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Activity of molybdenum phosphide for thiophene hydrodesulfurization

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Abstract

The high initial activity of Mo phosphide catalysts and the gradual increase in the activity during the reaction were studied during the thiophene hydrodesulfurization (HDS) at 573 K and atmospheric pressure. A series of unsupported Mo phosphides with various P/Mo ratios were prepared and reduced by temperature-programmed reduction (TPR) from 673 to 723 K (-1073 K) in a stream of H₂. The rate of thiophene HDS once decreased and then increased after 2-2.5 h for several of the studied catalysts. The reduction of the Mo(60)P(40) catalyst at 923 K exhibited the highest HDS rate of the other catalysts during the initial stage. The initial HDS activity of the catalysts is due to the presence of metallic Mo reduced by the TPR preparation. The increase in the HDS activity during the reaction was induced by the 823-1023 K-reduced Mo(60)P(40) and Mo(50)P(50) due to the formation of deficient phosphorus MoP from MoP with the phosphorus loss. The reduction and subsequent sulfidation increased neither the initial HDS activity nor the increase in the HDS activity.

Keywords

Mo phosphide; Hydrodesulfurization; Increase in HDS activity; Characterization.

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INTRODUCTION

Phosphorus enhances the performance of HDS catalysts for the removal of sulfur from gas oil^[1]. Mo phosphide exhibits a more stable activity than carbides and nitrides for hydrogenation and HDS^[2-11], similar to other transition-metal phosphides^[12-16] such as Ni₂P^[17-25], NiP/ Al_2O_3 ^[26,27], and W₂P^[28-30]. Recently, Oyama and coworkers^[2,3,5,7,9] have found that Mo phosphide is 1.2-fold more active than the sulfided Ni-Mo/ Al_2O_3 for HDS on the basis of the CO uptake^[9]. Phillips et al.^[4] reported that MoP/SiO₂ is 3.5-fold more active than the sulfided Mo/SiO₂ and that the activity of MoP/SiO₂ first decreases and then increases up to 60 h. This result shows an increase in the HDS activity during such a reaction. The surface of the MoP particles changes into a more active structure over the course of the 150-h activity measurement, but these changes have not been clearly accounted for.

Mo phosphide was sulfided on the surface of MoP/SiO₂ during the HDS resulting in it being highly active through the reversible exchange of phosphorus with many sulfur species^[6]. However, little or no explanation for the increase in the HDS activity by sulfidation has been established. The increase in the HDS activity might depend on the changes in the surface properties of the Mo phosphide caused by phosphorus release, a slight reduction in the Mo oxidation state of the phosphorus-deficient MoP originating from the MoP crystallites and by molybdenum sulfidation during the HDS reaction. Moreover, the release of phosphorus induces. In this study, the increase in the thiophene HDS activity is elucidated in terms of changes in the structure and surface properties of the Mo phosphide, which is prepared as a series of bulk Mo phosphides with several compositions. Mo phosphide and phosphorus compounds reduced at various temperatures were analyzed by XRD analysis. Furthermore, the extent

TABLE 1 : HDS rate and IRAT for the 923K-reduced catalysts with various phosphorus

Catalyst	P/Mo	HDS rate ^a (mmol/(min·g·cat))	IRAT ^b (-)
Mo(100)	-	26.3	negative
Mo(70)P(30)	0.428	7.05	negative
Mo(60)P(40)	0.667	36.7	1.06 <1.32>
Mo(50)P(50)	1.00	8.21	1.40

^aHDS rate at 8 h. ^bThe increasing HDS activity ratio (IRAT) is defined by the ratio of HDS rate at 8 h divided the low HDS rate at 2–2.5 h. ^c30 h at the reaction

of the phosphorus release and degree of molybdenum sulfidation of various catalysts were measured by X-ray photoelectron spectroscopy (XPS). The role of the active species of the Mo phosphide catalysts during the thiophene HDS is also discussed.

EXPERIMENTAL

Catalyst preparation

Mo phosphide precursors prepared using the physical mixtures of ammonium heptamolybdate ((NH₄)₆Mo₇O₂₄·4H₂O, Kishida Chemical Co.) and ammonium orthophosphate ((NH₄)₂HPO₄, Kishida Chemical Co.) at several P/Mo ratios were dissolved in distilled water and stirred until a white paste was produced. The resulting paste was dried at 393 K for approximately 12 h and calcined at 773 K for 5 h. The white phosphate precursor (0.12 g) was packed in a quartz tube reactor and dried in air for 1 h at 773 K. Catalysts were prepared by the temperature-programmed reduction from 673 to 723 K (-1023 K) at the rate of 10 K/min with H₂ at 0.9 l/h, and held at the final temperature for 3 h. The reduced Mo(50)P(50) was sulfided at 623 K for 3 h in a stream of 10% H₂S/H₂ (3 l/h) after the reduction at 923 K for comparison of the catalysts with a sulfided catalyst. The reduced or sulfided catalyst was subjected to the measurement of the thiophene HDS activity, XPS, and CO adsorption analysis without passivation. For the XRD analysis and BET measurement, the catalysts were passivated in 1% O₂/He (10 ml/min) for greater than 12 h at room temperature after the reduction, sulfidation, or HDS reaction. The catalysts were designated as follows: Mo(x)P(y), where x and y % are the MoO₃ and PO_{2.5} compositions, respectively. For example, Mo(60)P(40) denotes a MoO₃ content of 0.6 and a P₂O₅ content of 0.4.

Catalyst characterization

The structures of the catalysts before and after the reaction were determined by XRD analysis. The diffraction pattern was obtained using a RAD-II (Rigaku Co.) equipped with CuK_α radiation (λ = 1.542 Å). Peaks were

TABLE 2 : HDS rate and IRAT for the Mo(60)P(40) and Mo(50)P(50) reduced at various temperatures

Catalyst	Reduction temperature (K)	Surface area (m ² /g)	HDS rate (mmol/(min·g·cat)) ^a	IRAT (-) ^b
Mo(60)P(40)	723	1	20.3	negative
Mo(60)P(40)	823	5	9.36	1.14
Mo(60)P(40)	923	9	36.7	1.06 ^c
Mo(60)P(40)	1023	16	22.7	1.06
Mo(50)P(50)	723	ca. 1	23.4	negative
Mo(50)P(50)	823	5	8.19	1.00
Mo(50)P(50)	923	2	8.21	1.40
Mo(50)P(50)	1023	ca. 1	7.63	1.00

^aHDS rate at 8 h. ^bRatio of HDS rate at 8 h divided the low HDS rate at 2–2.5 h. ^c1.32 at 30 h

identified on the basis of the JCPDS card references: MoO₃ (JCPDS 35-609, 2θ = 23.3, 25.7, 27.3, and 39.0°; this study, 2θ = 23.3, 25.7, 27.4, and 39.0°), MoO₂ (JCPDS 32-671, 26.0, 37.0, 53.52°; 26.0, 37.2, 53.2), Mo metal (JCPDS 42-1120, 40.5, 69.9°; 39.4, 40.5, 58.7, 73.7), Mo₈P₅ (JCPDS 26-1274; 34.5, 40.7, 40.7; 34.6, 40.7, 41.6, 44.4, 57.4°) and MoP (JCPDS 24-771; 32.2, 43.1, 57.5°; 28.0, 31.9, 32.1, 43.0, 57.1, 64.9, 67.2, 74.2, 85.9, 93.9°). The average crystalline size of the catalysts was calculated using the Debye-Scherrer equation on the basis of the average particle sizes of three individual phases of MoO₃, MoO₂, Mo₈P₅, and MoP with high relative intensities. The Debye-Scherrer equation is expressed as D_c = 0.9λ/(B·cosθ), where λ = 1.542 Å, B is the full width at half-maximum corrected for instrumental broadening, and θ is the Bragg angle of the diffraction peak. All the X-ray diffraction patterns were obtained under identical conditions so that the peak intensities and peak widths of the patterns (more precise peak areas) reflected the crystallinity of a given phase. The temperature-programmed reduction was performed in situ using the Balzers QMS200 quadrupole mass spectrometer to determine how the processed Mo phosphides are formed from the oxidized precursors of Mo(60)P(40) during the TPR with hydrogen: the catalyst was heated from 323 to 923 K at the rate of 1 K/min with flowing hydrogen at 15 ml/min and analyzed by XRD analysis. The formation of the H₂O (m/Z = 18) from the catalysts was monitored using an on-line quadrupole mass spectrometer. The BET surface area of the catalysts was measured at 77 K using an Omnisorp 100X after the passivated catalysts were evacuated at 473 K for 2 h. The XPS P 2p binding energies of Mo(50)P(50) before the reaction and the XPS Mo 3d and S 2p of Mo(50)P(50) and Mo(60)P(40) before and after the reaction were determined using a Shimadzu ESCA3200 photoelectron spectrometer equipped with MgK_α radiation. The binding energies of P⁵⁺ and P⁰ were identified on the basis of the following references: 133.4 eV (133.8-9^[4,31], 132.5^[32],

TABLE 3 : The ratios of P/Mo, O/Mo, and S/Mo for the reduced Mo(50)P(50) and Mo(60)P(40) and 923 K-sulfided Mo(50)P(50) catalysts

Catalyst	P/Mo			O/Mo			S/Mo		
	br ^a	0.5	8.0	br ^a	0.5	8.0	br ^a	0.5	8.0
923 ^b Mo(50)P(50)	0.89	(Non)	0.85	0.93	(Non)	0.74	0	(Non)	0.17
923 ^b Mo(50)P(50)	0.82	(Non)	0.83	0.28	(Non)	0.24	0.52	(Non)	0.15
723 ^b Mo(60)P(40)	0.49	0.45	0.41	2.6	2.5	2.4	0	0.15	0.21
823 ^b Mo(60)P(40)	0.64	0.61	0.52	1.0	1.1	0.74	0	0.09	0.11
923 ^b Mo(60)P(40)	0.67	0.61	0.67	0.81	0.68	0.68	0	0.11	0.18
			0.59 ^c			0.65 ^c			0.20 ^c

^aBefore reaction. ^bReduced at 723, 823, or 923 K. ^c30 h

and 132.7 eV^[4] and 129.0 eV (129.1^[33] and 129.8-9 eV^[4,31,32]; (129.6 (P³⁻) and 130.4 eV (P⁰)^[35]). After carburization, the catalyst was cooled to room temperature in flowing 20% CH₄/H₂ and not exposed to air during the procedure from the catalyst pretreatment or the activity measurement to the XPS measurement. After the stopcocks at each end of the microreactor were closed, the microreactor was transferred to a glovebox in which the atmosphere was exchanged five times with argon (99.9999%), and then filled with argon. The catalyst was removed from the microreactor in the glovebox, mounted onto a sample-holder with carbon tape, and then placed in a vial while in the glovebox. The vial was then placed in the XPS prechamber attached glovebag in which the atmosphere was filled with argon. Furthermore, the catalyst on the sample-holder was taken out of the vial and then set on a sample-rod placed in the prechamber. The XPS analysis was typically done at a pressure of 5×10⁻⁶ Pa and at a scan speed of 0.33 eV s⁻¹. Argon etching was carried out for 3 min. All binding energies were referenced to the C_{1s} peak arising from the carbon (BE = 284.5 eV). The data were analyzed using Kratos of the ESCA3200 data station equipped with the Spark5 (Sun Microsystems Co.) workstation. Curve fitting was carried out using a least-squares fitting program.

Thiophene HDS activity measurement

The activity of the Mo phosphide catalysts for thiophene HDS was measured using a fixed-bed microreactor at 623 K and atmospheric pressure. Each oxide precursor (0.12g) was packed in the center of the reactor, and the temperature was monitored using a chromel-alumel thermocouple placed at the center of the reactor bed. After reduction or sulfidation, the catalysts were cooled to 623 K in a stream of 20% CH₄/H₂ or 10% H₂S/H₂ without exposure to air, then helium and subsequently hydrogen was passed over the catalyst before introduction of the reaction feed. The reaction feed consisting of a 3 vol% thiophene/H₂ mixture, was introduced into the microreactor at the rate of 3 l/h with an hourly gas space

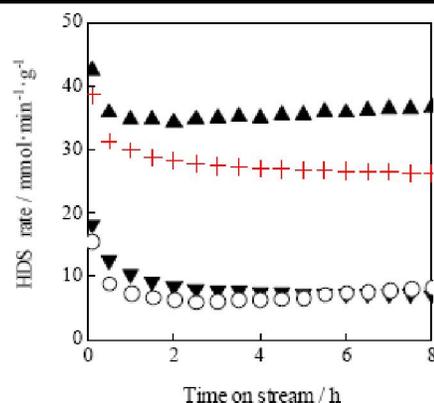


Figure 1 : Rate of thiophene HDS on 923-K-reduced Mo phosphides with various phosphorus at 573 K. (○) Mo(50)P(50), (▲) Mo(60)P(40), (▼) Mo(70)P(30), and (+) Mo(100)

velocity of 7600 /h. The reaction products and thiophene were analyzed on-line using a gas chromatograph equipped with a flame ionization detector using a 10% DC-550/Silica Uniport HP. The HDS rate was calculated from the of thiophene conversion rate.

RESULTS AND DISCUSSION

High initial HDS activity and increase in HDS activity

The rate of thiophene HDS for the 923 K-reduced Mo phosphides with various compositions is shown in figure 1. The HDS activity of the Mo phosphide catalysts at 8 h after the run decreased in the following order: Mo(60)P(40) > Mo(100) > Mo(50)P(50) > Mo(70)P(30). The HDS rate for Mo(60)P(40) reduced at 923 K was the highest of the other catalysts. The 923 K-reduced Mo(60)P(40) and Mo(50)P(50) exhibited an increase in the HDS activity during the reaction. Phillips et al.^[4] reported an increase in the activity of the 923 K-reduced 15 % Mo phosphide supported on silica during the thiophene HDS, and found the four-fold more active than the sulfided Mo/SiO₂ catalyst after 150 h. The difference in the HDS rate and the HDS rate at 8 h for the catalysts were considered to determine why the HDS activity increased during the reaction. The increasing HDS activity ratio (IRAT) is defined by the ratio of the low HDS rate at 2-2.5 h to the HDS rate at 8 h. The increase in the HDS activity ratios of the 923K-reduced catalysts are shown in TABLE 1. The IRATs of Mo(60)P(40) and Mo(50)P(50) were higher than unity, while Mo(70)P(30) was lower than unity. It should be noted that Mo(60)P(40) contained a slight excess of Mo, Mo(50)P(50) equal the amounts of Mo and phosphorus; and the two catalysts showed a markedly high activity during the reaction. The 923 K-reduced Mo phosphide catalysts were analyzed by XRD and are shown in Fig. 2. Mo(50)P(50) contained MoP crystallites with peaks at a high intensity while Mo(60)P(40) contained MoP crystallites with peaks

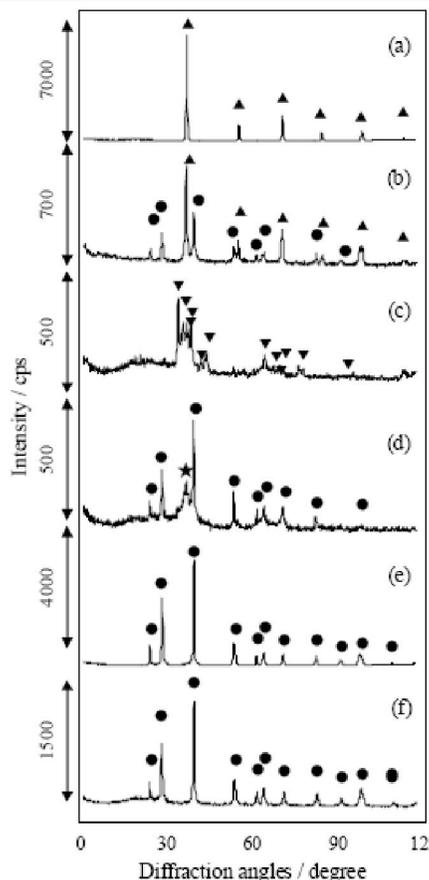


Figure 2 : XRD patterns of 923-K-reduced catalysts with various compositions before the reaction. (a) Mo(100), (b) Mo(70)P(30), (c) Mo(60)P(40), and (d) Mo(50)P(50). (▲) Mo metal, (●) MoP, (▼) Mo₈P₅, and (★) α-species

at a low intensity ranging from 40–42° (★ represents α-species). Mo(70)P(30) contained only Mo₈P₅ crystallites that were different from MoP and Mo metal.

Based on these results, the formation of the MoP crystallites and Mo₈P₅ crystallites lowered the HDS activity of the catalysts during the initial stage. The production of H₂O for the 923 K-reduced Mo(60)P(40) during the TPR for the catalyst preparation is shown in figure 3A. The temperature was increased from (a) 323 K (0 h after the start) to (b) 923 K (1 h), maintained at 923 K for (c) 1 and (d) 3 h, and then decreased to room temperature in flowing hydrogen. The catalysts were studied by XRD analysis. The remaining oxygen of Mo(60)P(40) was scarcely reduced at 923 K for 3 h due to the slight H₂O production and no formation of MoO₂ by the XRD analysis. Figure 3B shows the XRD patterns of the catalysts kept for 8 h. MoO₃ was only observed for the fresh catalyst (a). At 1 and 2 h (b and c) after the start, MoP was observed at 2q=34 and 43° together with MoO₂ at 2q=36.9° instead of MoO₃. An additional 2-h treatment at 923 K (d) increased the MoP intensity and generated new species, which were clearly observed by the peaks of α-species at 2q=

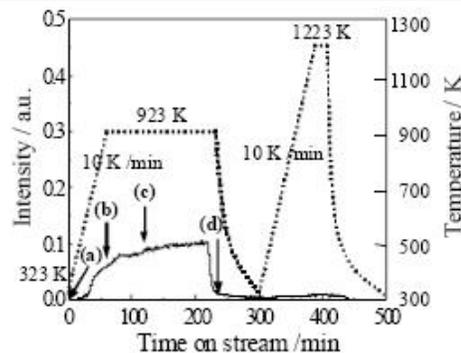


Figure 3(A) : H₂O production during TPR of 923-K-reduced Mo(60)P(40). Solid line represents H₂O desorption and dotted line represents catalyst temperature

37.9, 40.4, and 40.9° which are near metallic Mo. In figure 3B, the crystal growth of Mo metal was not observed despite a simultaneous decrease in the MoO₂ crystallites and an increase in the MoP crystallite formation. Thus, the generated α-species were active species during the initial stage of the HDS reaction and not Mo metal, but metallic Mo formed in the catalyst preparation of MoP by TPR. This species was deactivated to form Mo sulfide during the initial stage of the reaction. Consequently, the high HDS activity of the 923 K-reduced Mo(60)P(40) was probably due to the presence of the metallic Mo in the MoP_{1-x}. Furthermore, the 923 K-reduced Mo(60)P(40) exhibited similar XRD intensities before and after the reaction as shown in figure 3C. The α-species were also observed even 12 h after the reaction at 573 K. These results showed that the α-species did not change during the reaction, suggesting that no XRD analysis results could necessarily elucidate the behavior of the increasing HDS activity during the reaction.

Effect of reduction temperature on activities of Mo(60)P(40) and Mo(50)P(50) catalysts

The influence of the reduction temperature on the activities of Mo(50)P(50) and Mo(60)P(40) during the thiophene HDS is shown in figure 4. The Mo(60)P(40) reduced at 923 K was the most active of all the studied catalysts. The Mo(60)P(40) catalysts reduced at 723, 923, and 1023 K exhibited high HDS activities during the reaction, except for that at 823 K. The 723 K-reduced Mo(50)P(50) catalyst was the second-most-active catalyst while the 823–1023 K-reduced Mo(50)P(50) catalysts were the least active. The XRD patterns of the Mo phosphide catalysts reduced at 723, 823, and 1023 K are shown in figure 5 and at 923 K in figure 2. The 1023 K-reduced Mo(60)P(40) contained MoP crystallite together with metallic Mo, resulting in a high initial activity and significant increase in activity. However, the 1023 K-reduced Mo(50)P(50) consisted of only MoP crystallites, which induced the increase in HDS activity. The active species involved in the increased

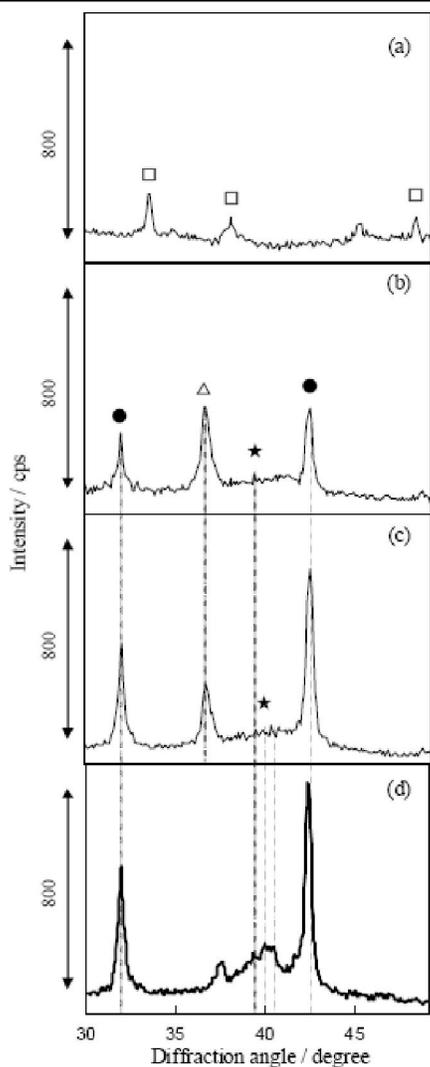


Figure 3(B) : XRD patterns of reduced Mo(60)P(40) catalyst which increased from (a) 323 to (b) 923 K and remained constant at 923 K for (c) 1 and (d) 3 h, and then cooled to room temperature in flowing hydrogen

HDS activity were the MoP crystallites based on the XRD analysis. Furthermore, the 823 K-reduced Mo(50)P(50) and Mo(60)P(40) contained both MoP crystallites and MoO₂, which induced the increase in the HDS activity during the reaction, but they exhibited a lower initial HDS activity due to the absence of the α -species. On the other hand, the IRATs of Mo(50)P(50) and Mo(60)P(40) (TABLE 2) reduced at 823, 923, and 1023 K were greater than unity. Thus, the reduction above 823 K highly promoted the formation of Mo(50)P(50) and Mo(60)P(40) during the reaction. On the other hand, the surface area of the 1023 K-reduced Mo(60)P(40) was 16 m²/g, three times greater than those of the 823 K-reduced Mo(60)P(40) and Mo(50)P(50). The 923 K-reduced Mo(60)P(40) had the second highest surface area (9 m²/g). These high-surface-area catalysts were active for the thiophene HDS, although the active 723 K-reduced Mo(50)P(50) and Mo(60)P(40) catalysts had low surface areas (approximately

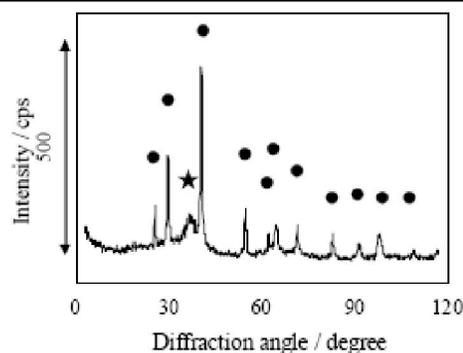


Figure 3(C) : XRD pattern of Mo(60)P(40) reduced 12 h after the reaction at 573 K. (□) MoO₃, (Δ) MoO₂, (●) MoP, and (★) α species

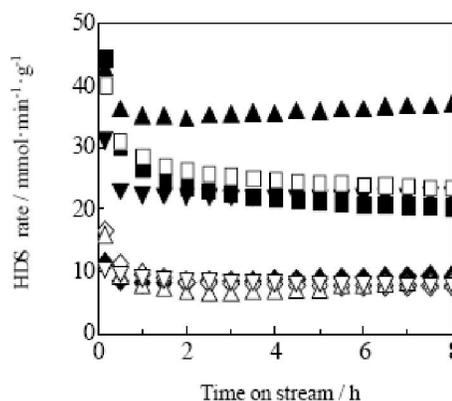


Figure 4 : Thiophene HDS on Mo(50)P(50) and Mo(60)P(40) reduced at various temperatures. Mo(50)P(50): (○) 723, (◇) 823, (Δ) 923, and (∇) 1023 K. Mo(60)P(40): (■) 723, (◆) 823, (▲) 923, and (▼) 1023 K

1 m²/g). Consequently, the surface area of the Mo phosphide did not depend on the HDS activity. Furthermore, the 723 K-reduced Mo(60)P(40) and Mo(50)P(50) contained amorphous Mo phosphoric oxides (reduced MoPO_{x-0.5}) with small amounts of MoO₂ and MoP, as shown in figure 6. Thus, both catalysts exhibited similar high initial HDS activities without increased IRATs during the initial stage of the thiophene HDS.

Surface active species determined by XPS and increased HDS activity during reaction

XPS can elucidate the surface active species of the 723 K-reduced Mo(50)P(50) and Mo(60)P(40) without IRATs, that of the 823 K-reduced Mo(60)P(40) with the low initial HDS rate and high IRAT, and those of the 923-1023 K-reduced Mo(60)P(40) with the high initial HDS rates and high IRATs. The XPS P_{2p} binding energies of Mo(50)P(50) and Mo(60)P(40) before the reaction are shown in Fig. 6. The P_{2p} binding energies at 133.4 and 129.0 eV were due to P⁵⁺ and P⁰, respectively. For the reduction at 823 K, Mo(50)P(50) contained both P⁵⁺ and P⁰, but Mo(60)P(40) contained P⁰. The latter catalyst had a higher IRAT than the former. The 823 K-reduced Mo(50)P(50) and Mo(60)P(40) contained MoO₂ and MoP

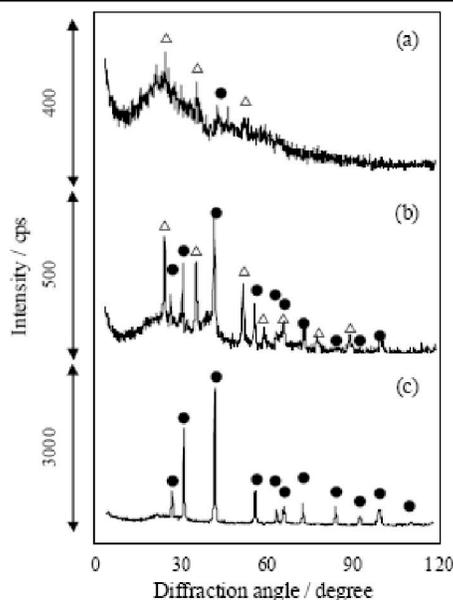


Figure 5(A)

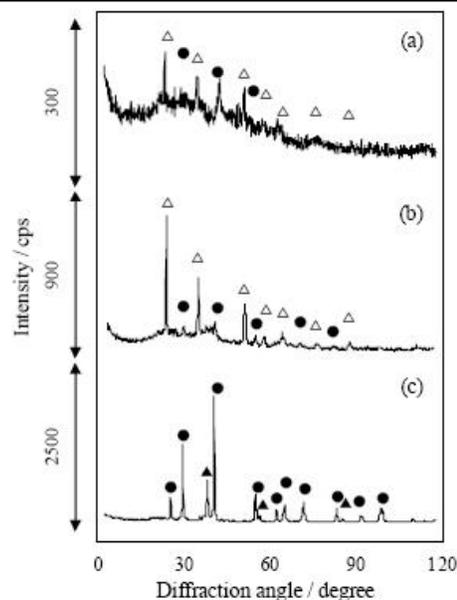


Figure 5(B)

Figure 5 : XRD patterns of (A) Mo(50)P(50) and (B) Mo(60)P(40) reduced at (a) 723, (b) 823, and (c) 1023 K. (Δ) MoO_3 , (\bullet) MoP, and (\blacktriangle) Mo metal

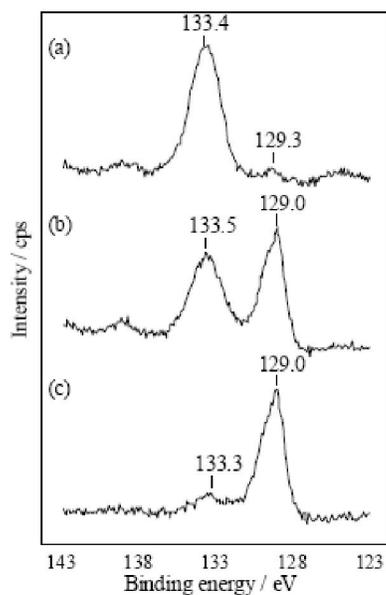


Figure 6(A)

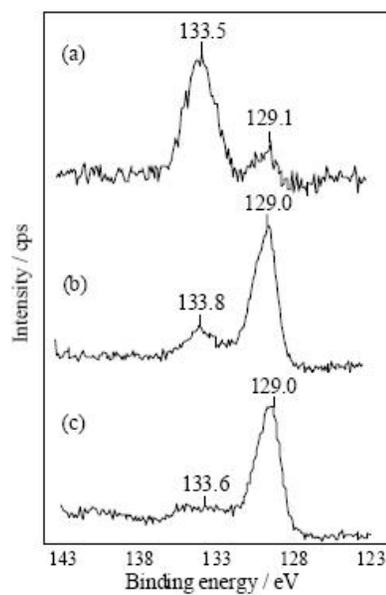


Figure 6(B)

Figure 6 : XPS P_{2p} binding energies of (A) Mo(50)P(50) and (B) Mo(60)P(40) reduced at (a) 723, (b) 823, and (c) 923 K before the reaction

crystallites. The reduction of the catalysts at 923 K formed P^0 species more than that at 823 K, which had a high initial activity and a high IRAT. Furthermore, the 723 K-reduced Mo(50)P(50) and Mo(60)P(40) contained P^{5+} with a small amount of P^0 . P^0 was contained in the deficient phosphorus MoP which is responsible for the increased HDS activity.

The P/Mo, S/Mo, and O/Mo ratios of the catalysts are shown in TABLE 3. For phosphorus, the P/Mo ratios of the 923 K-reduced Mo(50)P(50) (stoichiometric value of 1) and 823 and 923 K-reduced Mo(60)P(40) (0.66)

were 0.89, 0.64, and 0.72 before the reaction, respectively. This result showed the release of phosphorus during the TPR for the catalyst preparation. These results offered no observation of the highly active α -species. However, the P/Mo ratio of the 923 K-reduced Mo(50)P(50) were unchanged (slightly decreased from 0.89 to 0.85) before and after the reaction, but those of the 823 and 923 K-reduced Mo(60)P(40) decreased to 0.52 and 0.67, respectively. This result showed that the phosphorus of MoP crystallites for the catalysts reduced at 823-1023 K is released during the HDS reaction, resulting in the formation of a more deficient phosphorus MoP_{1-x} , i.e., $x=0.33$ for

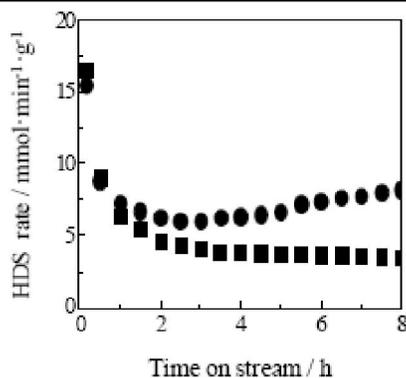
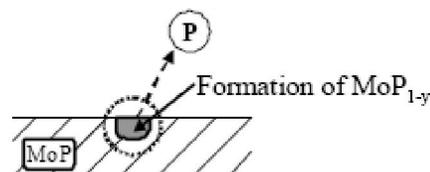
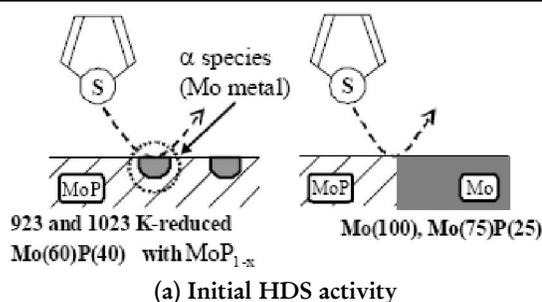


Figure 7 : Thiophene HDS on Mo(50)P(50) catalyst reduced at 923 K in (●) H₂ and subsequently sulfided at 623 K in (■) 10% H₂S/H₂

the 923K-reduced Mo(60)P(40). Furthermore, the S/Mo ratio increased with the increasing reaction time. The S/Mo ratio of the 923 K-reduced Mo(60)P(40) was 0.14 at 8h after the reaction and the catalyst was sulfided (MoS_{0.14}·MoP_{0.67}). However, the order of the increase in the S/Mo ratio (723 K > 923 K > 823 K) did not depend on the HDS activity (923 K > 723 K > 823 K). Sulfidation showed that sulfur, which was incorporated into the catalyst surface to form Mo sulfide or Mo phosphosulfide, was not responsible for the increase in the HDS activity. Phillips et al.^[4] and Oyama et al.^[2,3,5] reported the sulfidation of molybdenum, and Wu et al.^[6] reported the formation of Mo phosphosulfide on the surface of fresh MoP/SiO₂ after the HDS reaction. In addition, the surfaces of the MoP, Ni₃P, and Ni-Mo-P catalysts are partially sulfided while forming a phosphosulfide phase on the surface, but the bulk structures of the phosphides are maintained during the HDS^[10]. The 723 K-reduced catalyst exhibited a higher S/Mo ratio (0.21) than the 923 K-reduced catalyst. Since the P/Mo ratio of the 723 K-reduced catalyst decreased from 0.49 to 0.41 before and after the reaction, the O/Mo ratios were 2.6 and 2.4 before and after the reaction, respectively. The oxygen atoms of MoPO_x in the 723 K-reduced catalyst replaced the sulfur atoms that were removed from thiophene, since the O/Mo ratio of the 923 K-reduced catalyst decreased by 25 % after the sulfidation of the 923 K-reduced Mo(50)P(50) catalyst at a reaction temperature of 623 K. This sulfided/reduced Mo(50)P(50) catalyst was less active than the reduced Mo(50)P(50) catalyst, as shown in figure 7. Stinner et al.^[35] and Jian et al.^[36] reported that the HDN activity of the unsupported Mo phosphide is low in the presence of H₂S due to the blocking of the surface catalytic sites.

The mechanisms of the increase in the HDS activity are shown in figure 8. A phosphorus loss was observed during the activation of Mo(50)P(50) and Mo(60)P(40) reduced at 923 K at 8 h (for Mo(60)P(40) even at 30 h in TABLE 3). The growth of the MoP crystallites in the 923



(b) Increase in HDS activity (IRAT) of Mo(50)P(50) and Mo(60)P(60) reduced at 823-1023 K

Figure 8 : Formation of active species with increase in HDS activity of Mo phosphide during thiophene HDS

K-reduced Mo(50)P(50) was less active than that in the 923 K-reduced Mo(60)P(40). The increase in the HDS activity was due to the presence of the deficient phosphorus of MoP (MoP_{1-x}; x = 0.28 for 923K-reduced Mo(60)P(40)) species during the reduction of the MoP crystallites and the subsequent formation of active MoP_{1-x} during the reaction. The gradual increase in the HDS activity was due to the formation of the active MoP_{1-x} species induced by phosphorus loss during the reaction. Furthermore, the mechanisms of the high initial HDS activity of Mo(60)P(40) is shown in figure 8. The high initial HDS activity of the 923 K-reduced Mo(60)P(40) was due to the formation of metallic Mo (α -species) during the initial step of HDS reaction. The metallic Mo was easily deactivated to form Mo sulfide, but supplied by phosphorus release.

CONCLUSIONS

The high activity of Mo phosphide catalysts during the initial stage and the gradual increase in the HDS activity during the thiophene HDS at 573 K and atmospheric pressure were studied. Mo(60)P(40) consisted of two types of highly active species. (1) The HDS activity during the initial stage of the reaction is due to the presence of metallic Mo on the catalysts reduced on the catalyst preparation. (2) The increase in the HDS activity is due to the formation of the deficient phosphorus MoP (MoP_{1-x}) from the phosphorus loss during the reaction. (3) The sulfidation of the 923 K-reduced Mo(50)P(50) increased neither the gradual increase in the HDS activity nor the increase in IRAT. This result indicated that the formed Mo sulfide or phosphosulfide during the reaction was not active for the gradual increase in the HDS activity.

REFERENCES

- [1] R.Iwamoto, J.Glimblot; *Adv.Catal.*, **44**, 417 (1999).
- [2] W.Li, B.Dhandapani, S.T.Oyama; *Chem.Lett.*, 207 (1998).
- [3] P.A.Clark, X.Wang, S.T.Oyama; *J.Catal.*, **207**, 256 (2002).
- [4] D.C.Phillips, S.J.Sawhill, R.Self, M.E.Bussell; *J.Catal.*, **207**, 266 (2002).
- [5] P.A.Clark, S.T.Oyama; *J.Catal.*, **218**, 78 (2003).
- [6] Z.Wu, F.Sun, W.Wu, Z.Feng, C.Liang, Z.Wei, C.Li; *J.Catal.*, **202**, 41 (2004).
- [7] S.T.Oyama; *J.Catal.*, **216**, 343 (2003).
- [8] M.Jian, R.Prins; *Bull.Soc.Chim.Belg.*, **104**, 231 (1995).
- [9] S.T.Oyama, P.Clark, V.L.S.Teixeira da Silva, E.J.Lede, F.G.Requejo; *J.Phys.Chem.B*, **105**, 4961 (2001).
- [10] F.Sun, W.Wu, Z.Wu, J.Guo, Z.Wei, Y.Yang, Z.Jiang, F.Tian, C.Li; *J.Catal.*, **228**, 298 (2004).
- [11] E.L.Muetterties, J.C.Sauer; *J.Am.Chem.Soc.*, **96**, 3410 (1974).
- [12] E.L.Muetterties, F.J.Hirsekor; *J.Am.Chem.Soc.*, **96**, 4063 (1974).
- [13] A.L.Hector, I.P.Parkin; *J.Mater.Chem.*, **4**, 279 (1994).
- [14] C.Stinner, R.Prins, Th.Weber; *J.Catal.*, **202**, 187 (2001).
- [15] X.Wang, P.Clark, S.T.Oyama; *J.Catal.*, **208**, 321 (2002).
- [16] Y.Brik, M.Kacimi, M.Ziyad, F.Bozon-Verduraz; *J.Catal.*, **202**, 118 (2001).
- [17] F.Nozaki, R.Adachi; *J.Catal.*, **40**, 166 (1975).
- [18] F.Nozaki, T.Kitoh, T.Sodesawa; *J.Catal.*, **62**, 286 (1980).
- [19] F.Nozaki, M.Tokumi; *J.Catal.*, **79**, 207 (1983).
- [20] W.R.A.M.Robinson, J.N.M.Van Gestel, T.I.Koranyi, S.Eijsbouts, A.M.Van der Kraan, J.A.R.Van Veen, V.H.J.de Beer; *J.Catal.*, **161**, 279 (1996).
- [21] S.T.Oyama, X.Wang, Y.K.Lee, K.Bando, F.G.Requejo; *J.Catal.*, **210**, 207 (2002).
- [22] C.Stinner, Z.Tang, M.Haouas, Th.Weber, R.Prins; *J.Catal.*, **208**, 456 (2002).
- [23] S.T.Oyama, X.Wang, F.G.Requejo, T.Sato, Y.Yoshimura; *J.Catal.*, **209**, 1 (2002).
- [24] S.J.Sawhill, D.C.Phillips, M.E.Bussell; *J.Catal.*, **215**, 208 (2003).
- [25] S.T.Oyama, X.Wang, Y.K.Lee, W.J.Chun; *J.Catal.*, **218**, 78 (2003).
- [26] A.L.Agudo, R.L.Cordero, J.M.Palacios, J.L.Fierro; *Bull.Soc.Chim.Belg.*, **104**, 237 (1995).
- [27] F.Nozaki, T.Sekura, M.Kawai; *Chem.Lett.*, 967 (1976).
- [28] P.Clark, X.Wang, P.Deck, S.T.Oyama; *J.Catal.*, **210**, 116 (2002).
- [29] P.Clark, W.Li, S.T.Oyama; *J.Catal.*, **200**, 140 (2001).
- [30] S.T.Oyama, P.Clark, X.Wang, T.Shido, Y.Iwasawa, S.Hayashi, J.M.Ramallo-López, F.G.Requejo; *J.Phys.Chem.B*, **106**, 1913 (2002).
- [31] T.I.Koranyi; *Appl.Catal.A*, **239**, 253 (2003).
- [32] J.N.Balarayu, C.Anandan, K.S.Rajam; *Surf.Coat.Tech.*, **200**, 3675 (2006).
- [33] P.Perez-Romo, C.Potvin, J.M.Manoli, M.M.Chehimi, G.Djega-Mariadassou; *J.Catal.*, **208**, 187 (2002).
- [34] P.Peeters, G.v.d.Hoorn, T.Daenen, A.Kurowski, G.Saikov; *Electrochim.Acta*, **47**, 161 (2001).
- [35] C.Stinner, R.Prins, Th.Weber; *J.Catal.*, **191**, 438 (2002).
- [36] M.Jian, J.L.Ricocerca, R.Prins; *Bull.Soc.Chim.Belg.*, **104**, 225 (1995).