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Inhibiting effects of H_2S on HDS activity of CoMo-, NiMo-, and Mo/Al_2O_3

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Abstract

In order to clarify the relationship between the inhibiting effect of H_2S and the promoting effects of Co and Ni on hydrodesulfurization (HDS) activity, HDS reactions of benzothiophene (BT) and dibenzothiophene (DBT) over sulfided $CoMo/Al_2O_3$, $NiMo/Al_2O_3$, Mo/Al_2O_3 were carried out in the stream of H_2 or 5% H_2S/H_2 using a conventional fixed bed flow reactor. Both the inhibiting effect of H_2S and the promoting effect of Co (or Ni) on an HDS reaction were observed in the reaction of both reactants on every catalyst examined here. HDS activity of Mo/Al_2O_3 was most severely inhibited by the addition of H_2S. $NiMo/Al_2O_3$ was more susceptible to the inhibiting effect of H_2S than $CoMo/Al_2O_3$. The promoter eased the inhibiting effect of H_2S on HDS activity of these promoted catalysts. HDS of DBT was more sensitive to the promoting effect of Co and Ni, and to the inhibiting effect of H_2S, than that of BT. The present results supply new points of view with respect to the promoting effects of Co and Ni in this catalysis.

Keywords: Hydrogen sulfide; Cobalt; Nickel; Hydrodesulfurization activity

1. Introduction

H_2S inhibits the hydrodesulfurization (HDS) activity of sulfided $CoMo/Al_2O_3$ catalyst, although H_2S is usually used for activation of the catalyst during the pretreatment. It has been reported that, by addition of H_2S, HDS reactions of thiophene [1,2], benzothiophene [3,4], and dibenzothiophene [5,6] are inhibited. This inhibiting effect, however, has not been investigated in detail, especially concerning with the role of promoter Co.

On the other hand, many efforts have been made to understand the origin of promotional effects of Co and Ni on the catalyst performance of Mo/Al_2O_3. Some model structures of active sites have been proposed, aiming at explaining the role of promoter [7,8]. Among these, the Co–Mo–S model by Topsøe et al. [7], in which the Co atoms occupy the edge positions of MoS_2 clusters, and the remote control model by Delmon [8], in which H_2 is dissociated over Co_9S_8 to spill-over, are well known. More detailed information regarding the role of Co, however, has not yet been clarified.

The present work was done to clarify the relationship between the inhibiting effect of H_2S and the promoting effect of Co or Ni. For this purpose, HDS of benzothiophene and dibenzothiophene were carried out over sulfided $CoMo/Al_2O_3$, sulfided $NiMo/Al_2O_3$, sulfided

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Mo/Al_2O_3, in streams of both H_2 and 5% H_2S/H_2.

2. Experimental

2.1. Catalysts

Catalysts examined here were prepared by the incipient wetness method using aqueous solutions of ammonium heptamolybdate, cobalt nitrate, and nickel nitrate. Mo/Al_2O_3 (MoO_3, 15.8 wt%), Co/Al_2O_3 (CoO, 5.2 wt%), and Ni/Al_2O_3 (NiO, 5.2 wt%) were prepared by impregnating γ-Al_2O_3 (60/100 mesh) with each solution described above, followed by drying at 120°C for 16 h and calcination at 520°C for 12 h. $CoMo/Al_2O_3$ (CoO, 4.4 wt%; MoO_3, 15.1 wt%) and $NiMo/Al_2O_3$ (NiO, 4.4 wt%; MoO_3, 15.1 wt%) were prepared by impregnating the Mo/Al_2O_3 with the solution of cobalt nitrate or nickel nitrate, followed by drying at 120°C for 16 h and calcination at 520°C for 12 h. A commercial $CoMo/Al_2O_3$ (Ketjenfine 742, CoO, 4.42 wt%; MoO_3, 14.9 wt%) was also used as a reference.

Before the activity test, the catalysts were sulfided in situ in a conventional fixed bed flow system in a stream of 1 MPa 5% H_2S/H_2, initially at room temperature for 1 h, then the temperature was raised to 400°C (10°C/min) and held at 400°C for 2 h.

2.2. Activity test

HDS activity tests were undertaken immediately after the catalyst sulfiding mentioned above using a conventional fixed bed flow system. Benzothiophene (BT) dissolved in *n*-dodecane at 5 mol% (sulfur, 0.95 wt%) and dibenzothiophene (DBT) dissolved in decalin at 2.5 mol% (sulfur, 0.57 wt%) were used as the feed. The reaction was carried out under the following conditions: 300°C, 5 MPa H_2 (or 5% H_2S/H_2), gas-flow rate 300 ml/min, H_2/feed 1000 v/v, LHSV 7.5–6800 h^{-1}. LHSV was varied by changing the weight of catalyst used. Products were analyzed by GC (FID) and GC–MS. Details of the apparatus were described in our preceding papers [4,9].

3. Results

3.1. Promoting effects of Co and Ni on HDS of benzothiophene

Over every sulfided catalyst examined in the stream of H_2, ethylbenzene (EB) and 2,3-dihydrobenzothiophene (DHBT) were mainly produced. Our previous paper indicated that HDS of BT proceeds by two parallel pathways, as a result of numerical analysis [10], that is, one in which EB is produced through DHBT, and the other in which EB is produced directly from BT (Fig. 1). The product yields of EB and DHBT with increasing 1/LHSV (i.e., with increasing the charge of the catalyst) observed over sulfided $CoMo/Al_2O_3$, $NiMo/Al_2O_3$, and Mo/Al_2O_3 in H_2 stream are shown in Fig. 2a and b, respectively. The EB yield of $CoMo/Al_2O_3$ (or $NiMo/Al_2O_3$) is much higher than the simple sum of that of Co/Al_2O_3 and Mo/Al_2O_3 (or Ni/Al_2O_3 and Mo/Al_2O_3). The addition of Co or Ni on Mo/Al_2O_3 drastically promotes EB formation. Comparing Fig. 2a with b, we see that EB is selectively produced on both Co- and Ni-promoted catalysts, while EB and DHBT are comparably produced on Mo/Al_2O_3.

In order to clarify the characteristics of the catalysts examined, HDS selectivity (EB/(EB

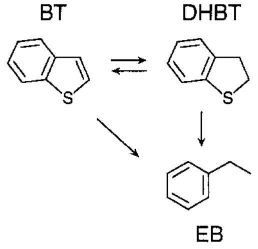

Fig. 1. Reaction paths of benzothiophene HDS.

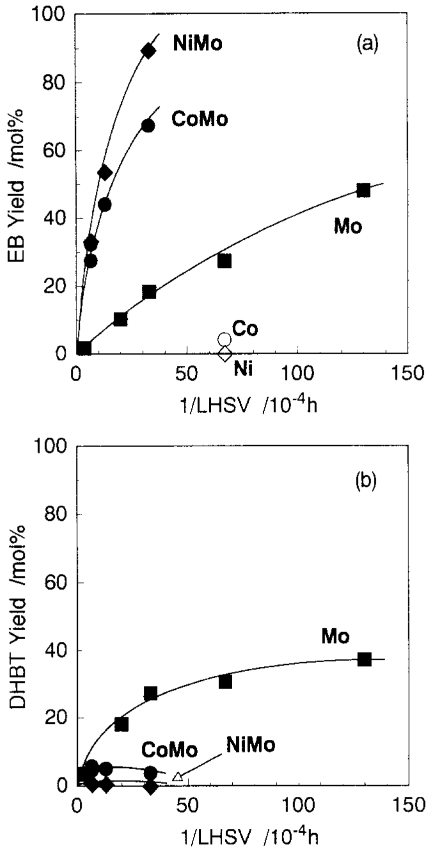

Fig. 2. EB yield vs. 1/LHSV in the stream of H_2 (a), and DHBT yield vs. 1/LHSV in the stream of H_2 (b). ●, $CoMo/Al_2O_3$; ◆, $NiMo/Al_2O_3$; ■, Mo/Al_2O_3; ○, Co/Al_2O_3; ◇, Ni/Al_2O_3.

+ DHBT)) was plotted against BT conversion, as is shown in Fig. 3 with the results observed over Co/Al_2O_3 and Ni/Al_2O_3. The HDS selectivities of $NiMo/Al_2O_3$ and $CoMo/Al_2O_3$ are higher than those of Mo/Al_2O_3, Co/Al_2O_3, or Ni/Al_2O_3. The addition of Co or Ni clearly changes the HDS characteristics of Mo/Al_2O_3.

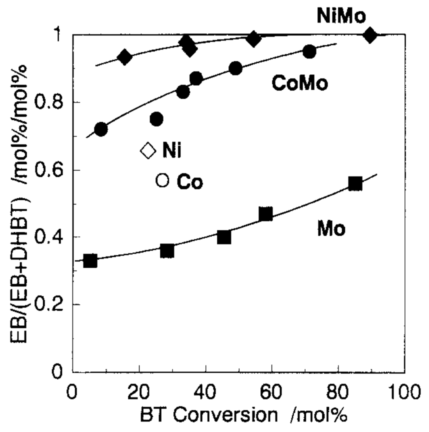

Fig. 3. HDS selectivity vs. BT conversion in the stream of H_2. ●, $CoMo/Al_2O_3$; ◆, $NiMo/Al_2O_3$; ■, Mo/Al_2O_3; ○, Co/Al_2O_3; ◇, Ni/Al_2O_3.

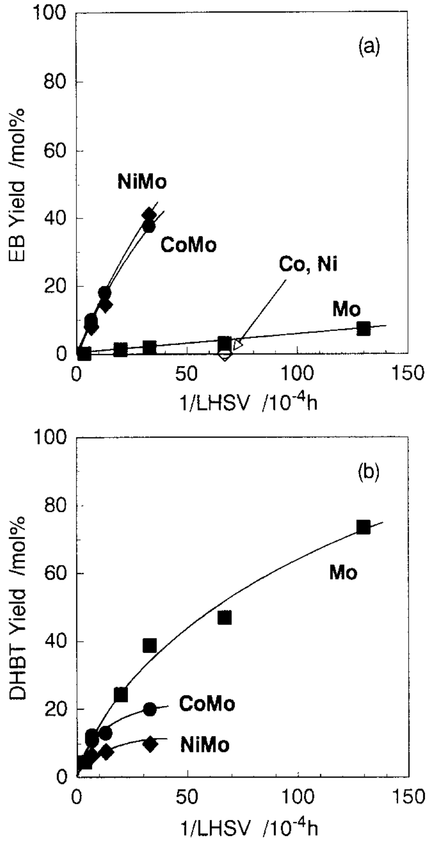

Fig. 4. EB yield vs. 1/LHSV in the stream of 5% H_2S/H_2 (a), and DHBT yield vs. 1/LHSV in the stream of 5% H_2S/H_2 (b). ●, $CoMo/Al_2O_3$; ◆, $NiMo/Al_2O_3$; ■, Mo/Al_2O_3; ○, Co/Al_2O_3; ◇, Ni/Al_2O_3.

3.2. *Inhibiting effect of H_2S on HDS of benzothiophene*

To clarify the relationship between the role of Co (or Ni) and the effect of H_2S on the HDS reaction, the HDS activity of the promoted catalysts was examined in the stream of 5% H_2S/H_2. The yields of EB and DHBT as a function of 1/LHSV in this stream are shown in Fig. 4a and b, respectively. As in the stream of H_2, the addition of Co and Ni on Mo/Al_2O_3 clearly promotes EB yield. Moreover, there is only a small difference in the EB yield between

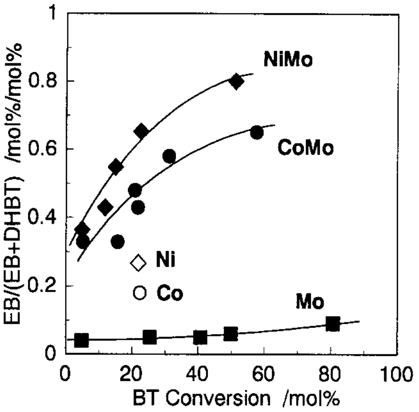

Fig. 5. HDS selectivity vs. BT conversion in the stream of 5% H_2S/H_2. ●, $CoMo/Al_2O_3$; ◆, $NiMo/Al_2O_3$; ■, Mo/Al_2O_3; ○, Co/Al_2O_3; ◇, Ni/Al_2O3.

these two catalysts in the stream of 5% H_2S/H_2, while the EB yield on $NiMo/Al_2O_3$ is clearly higher than that on $CoMo/Al_2O_3$ in the stream of H_2 (Fig. 2a). This suggests that Ni-promoted catalyst is more susceptible to the inhibiting effect of H_2S than Co-promoted catalyst.

Comparing Fig. 4 with Fig. 2 shows that the added H_2S remarkably decreases the EB yield and increases the DHBT yield in all catalysts examined. On Mo/Al_2O_3, DHBT is selectively produced. This effect of H_2S is consistent with our previous paper [10], in which the addition of H_2S depressed the hydrogenolysis rate of the C–S bond, whereas it promoted the hydrogenation rate.

Fig. 5 shows the selectivity–conversion profile in the stream of 5% H_2S/H_2. The addition of Co or Ni on Mo/Al_2O_3 clearly promotes HDS selectivity. Compared with Fig. 3, the HDS selectivity definitely decreases by the addition of H_2S to the stream of H_2. Especially, considering that the HDS selectivity of Mo/Al_2O_3 is very low, it can be said that the addition of Co or Ni more profoundly promotes HDS selectivity than in the stream of H_2. It is noted that, in both streams, the HDS activity and selectivity of $CoMo/Al_2O_3$ and $NiMo/Al_2O_3$ are enhanced by the synergic effect of Co (or Ni) and Mo.

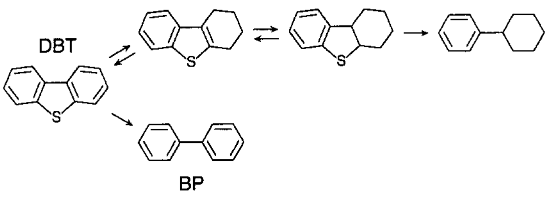

Fig. 6. Reaction paths of dibenzothiophene HDS.

3.3. Inhibiting effect of H_2S on HDS of dibenzothiophene

HDS of DBT was carried out in the stream of H_2 and 5% H_2S/H_2, for the purpose of understanding the relationship between the inhibiting effect of H_2S and the promoting effect of Co or

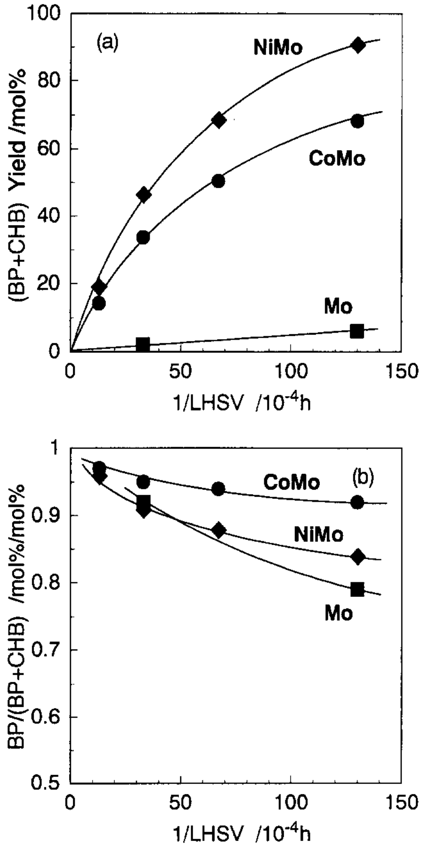

Fig. 7. HDS yield (= BP + CHB yield) vs. 1/LHSV in the stream of H_2 (a), and BP/(BP + CHB) ratio vs. 1/LHSV in the stream of H_2 (b). ●, $CoMo/Al_2O_3$; ◆, $NiMo/Al_2O_3$; ■, Mo/Al_2O_3.

Table 1
Rate constants and related factors in HDS of BT

Catalyst	in H_2		in 5% H_2S/H_2		k in H_2S/k in H_2
	k (h^{-1})	Promoting factor [a]	k (h^{-1})	Promoting factor [a]	
$CoMo/Al_2O_3$	370	7	140	25	0.38
$NiMo/Al_2O_3$	670	13	150	27	0.22
Mo/Al_2O_3	50	1	5.5	1	0.11

[a] Ratio of rate constant based on Mo/Al_2O_3.

Ni more deeply. On every catalyst examined, biphenyl (BP) and cyclohexylbenzene (CHB) were mainly produced. In addition, a trace amount of 1,2,3,4-tetrahydrodibenzo-thiophene and 1,2,3,4,4*a*,9*b*-hexahydro-dibenzothiophene were detected. A reaction path in HDS of DBT has been proposed, as is shown in Fig. 6 [11,12]. In Fig. 7a, the sums of the yields of BP and CHB, which are HDS products, on $CoMo/Al_2O_3$, $NiMo/Al_2O_3$, and Mo/Al_2O_3 in the stream of H_2 are plotted against 1/LHSV. The HDS yield (= BP + CHB yield) of $NiMo/Al_2O_3$ is the highest and the addition of Co or Ni drastically increases the HDS yield. For all catalysts examined, as can be seen from BP/(BP + CHB) ratio of Fig. 7b, BP is predominantly produced under this condition (5 MPa, 300°C).

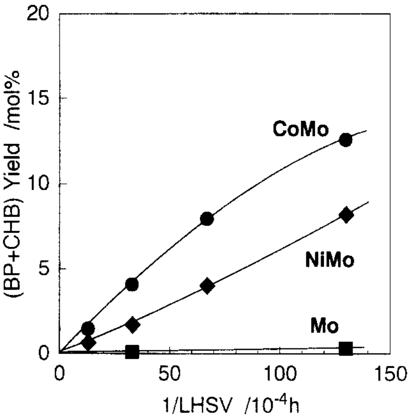

Fig. 8. HDS yield (= BP+CHB yield) vs. 1/LHSV in the stream of 5% H_2S/H_2. ●, $CoMo/Al_2O_3$; ♦, $NiMo/Al_2O_3$; ■, Mo/Al_2O_3.

In order to examine the inhibiting effect of H_2S on the HDS yield, the reaction of DBT was also carried out in the stream of 5% H_2S/H_2. The results observed over $CoMo/Al_2O_3$, $NiMo/Al_2O_3$, and Mo/Al_2O_3 are shown in Fig. 8. Comparing Fig. 8 with Fig. 7a, we see that the added H_2S depresses, to a great extent, the HDS yield. It is noted that, in the stream of 5% H_2S/H_2, the HDS yield of $CoMo/Al_2O_3$ is higher than that of $NiMo/Al_2O_3$, and that Mo/Al_2O_3 is almost inactive. On $CoMo/Al_2O_3$ and $NiMo/Al_2O_3$, BP was pri-

Table 2
Rate constants and related factors in HDS of DBT

Catalyst	in H_2		in 5% H_2S/H_2		k in H_2S/k in H_2
	k (h^{-1})	Promoting factor [a]	k (h^{-1})	Promoting factor [a]	
$CoMo/Al_2O_3$	110	22	12	50	0.11
$NiMo/Al_2O_3$	180	36	6	25	0.03
Mo/Al_2O_3	5	1	0.24	1	0.05
$CoMo/Al_2O_3$ (commercial)	63	13	8.3	35	0.13
$CoMo/Al_2O_3$ (commercial)	730 [b]		230 [b]		0.32 [b]

[a] Ratio of rate constants based on Mo/Al_2O_3.

[b] Value in HDS of BT (BT dissolved in decalin at 2.5 mol%).

marily produced in the stream of 5% H_2S/H_2 as in that of H_2.

4. Discussion

In both the HDS of BT and that of DBT, the addition of H_2S to the stream of H_2 clearly decreases HDS yields on every sulfided catalyst examined. In order to clarify the relationship between the inhibiting effect of H_2S and the promoting effect of Co or Ni, pseudo-first-order rate constants were calculated. The obtained rate constants in HDS of BT (for EB formation) and DBT (for BP and CHB formation) are summarized in Tables 1 and 2, respectively. In addition, the promoting factor, which is defined as the ratio of the rate constant of the promoted catalyst to that of Mo/Al_2O_3, is shown in these tables. The ratio of the rate constant in the stream of 5% H_2S/H_2 to that in the stream of H_2 is also shown in these tables, showing the catalyst sensitivity to the inhibiting effect of H_2S.

In the case of HDS of BT (Table 1), it is noticeable that the promoting factors of $CoMo/Al_2O_3$ and $NiMo/Al_2O_3$ in the stream of 5% H_2S/H_2 are much larger than that in the stream of H_2. The promoting effects of Co and Ni appear more clearly in the stream of 5% H_2S/H_2. As can be seen from the ratio of the rate constant in the stream of 5% H_2S/H_2 to that in the stream of H_2, the susceptibility to the inhibiting effect of H_2S decreases in the following order: $Mo/Al_2O_3 > NiMo/Al_2O_3 > CoMo/Al_2O_3$. That is, by the addition of Co or Ni, the inhibiting effect of H_2S on HDS activity is suppressed and the degree of suppression over the Co-promoted catalyst is higher than that over the Ni-promoted catalyst.

On the other hand, in the case of HDS of DBT (Table 2), it is noted that, on $CoMo/Al_2O_3$, the promoting factor in the stream of 5% H_2S/H_2 is about twice as high as that in the stream of H_2, whereas on $NiMo/Al_2O_3$, this factor in the stream of 5% H_2S/H_2 is lower than that in the stream of H_2. As can be seen from the ratio of the rate constant in the stream of 5% H_2S/H_2 to that in the stream of H_2, the Ni-promoted catalyst is more susceptible to the inhibiting effect of H_2S than the unpromoted catalyst is. Moreover, the results observed over commercial $CoMo/Al_2O_3$ under the same condition (BT dissolved in decalin at 2.5 mol%) indicate that the added H_2S inhibits the reaction of DBT more drastically than that of BT.

Comparing Table 2 with Table 1 shows that the promoting factors of $CoMo/Al_2O_3$ and $NiMo/Al_2O_3$ in the stream of H_2 are much higher in the case of DBT than that of BT. By comparison of both the BP and CHB formation and the BP formation, the same tendency was shown. HDS of DBT is more sensitive to promoting effects of Co and Ni.

References

[1] C.N. Satterfield and G.W. Roberts, AIChE J., 14 (1968) 159.

[2] F.E. Massoth, J. Catal., 47 (1977) 316.

[3] H. Gissy, R. Bartsch and C. Tanielian, J. Catal., 65 (1980) 158.

[4] M. Yamada, Y.-L. Shi, T. Obara and K. Sakaguchi, Sekiyu Gakkaishi, 33 (1990) 227.

[5] D.H. Broderick and B.C. Gates, AIChE J., 27 (1981) 663.

[6] G.H. Singhal, R.L. Espino, J.E. Sobel and G.A. Huff, Jr., J. Catal., 67 (1981) 457.

[7] H. Topsøe and B.S. Clausen, Catal. Rev. Sci. Eng., 26(3,4) (1984) 395.

[8] B. Delmon, Bull. Soc. Chim. Belg., 88 (1979) 979.

[9] M. Yamada, A. Saito, T. Wakatsuki, T. Obara, J.-W. Yan and A. Amano, Sekiyu Gakkaishi, 30 (1987) 412.

[10] S. Kasahara, Y.-L. Shi, J. Zou, K. Kawahara and M. Yamada, Sekiyu Gakkaishi, 37 (1994) 194.

[11] M. Houalla, N.K. Nag, A.V. Sapre, D.H. Broderick and B.C. Gates, AIChE J., 24 (1978) 1015.

[12] M. Nagai and T. Kabe, J. Catal., 81 (1983) 440.