The Selectivity of Sulfided NiW/Al_2O_3 Catalyst in the Hydrodesulfurization of Dibenzothiophene

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Synopsis. The selectivity of a sulfided NiW/Al_2O_3 catalyst for hydrodesulfurization has been studied at 300 °C and 10.1 MPa total pressure. The presence of oxygen and sulfur compounds depressed the desulfurization of dibenzothiophene, but not the hydrogenation. The addition of large amounts of acridine improved the catalytic activity significantly for the desulfurization of dibenzothiophene to biphenyl while preventing hydrogenation.

The hydrodesulfurization of petroleum residue is widely practiced and the need for a similar technology for coal-derived liquids is well recognized. Heavy feedstocks contain small amounts of nitrogen compounds and sulfur compounds as impurities. Catalyst poisoning by nitrogen compounds is a serious problem during hydroprocessing treatment.

Several researchers have studied the effect of nitrogen compounds on the hydrodesulfurization reactions in order to obtain more detailed information about the poisoning mechanism. A previous study1) revealed that the presence of nitrogen compounds depressed the hydrogenation of dibenzothiophene on a sulfided Mo/Al_2O_3 catalyst. Neither an increase in the conversion, nor an improvement in the catalytic activity for the desulfurization, was observed during the reaction. Cowley and Massoth2) also found that the addition of pyridine greatly decreased the conversion of thiophene on a sulfided Mo/Al_2O_3 catalyst. Moreover, Urimoto and Sakikawa3) reported that the presence of pyridine inhibited the hydrodesulfurization activity of MoS_2, WS_2, CoS, and NiS catalysts. Thus, the presence of nitrogen compounds greatly decreased the conversion, and diminished the catalytic activity of the molybdenum (or nickel or tungsten) sulfided catalyst which did not contain any promoting metals.

However, we have studied the poisoning effect of nitrogen compounds on the hydrodesulfurization of dibenzothiophene on a sulfided NiMo/$Al_2O_3$4) and NiW/$Al_2O_3$5) catalyst and found that the presence of large amounts of acridine markedly enhanced the desulfurization activity of the catalysts, together with a decrease in the hydrogenation activity. The behavior of these catalysts appeared to be different from the sulfided Mo/Al_2O_3 catalysts or metal sulfide catalysts without a promoter in the presence of nitrogen compounds.

In the present work, the hydrodesulfurization of dibenzothiophene on the sulfided NiW/Al_2O_3 catalyst at 300 °C and 10.1 MPa total pressure was investigated in the presence of CS_2 and xanthene as well as acridine. The selectivity of the sulfided NiW/Al_2O_3 catalyst for hydrogenation and desulfurization is discussed.

Experimental

Acridine (Ultra pure grade, Tokyo Kasei Chemical), dibenzothiophene, xanthene and carbon disulfide (Extra pure grade), and xylene (Chemically pure grade) were used without purification. Hydrogen (99.9%, To-Ei Chemical) was passed through 13X Molecular Sieves before use. Hydrogen sulfide (99.5%) was used without purification.

Two grams of a NiW/Al_2O_3 (6.5%, NiO and 21% WO_3, Ketjenfine; 14—20 mesh) were packed into the central portion (length 3.6 cm) of the reactor and were oxidized in air at 450 °C for more than 24 h. The catalyst was reduced in situ at 400 °C for 4 h at a pressure of 10.1 MPa of hydrogen, then at 30 L h^{-1}. After presulfidation, the catalyst was sulfided at a 10% H_2S/H_2 atmosphere, then at 30 L h^{-1} and 400 °C for 3 h. The experiment was carried out in a continuous-flow microreactor at 300 °C and 10.1 MPa total pressure. The hydrogen (gas ntp)/dibenzothiophene ratio was 320. The weight hourly space velocity (WHSV) was 7.5. After a solution containing 5 wt% dibenzothiophene in xylene was introduced into the reactor, a steady state was achieved within about 3 h. This standard condition was run before the start of each set of experiments with a particular additive.

When measuring the selective effect on the hydrodesulfurization by an additive, a series of feeds containing increasing concentrations of additive was used. The catalyst attained steady activity within about 1 h when additive concentrations were increased. The liquid products were separated by a high-pressure separator into gaseous products. The liquid products, which had higher boiling points than xylene, were analyzed by FID gas chromatography. Biphenyl, cyclohexylbenzene, and 2-ethylbicyclo[4.4.0]decane were identified by comparisons with data from authentic samples by GC and high-resolution mass spectrometry. The hydrogenated dibenzothiophene compounds, cyclohexylbenzene and methyl- and dimethyl dibenzothiophene, were analyzed by GC-MS.

Results and Discussion

Promoting Effect of Acridine. The change in the product distribution in dibenzothiophene hydrodesulfurization in the presence of acridine at 300 °C and 10.1 MPa total pressure is shown in Fig. 1. The concentrations of the unreacted dibenzothiophene and cyclohexylbenzene remained constant at 0.1 wt% of acridine, though but further additions led to a great increase in the conversion of dibenzothiophene. This observation indicates that a large amount of acridine enhances the selective desulfurization of dibenzothiophene to biphenyl and depresses hydrogenation. Above 320 °C, conversion is not influenced by acridine. This appears to be caused either by diffusional limitations or by a competitive C–N hydrogenolysis of perhydroacridine, which is formed from acridine hydrogenation.

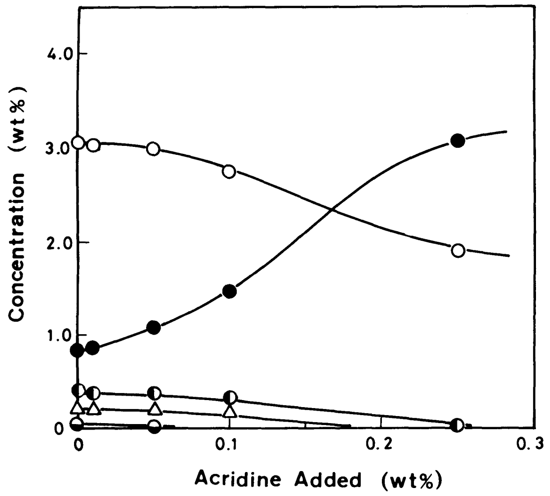

Fig. 1. Change in the product distribution of dibenzothiophene hydrodesulfurization on the addition of acridine at 300 °C. ◒, Methyl- and dimethyldibenzothiophene; ○, Dibenzothiopohene; ●, biphenyl; △, cyclohexylbenzene; ◐, 1,1′-bicyclohexyl, hydrogenated dibenzothiophenes, and other hydrocarbons which have higher boiling point than 1,1′-bicyclohexyl.

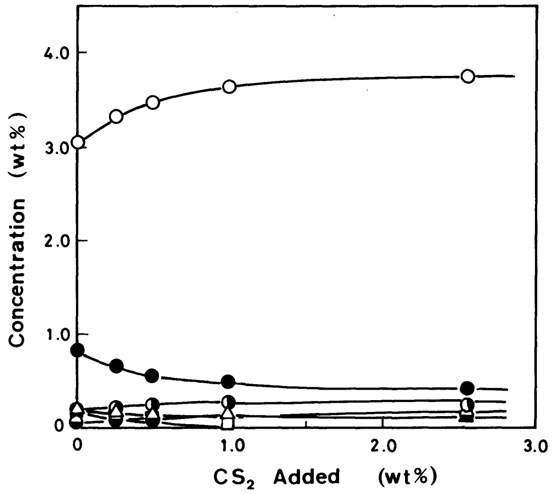

Fig. 2. Effect of CS_2 on product distribution of dibenzothiophene hydrodesulfurization at 300 °C. ◑, Hydrogenated dibenzothiophene compounds; □, 1,1′-bicyclohexyl and other hydrocarbons which have higher boiling point than 1,1′-bicyclohexyl. See Fig. 1 for the other symbols.

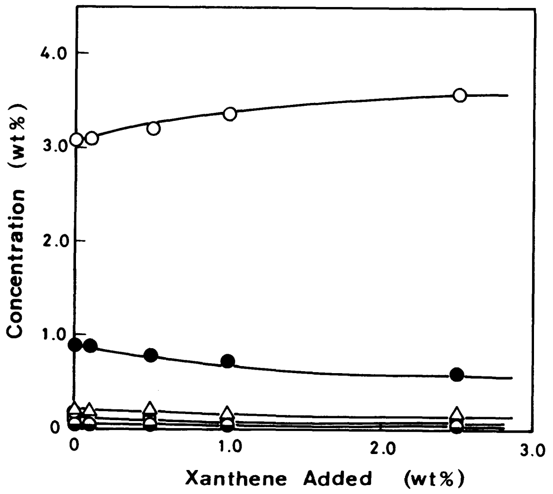

Fig. 3. Effect of xanthene on product distribution of dibenzothiophene hydrodesulfurization at 300 °C. See Fig. 1 for the symbols.

The addition of acridine greatly improved the carbon material balance on dibenzothiophene, even at higher temperatures, since the formation of the many small amounts of by-products decreased. The material balance was initially 29 and 57% at 320 and 360 °C, respectively, but rose to 80% after the addition of acridine.

Several authors have proposed shcemes for the electron-transfer reactions between nickel and tungsten ions responsible for generating the desulfurization sites.[1-8] Ni(II) ions should be more easily reduced than WS_2 by hydrogen:

$$\mathrm{Ni(II)} + \mathrm{e} = \mathrm{Ni(I)} \tag{1}$$

and

$$\mathrm{Ni(I)} + \mathrm{W(IV)} = \mathrm{Ni(II)} + \mathrm{W(III)}. \tag{2}$$

The removal of sulfur from dibenzothiophene by W(III) could be followed by reduction with hydrogen to complete the catalytic cycle

$$2\mathrm{W(III)} + \mathrm{RS} + (\mathrm{H_2}) = 2\mathrm{W(IV)} + \mathrm{RH_2} + \mathrm{S^{2-}}, \tag{3}$$

$$\mathrm{S^{2-}} + 4\mathrm{W(IV)} = 1/8\mathrm{S_8} + 4\mathrm{W(III)}, \tag{4}$$

or

$$2\mathrm{S^{2-}} + 2\mathrm{H_2} + 4\mathrm{W(IV)} = 2\mathrm{H_2S} + 4\mathrm{W(III)}. \tag{5}$$

The addition of acridine yielded sulfur in solution as well as a high desulfurization activity to the catalyst. When the reaction solution in the presence of 0.25 wt% acridine was cooled to 0 °C, the solution changed from colorless to orange. Sulfur precipitated from the solution within a couple of days. The orange color was caused by amine complexes,[9] such as hydrogenated acridine compounds with sulfur. The amines, to which acridine was easily hydrogenated, appears to help with the formation of sulfur from a sulfide anion to form an active site W(III) and/or with the desorption of hydrogen sulfide.

Depressing Effect of Carbon Disulfide and Xanthene. Figure 2 shows the effect of CS_2 on dibenzothiophene hydrodesulfurization at 10.1 MPa and 300 °C. The presence of CS_2 apparently depressed the desulfurization of dibenzothiophene to biphenyl and of hexahydrodibenzothiophene to cyclohexylbenzene. This result gives rise to an increase in concentration of tetrahydro- and hexahydrodibenzothiophene before desulfurization. The presence of an added sulfur compound depresses the desulfurization reaction along with a competitive adsorption of both dibenzothiophene and the hydrogenated compounds, but does not depress the hydrogenation. Singhal et al.[10] and Broderick et al.[11] also found that H_2S (generated from CS_2) did not inhibit dibenzothiophene hydrogenation on the sulfided $CoMo/Al_2O_3$ catalysts.

The concentrations of methyl- and dimethyl dibenzothiophene was increased by the addition of CS_2. This result indicates that the presence of CS_2 enhanced the alkylation of dibenzothiophene and hampered the desulfurization. These compounds were produced in the reaction with the Co/HY zeolite catalyst,[12] which had stronger acid sites. Therefore, the sulfided NiW/Al_2O_3 catalyst appears to have stronger acid sites than the sulfided $NiMo/Al_2O_3$, $CoMo/Al_2O_3$, and Mo/Al_2O_3 catalysts.

The change in the products of dibenzothiophene hydrodesulfurization in the presence of xanthene at 300 °C is shown in Fig. 3. The presence of xanthene depressed the formation of both biphenyl and cyclohexylbenzene with decreasing the conversion of dibenzothiophene, while methyldibenzothiophenes remained unchanged. Thus, the inhibitory effect of an oxygen compound on the sulfided NiW/Al_2O_3 catalyst closely parallels that of CS_2, except for an enhancement of the alkylation of dibenzothiophene.

These results indicated that there are two different sites on the sulfided NiW/Al_2O_3 catalyst; hydrogenation and desulfurization sites. Hydrogenation sites were inhibited by acridine but neither by CS_2 nor by xanthene, whereas desulfurization sites were promoted by acridine. The presence of a nitrogen compound promotes the catalytic activity of the sulfided NiW/Al_2O_3 catalyst for the desulfurization.

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