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The Effect of Hydrogen Sulfide on Acridine Hydrodenitrogenation on a Sulfided $NiMo/Al_2O_3$ Catalyst

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(Received June 14, 1990)

Synopsis. The effect of hydrogen sulfide on acridine hydrodenitrogenation over a sulfided $NiMo/Al_2O_3$ catalyst at 280—380 °C and 10.1 MPa total pressure was studied. The result showed that the presence of H_2S depressed the total C–N hydrogenolysis at a low P_{H_2S}/P_{H_2} ratio of $1.1—79\times10^{-5}$, but that it rarely affected the C–N hydrogenolysis at a ratio above 0.003.

Previous studies[1,2] have shown that the presence of various sulfur compounds depressed the C–N hydrogenolysis reactions in the hydrodenitrogenation of acridine and carbazole on the Mo/Al_2O_3 catalysts at 10.1 MPa total pressure. Satterfield *et al.*[3,4] reported, however, that the presence of hydrogen sulfide increased the overall rate of hydrodenitrogenation of pyridine or quinoline on sulfided $NiMo/Al_2O_3$ catalysts. Recently, Yan *et al.*[5] reported the promoting effect on quinoline hydrodenitrogenation over a sulfided $CoMo/Al_2O_3$ catalyst. Nickel- or cobalt-promoted molybdenum catalysts might be more active for the C–N hydrogenolysis of nitrogen compounds in the presence of H_2S, as well as the C–S hydrogenolysis. Moreover, the presence of H_2S at a high H_2S/H_2 ratio not only changed the sulfided state of the catalyst's surface[6] but also caused the reduction of organic compounds on MoS_2.[7] In the present work, the effect of the presence of H_2S on acridine hydrodenitrogenation on a sulfided $NiMo/Al_2O_3$ catalyst is discussed on basis of changes in the ratio of P_{H_2S}/P_{H_2} and the reaction temperature.

Experimental

The study was carried out in a continuous-flow fixed-bed reactor, using the $NiMo/Al_2O_3$ catalyst and procedures described previously.[1] The catalyst was preheated in air at 450 °C in the reactor before pretreatment. Sulfiding was accomplished *in situ* in a flowing 10 vol% H_2S/H_2 atmosphere (6 $dm^3\,h^{-1}$) at 400 °C for 3 h after the oxidized catalyst was reduced at 400 °C and 10.1 MPa pressure for 3 h. The experiment was performed at 280—380 °C and 10.1 MPa total pressure. A solution of xylene containing 0.25 wt% acridine was fed at a rate of 20 $cm^3\,h^{-1}$ into the reactor with flowing hydrogen at 30 $dm^3\,h^{-1}$. Ethanethiol (0.1 kPa) was added to the feed in order to maintain the sulfided state of the catalyst during the reaction. Ethanethiol was readily decomposable to form H_2S at 10.1 MPa total pressure. No ethanethiol was observed in the reaction products. The reaction reached a steady state in about 3 h. The liquid reaction products were analyzed by FID gas chromatography.

Results and Discussion

The major denitrogenated product was dicyclohexylmethane with a small amount of benzylcyclohexane. Acridine was completely hydrogenated to yield perhydroacridine through *cis*- and *trans*-1,2,3,4,4a,9,9a,10-octahydroacridines, even at 280 °C, while 1,2,3,4,5,6,7,8-octahydroacridine was formed preferentially rather than the 1,2,3,4,4a,9,9a,10-octahydro compounds above 300 °C.

The effect of H_2S on acridine hydrodenitrogenation on the sulfided catalyst at 330 °C is shown in Fig. 1. The presence of H_2S decreased the concentration of dicyclohexylmethane and increased those of octahydroacridine and perhydroacridine. This result showed that the presence of H_2S depressed the C–N hydrogenolysis of perhydroacridine to dicyclohexylmethane at 330 °C. The concentration of dicyclohexylmethane was decreased to 0.18 wt% from 0.2 wt% by the addition of P_{H_2S} of 7.0 kPa from 0.10 kPa at 330 °C, which corresponded to a ratio of P_{H_2S}/P_{H_2} varying from 7.9×10^{-4} to 1.1×10^{-5}. Figure 2 shows, however, that at 280 °C the presence of H_2S decreased the concentrations of perhydroacridine and dicyclohexylmethane and increased that of octahydroacridine. The presence of H_2S depressed the hydrogenation of octahydroacridine to perhydroacridine and resulted in a reduced

Table 1. The Effects of H_2S on Hydrodenitrogenation

Compound	Catalyst	Reaction temperature	H_2S pressure	H_2S/H_2 ratio	Effect[a]	Reference
		°C	kPa			
Acridine	Mo/Al_2O_3	280—380	0.3	0.0008	−	1
Carbazole	Mo/Al_2O_3	280—360	0.3	0.0003	−	2
Acridine	$NiMo/Al_2O_3$	280—340	0.1—7	$1.1—79\times10^{-5}$	−	Present work
Acridine	$NiMo/Al_2O_3$	300—380	17.8	0.003	+−	Present work
Quinoline	$NiMo/Al_2O_3$	350—390	13.8—110	$2—16\times10^{-2}$	+−	3,4
Quinoline	$NiMo/Al_2O_3$	400	0.25	0.052	+	5
SCRII	$CoMo/Al_2O_3$	400	0.84	0.1	+	7
Benzophenone	MoS_2	200	7.5	1	++	8

a) +, promoting effect; −, depressing effect; +−, a slightly promoting or depressing effect depends on reaction temperature.

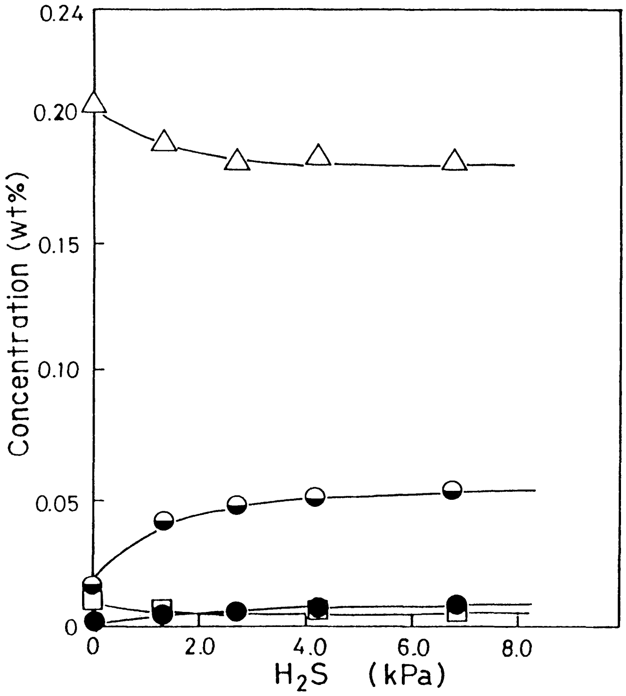

Fig. 1. The effect of H_2S on acridine hydrodenitrogenation on the sulfided $NiMo/Al_2O_3$ catalyst at 330 °C and 10.1 MPa total pressure. ●, 1,2,3,4,5,6,7,8-octahydroacridine; ◒, perhydroacridine; △, dicyclohexylmethane; □, benzylcyclohexane.

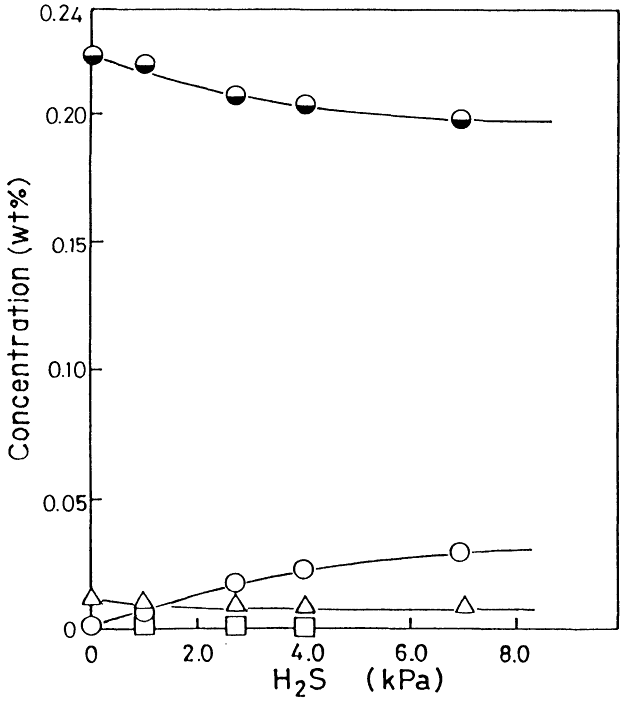

Fig. 2. The effect of H_2S on acridine hydrodenitrogenation on the sulfided $NiMo/Al_2O_3$ catalyst at 280 °C and 10.1 MPa total pressure. ○, *cis-* and *trans-*1,2,3,4,4a,9,9a,10-octahydroacridines; See Fig. 1 for other symbols.

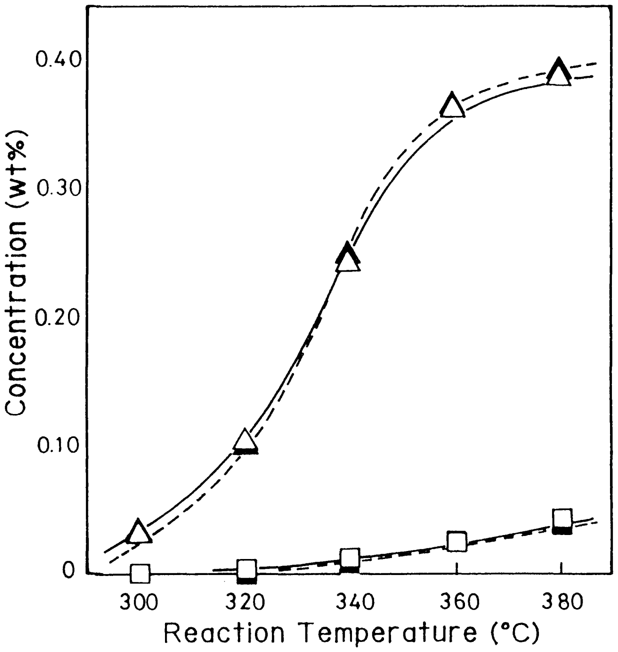

Fig. 3. The hydrodenitrogenation of acridine on the sulfided $NiMo/Al_2O_3$ catalyst at 10.1 MPa total pressure when 0.3 kPa (3×10^{-5} P_{H_2S}/P_{H_2}) (– – –) and 17.8 kPa (0.003 P_{H_2S}/P_{H_2} ratio) (——) of H_2S were added to the feed; See Fig. 1 for symbols.

C-N hydrogenolysis at lower temperature. These results suggest that the stability of the surface of the sulfided catalyst is probably changed at the reaction temperature.

In order to determine the effect of H_2S on C-N hydrogenolysis at a high ratio of P_{H_2S}/P_{H_2}, the study was carried out at 10.1 MPa total pressure and an H_2S/H_2 ratio of 0.003. The concentration of dicyclohexylmethane was slightly increased at 380 °C and remained unchanged up to 360 °C. In this case, the presence of H_2S slightly increased the C-N hydrogenolysis at high temperature, but remained unchanged at low temperature. This observation is in agreement with the results obtained by Satterfield and coworkers[3,4] in studies of the hydrodenitrogenation of pyridine and quinoline at 6.9 MPa total pressure and the P_{H_2S}/P_{H_2} ratio of 0.002. Yan et al.[5] reported the promoting effect of H_2S on quinoline hydrodenitrogenation at a H_2S/H_2 ratio of 0.052. Hirschon and Lain[8] also reported the promoting effect on SRCII hydroliquefaction over a $CoMo/Al_2O_3$ catalyst at a H_2S/H_2 ratio of 0.1. Moreover, Itabashi et al.[7] found that the presence of H_2S extremely enhanced the reduction of carbonyl compounds to hydrocarbons over a MoS_2 catalyst at 200 °C and about 7.5 MPa H_2S pressure. The promoting effect on the hydrodenitrogenation was carried out at a high ratio of H_2S/H_2 (above 0.003). Consequently, the presence of H_2S depressed the C-N hydrogenolysis at a low P_{H_2S}/P_{H_2} ratio of below 7.9×10^{-4}, but promoted C-N hydrogenolysis at a higher ratio. The total C-N hydrogenolysis remains unchanged at a ratio of about 0.003, though the effect of H_2S depends on the reaction temperature. The stability of the sulfided catalyst is probably changed thermodynamically in an H_2S/H_2 atmosphere and at the reaction temperature.

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