. The presence of acridine lowered the amount of cyclohexylbenzene, and enhanced the amount of biphenyl, which reached constant values of 0.2% and 0.05%, respectively. The selective pattern was similar to the results of acridine addition in the xylene solvent: The presence of acridine inhibited the hydrogenation sites and resulted in increased biphenyl formation. However, more than 22% tetralin was adsorbed competitively on the active sites for the direct C–S hydrogenolysis of dibenzothiophene to biphenyl, as well as on the active sites for successive hydrogenation of dibenzothiophene. The presence of acridine slightly enhanced biphenyl formation.

In summary, the HDS of dibenzothiophene was catalyzed on two kinds of active sites on the sulfided Mo/$Al_2O_3$ catalyst: Site I was active for hydrogenation and was very sensitive to poisoning by nitrogen bases, while Site II was active for HDS (C–S hydrogenolysis), and was less susceptible to acridine poisoning. The presence of a small amount of tetralin hindered the hydrogenation of dibenzothiophene, but a large amount of tetralin depressed the C-S hydrogenolysis as well as the hydrogenation reaction.

Several researchers have found it necessary to postulate the existence of two kinds of catalytic sites on molybdenum sulfide catalysts. Massoth and coworkers[7–9] proposed that at least two HDS sites exist, one being poisoned and the other unaffected by pyridine. Hydrogenation was more strongly affected by pyridine than HDS. They suggested that the three reactions (HDS, hydrogenation, and cracking) appeared to take place on different sites.[7] Gates and coworkers[2,10,11] studied the HDS reaction network of dibenzothiophene and found that $H_2S$ depressed hydrogenolysis but left hydrogenation unchanged. They also proposed that there was competitive adsorption of $H_2S$ and the sulfur-containing reactant on one kind of catalytic site and noncompetitive adsorption of hydrogen on another kind of site. Furthermore, Shimada et al.[12] found that two-dimensional polymolybdate structures were favorable for high hydrogenation activity while electronegative molybdenum which induces Brønsted activity was required for high hydrogenolysis activity. They also reported that HDS of dibenzothiophene can be catalyzed on both kinds of active sites.

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