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Hydrodesulfurization of dibenzothiophene over alumina-supported nickel molybdenum phosphide catalysts

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Abstract

The activity of nickel molybdenum phosphide catalysts was studied for the hydrodesulfurization of dibenzothiophene at 573 K and total pressure of 2.0 MPa. The Al_2O_3-supported NiMo phosphide catalysts were prepared by successive and simultaneous methods. The effect of the reduction temperature on the catalyst activity was also studied. The simultaneous preparation was determined to be the best method for the preparation of the active supported catalyst for dibenzothiophene HDS. The 623 K-reduced catalyst had the highest HDS rate of the catalysts. Nickel migrated from the inside to the surface during the reaction and promoted the HDS activity. The active species in the dibenzothiophene HDS and the oxidation states of Mo, Ni and P in the catalyst before and after reaction and of S after the reaction were studied on the basis of an XPS analysis.

Keywords: Dibenzothiophene; Hydrodesulfurization; NiMo phosphide; XPS

1. Introduction

Hydrodesulfurization (HDS) is one of the most important processes in petroleum refineries. Most commercial HDS catalysts contain a mixture of MoS_2 and Ni or Co. More recently, transition metal phosphides has been extensively studied and reported to be active for HDS and HDN. Phillips et al. [1] reported that MoP/SiO_2 was four times more active than MoS_2/SiO_2 at 150 h per catalyst gram during thiophene HDS. Bulk MoP was floated on the SiO_2 of MoP/SiO_2 in the TPR study of MoP/SiO_2 [2]. On the other hand, there are few studies on the Al_2O_3-supported MoP. Phosphorus oxide reacted with Al_2O_3 to form $AlPO_4$, and the Mo oxide was changed to Mo metal below 750 K [3]. Above 1023 K, the phosphorus of $AlPO_4$ was released and reacted with Mo metal to form MoP crystallites. Furthermore, the addition of phosphorus to alumina reacts with Lewis acids [4], that leads to weakening the interaction of the Mo atom and alumina [5], increasing the sulfidity of the catalyst [6], forming larger MoS_2 crystallites with a lower dispersion of the active metal on the support [7,8] and a higher stacking of MoS_2 crystallite [9]. Although there are many studies on the activity of single transition metal phosphide catalysts for HDS, there are few studies on the effect of the preparation methods on the HDS activity and the change in the surface compositions of Ni and Mo phosphides during the reaction. In this study, alumina-supported NiMo phosphide catalyst was prepared by successive and simultaneous methods, and subjected to the HDS measurement of dibenzothiophene. The active species in the dibenzothiophene HDS and the oxidation states of Mo, Ni and P in the catalyst before and after reaction and of S after the reaction were studied on the basis of an XPS analysis.

2. Experimental

2.1. Catalyst preparation

A nickel molybdenum phosphide (mole composition, Ni:Mo:P = 1:1:1; NiO: 5.2 wt%, MoO_3: 9.8 wt%, P_2O_5:

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5.0 wt%) supported on Al_2O_3 was prepared using three kinds of successive impregnation and simultaneous methods; in the former method, alumina was injected into an aqueous solution of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ and $(NH_4)_2HPO_4$, dried at 393 K and then oxidized in dry air at 773 K for 5 h. An aqueous solution of $Ni(NO_3)_2\cdot 6H_2O$ was added to the oxidized solid which was dried at 393 K then calcined in dry air at 773 K for 5 h (this catalyst was denoted as Ni/MoP/Al_2O_3). In the successive impregnation method, Al_2O_3 was first added to the aqueous $Ni(NO_3)_2$ solution, dried at 393 K and then calcined in dry air at 773 K for 5 h. The Ni/Al_2O_3 was impregnated with the aqueous solution of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ and $(NH_4)_2HPO_4$, dried at 393 K and then calcined in dry air at 773 K for 5 h. This catalyst was denoted as MoP/Ni/Al_2O_3. In the simultaneous method, three aqueous solutions containing molybdenum, nickel and phosphorus were mixed with the pH adjusted to 2 using 0.1 M HNO_3 into which Al_2O_3 had been added. The corresponding solid was dried at 393 K and calcined in dry air at 773 K for 5 h (NiMoP/Al_2O_3). For the reduction of the prepared catalysts, the catalysts were oxidized in dry air at 773 K, cooled to 573 K and heated by a temperature-programmed reduction method with H_2 from 573 to 623 K (−1073) K at the rate of 60 K h^{-1}, and maintained at a final temperature for 3 h. The reduced catalysts were cooled to room temperature in flowing H_2 which was switched to an Ar flow at room temperature for 1 h.

2.2. Activity measurement

The HDS of dibenzothiophene was carried out using a fixed-bed microreactor in a high-pressure flow system. A 1.0 g quantity of the reduced (not presulfided) catalyst (0.85–1.70 mm) was placed in the middle of the reactor. The solution of 1 wt% dibenzothiophene in xylene was introduced into the reactor at 10 mL h^{-1} with a hydrogen flow of 4 L h^{-1} at 513–573 K and total pressure of 2 MPa. Hydrogen was dried by passing it through a Linde 13× molecular sieve trap. The feed and reaction products were quantitatively analyzed by FID gas chromatography with a 2% silicon OV-17 column.

2.3. Characterization

The catalyst was not exposed to air during the procedure from the catalyst pretreatment to the XPS measurement. The XPS spectra of the Mo 3d, Ni 2p and P 2p lines before and after the reaction and S 2p lines after the reaction were obtained using a Shimadzu ESCA 3200 spectrometer with monochromatic Mg Kα exciting radiation. The binding energy values for the catalysts were referenced to the Al 2p line of Al_2O_3 at 74.7 ± 0.2 eV. The Mo 3d spectra (Mo $3d_{5/2}$ and $3d_{3/2}$) were curve-fitted into six different Mo species of the Mo doublets of the catalysts [10,11]. The Ni 2p envelope was deconvoluted into four Ni 2p binding energies (Ni^0, Ni^{2+}, Ni^{3+}, Ni^{2+} satellite) [12,13]. The S 2p binding energy of the catalysts after the HDS reaction was deconvoluted into S^{2-}, S_2^{2-} and S^0 [14,15] and the P 2p was analyzed to P^0, P^{3+} and P^{5+} [16,17]. The baseline corrections for the Ni $2p_{3/2}$ and Mo 3d peaks were carried out using the Shirly method.

3. Results and discussion

3.1. Dibenzothiophene HDS over NiMo phosphides reduced at various temperatures

The HDS of dibenzothiophene over the NiMoP/Al_2O_3 catalysts reduced at various temperatures and total pressure of 2.0 MPa and at 573 K is shown in Fig. 1 and Table 1. The 623 K-reduced catalyst had the highest HDS rate of the catalysts. The HDS rate of the catalysts decreased with the increasing reduction temperature. The 573 K-reduced catalyst was less active than the 623- and 973 K-reduced catalysts. The reaction products were biphenyl (BPN) and cyclohexylbenzene (CHB). Bicyclohexyl and tetrahydrodibenzothiophene were formed in a small amount but scarcely formed at a high conversion. The selectivities of the desulfurization (BPN/CHB ratio) for the 623 K-reduced catalyst was low (9.2) but for the other catalysts, it was slightly higher (10–11), indicating that all the catalysts exhibited a similar selectivity of the 723–973 K-reduced catalysts for the desulfurization–hydrogenation. Thus, the HDS activity of the 723–923 K-reduced catalysts decreased with increasing reduction temperature while maintaining the same distribution of the active sites.

3.2. Preparation method

The HDS of dibenzothiophene over the Al_2O_3-supported 973 K-reduced nickel molybdenum phosphide catalysts prepared by the three methods was studied. The order of the HDS rates at 573 K for the supported catalysts is as

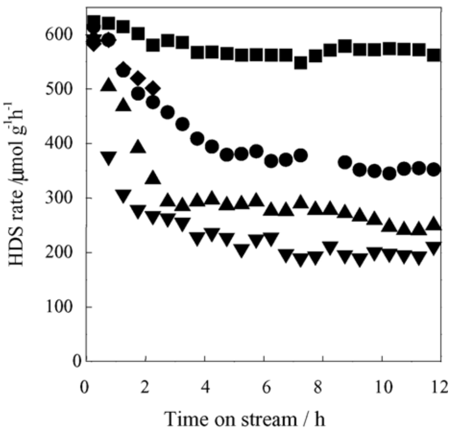

Fig. 1. Dibenzothiophene HDS over NiMo phosphide catalysts reduced at (◆) 573, (■) 623, (●) 723, (▲) 823 and (▼) 923 K at total pressure of 2.0 MPa and 573 K.

Table 1
HDS rate and BPN/CHB ratio at 0.5 and 12 h for NiMoP/Al_2O_3 reduced at 623, 723, 823 and 923 K

Reduction temperature (K)	HDS rate (μmol g^{-1} h^{-1}) Reaction time (h)		BPN/CHB ratio Reaction time (h)
	0.5	12	12
573	582	501	10.1
623	623[a]	562[b]	9.2[b]
723	614	352	11.2
823	594	249	10.8
923	591	210	11

WHSV: 8 h^{-1}.

[a] Conversion: 100% at 0.5 h.

[b] Conversion: 90.2% at 12 h.

Table 2
Ni/(Ni + Mo) and Mo/(Ni + Mo) atomic ratios[a] of NiMoP/Al_2O_3 reduced at 623–923 K before and after the reaction

Reduction temperature (K)	Ni/(Ni + Mo)		Mo/(Ni + Mo)		P/(Ni + Mo)	
	b.r.[b]	a.r.[c]	b.r.	a.r.	b.r.	a.r.
623	0.385	0.688	0.615	0.312	0.745	0.569
723	0.749	0.653	0.251	0.347	0.410	0.275
823	0.739	0.304	0.261	0.696	0.333	0.015
923	0.732	0.219	0.268	0.781	0.057	0.009

[a] M/(Ni + Mo) was caluculated on the basis of M/Al atomic ratio obtained by XPS. M is Ni, Mo, P and S. M/Al atomic ratio is $(A_M/f_M)/(A_{Al}/f_{Al})$, where A is peak area and f is factor of sensitivity of each atom and the device.

[b] Before the reaction.

[c] After the reaction.

follows: NiMoP/Al_2O_3 (191 mmol g^{-1} h^{-1}) > Ni/MoP/Al_2O_3 (166 mmol g^{-1} h^{-1}) > MoP/Ni/Al_2O_3 (152 mmol g^{-1} h^{-1}). The simultaneous preparation afforded the best preparation method of the active Al_2O_3-supported catalyst for the dibenzothiophene HDS. The simultaneous preparation method produced the mixture of NiMo oxide. Alumina had a strong interaction by alumina and the phosphorus probably blocked a wide dispersion of the NiMo oxide on alumina, and probably resulted from pile up the active NiMoS species for the HDS reaction after sulfidation.

3.3. XPS analysis and active species of NiMo phosphide catalysts

The compositions of molybdenum, nickel and phosphorus in the catalysts before and after the reaction based on an XPS analysis are shown in Table 2. The ratios of Mo/(Ni + Mo) and Ni/(Ni + Mo) of the 723–923 K-reduced catalysts did not change at all the reduction temperatures, while the Ni/(Ni + Mo) increased after the reaction. The 623 K-reduced catalyst after the reaction exhibited a higher Ni/(Ni + Mo) than that before the reaction. These results indicated that nickel migrated to the surface during the reaction and promoted the HDS activity. The P/(Ni + Mo) ratio was affected by the reduction temperature. The P/(Ni + Mo) ratio of the 923 K-reduced catalyst was lower than all the reduced catalysts before the reaction and for all the catalysts it decreased after the reaction. This is due to the phosphorus release with hydrogen at the high reduction temperature and after the reaction. Concerning the Mo oxidation state in Table 3, Mo^{5+} in the catalyst before the reaction was predominant for the reduction at 623 K. The Mo^{4+} ion increased, but the Mo^{5+} and Mo^{6+} ions decreased after the reaction to form Mo sulfide (Mo^{4+} sulfide). The 723 K-reduced catalyst had the highest ratio of BPN/CHB (11.2) and the least $Mo^{5+}(Mo^{6+})/Mo^{4+}$ ratio. This result shows that the formation of Mo sulfide facilitates the direct desulfurization of dibenzothiophene to BPN. For the Ni valence of the 623 K-reduced catalyst after the reaction, Ni^0 and Ni^{2+} increased but those for the 923 K-reduced catalyst decreased. This increase in the distribution of Ni^0 and Ni^{2+} probably brought about the high HDS activity.

The change in the composition of the 623 K-reduced catalyst by the preparation method is shown in Table 4. The NiMoP/Al_2O_3 catalyst after the reaction had the largest Ni/(Ni + Mo), therefore, the Mo composition was the least. The P/(Ni + Mo) ratios for Ni/MoP/Al_2O_3 and NiMoP/Al_2O_3 were lower than for MoP/Ni/Al_2O_3, which was the least active of three catalyst. This lower intensity of phosphorus amount on the surface showed that phosphorus strongly interacted with alumina in the first simultaneous impregnation of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ and $(NH_4)_2HPO_4$ and the subsequent reduction. Furthermore, the P^{5+} ion was distributed more than the P^{3+} ion for all the catalysts in

Table 3
Distribution of Mo oxidation sites for NiMoP/Al_2O_3 reduced at 623–723 K before and after the reaction

Sample		Distribution										
		Mo^0	Mo^{2+} Mo^{3+}	Mo^{4+}	Mo^{5+}	Mo^{6+}	Ni^0	Ni^{2+}	Ni^{3+}	Ni^2 satellite	P^{3+}	P^{5+}
623R	b.r.	–	–	0.281	0.494	0.225	0.306	0.091	0.016	0.588	0.381	0.619
	a.r	–	–	0.607	0.319	0.074	0.445	0.187	0.105	0.264	0.113	0.686
723R	b.r.	0.054	–	0.332	0.529	0.085	0.520	0.132	0.061	0.287	0.325	0.675
	a.r.	0.148	–	0.559	0.259	0.034	0.515	0.143	0.098	0.245	0.215	0.519
823R	b.r.	0.010	–	0.446	0.422	0.123	0.545	0.148	0.038	0.270	0.213	0.470
	a.r.	–	–	0.574	0.322	0.103	0.480	0.146	0.223	0.151	0.269	0.638
923R	b.r	0.139	–	0.561	0.273	0.027	0.550	0.132	0.068	0.250	0.423	0.577
	a.r	0.079	–	0.529	0.300	0.091	0.307	0.121	0.349	0.223	0.341	0.659

Table 4
The atomic ratios of Ni, Mo, S and P to (Ni + Mo) for the three NiMo phosphide catalysts reduced at 623 K before and after the reaction

Catalysts	BPN/CHB ratio	Ni/(Ni + Mo)		Mo/(Ni + Mo)		S/(Ni + Mo)		P/(Ni + Mo)
		b.r.	a.r.	b.r.	a.r.	a.r.	b.r.	a.r.
$Ni/MoP/Al_2O_3$	11.5[a]	0.319	0.390	0.681	0.610	0.826	0.252	0.714
$MoP/Ni/Al_2O_3$	11.2[b]	0.457	0.433	0.543	0.567	0.425	1.047	1.511
$NiMoP/Al_2O_3$	9.2[c]	0.384	0.688	0.615	0.312	0.480	0.739	1.389

[a] HDS rate at 12 h were 562 $\mu mol\ g^{-1}\ h^{-1}$.
[b] HDS rate at 12 h were 490 $\mu mol\ g^{-1}\ h^{-1}$.
[c] HDS rate at 12 h were 480 $\mu mol\ g^{-1}\ h^{-1}$.

Table 3. The P^{5+} ion increased after the reaction. The increase in phosphorus after the reaction is probably due to the migration of phosphorus from the inside to the surface and then phosphorus release. The average Mo valence (5.0) of $NiMoP/Al_2O_3$ was higher than that (3.6) of the phosphorus-undoped $NiMo/Al_2O_3$, suggesting a softening effect (sulfiding [6]) of phosphorus on the maintenance of a high Mo valence. Furthermore, the S/(Ni + Mo) ratio for $Ni/MoP/Al_2O_3$ was higher than that for $NiMoP/Al_2O_3$ in spite of a low conversion, probably due to an individual sulfidation of Ni and Mo atoms without the full formation of active NiMoS species. Since the $Ni/MoP/Al_2O_3$ had the lowest phosphorus content in spite of the highest sulfur content, Mo sulf-phosphide was not formed but sulfided. S_2^{2-} was significantly present for the 623-reduced catalyst but it decreased with the increasing reduction temperature. Sulfur deposits on the catalyst and sulfided the NiMo phosphorus catalyst to readily form a sulfide by phosphorus [6]. The Ni and Mo sulfide containing S_2^{2-} was an active species. Mo^{5+} and Mo^{6+} after the reaction decreased but Mo^{4+} increased, and for the Ni valence, the Ni^{3+} decreased to Ni^{2+}. Ferdous et al. [6] also reported the presence of Ni^{2+} in sulfided form of 2.7% P-doped 3% Ni-14%Mo/Al_2O_3 catalyst, confirmed by XPS.

In order to deconvoluted the Mo 3d and Ni 2p binding energies, the Mo oxidation states before and after the reaction did not have any good relationship between the Mo valance and the HDS rate. However, the Ni^{2+} ion of the catalysts after the reaction was correlated to the HDS rate in Fig. 2, although the percentage of Ni was low on the surface before the reaction. This result indicated that Ni^{2+} of the NiMo sulfide species was active for the dibenzothiophene HDS. Phosphorus (P^{5+}) blocked the high dispersion of the Ni and Mo species on Al_2O_3 by the interaction of phosphorus with Al_2O_3, and the NiMo sulfide piled up on the surface. Sun et al. [9] also reported that since phosphorus eliminated the stronger alumina surface sites the Ni^{2+} also interact more weakly with the alumina. Phosphorus can be more efficiently sulfided and form more Ni atom along the edges of MoS_2 crystallite in the catalytically active Ni–Mo–S phase.

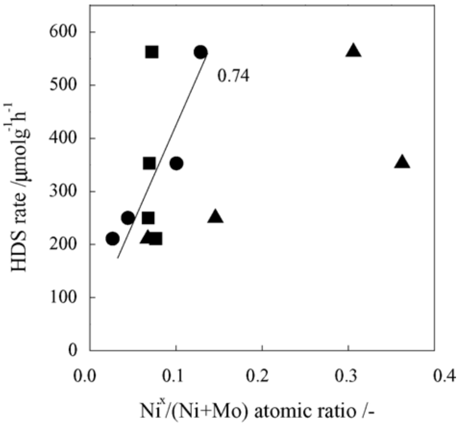

Fig. 2. Relationship between HDS rate and Ni^{n+}/(Ni + Mo) (n = 0, 2 and 3) atomic ratio of NiMo phosphide catalysts reduced at 623–923 K after the reaction. (■) Ni^{3+}, (●) Ni^{2+} and (▲) Ni^0.

4. Conclusion

The order of the HDS activities of the Al_2O_3-supported catalysts is as follows: $NiMoP/Al_2O_3 > MoP/Ni/Al_2O_3 > Ni/MoP/Al_2O_3$. The simultaneous preparation method produced the best preparation of the active supported catalyst for the dibenzothiophene HDS. The HDS rate of the catalysts decreased with the increasing reduction temperature. For the 723–923 K-reduced catalysts, the Ni/(Ni + Mo) decreased after the reaction. The 623 K-reduced catalyst after the reaction exhibited a higher Ni/(Ni + Mo) than that before the reaction. This result indicated that nickel migrated form the inside to the surface during the reaction and promoted the HDS activity. For the Ni valence of the 623 K-reduced catalyst, the Ni^0 and Ni^{2+} increased after the reaction but the 923 K-reduced catalyst decreased. The Ni^{2+} ion of the catalysts after the reaction was correlated to the HDS rate, although the percentage of Ni was low on the surface before the reaction. Ni^{2+} of the NiMo sulfide species was active for the dibenzothiophene HDS. Phosphorus (P^{5+}) blocked the high dispersion of the Ni and Mo species on Al_2O_3 by the interaction of phosphorus with Al_2O_3, and the NiMo sulfide piled up on the surface.

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