

XPS Study of Nitrided Molybdena/Titania Catalyst for the Hydrodesulfurization of Dibenzothiophene

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Received: June 8, 1999; In Final Form: September 10, 1999

The relationship between the molybdenum species of nitrided Mo/TiO₂ catalysts and the HDS activity of the catalysts was studied by XPS and X-ray diffraction. The HDS of dibenzothiophene was carried out in a fixed-bed microreactor at 573 K and 10.1 MPa of total pressure. The 10.3% MoO₃/TiO₂ catalyst was nitrided by a temperature-programmed reaction with ammonia at 4 L h⁻¹ at various temperatures. The 1023 K nitrided catalyst held the highest TOF (based on CO adsorption). From XPS analysis, it was found that the 1023 K nitrided molybdenum catalyst was significantly difficult to sulfide the surface molybdenum species of the nitrided catalyst. The 773 K nitrided catalyst had more sulfur accumulation and less nitrogen release than the 1023 K nitrided catalyst. For the Mo/TiO₂ nitrided above 973 K, titania was reduced and nitrided to form TiO and TiN but was not transformed to rutile. The molybdenum oxidation states of the nitrided Mo/TiO₂ catalysts decreased with increasing nitriding temperature, and Mo²⁺ and Mo⁰ ions are predominant on the surface of the 1023 K nitrided catalyst. The Mo²⁺ and Mo⁰ ions were the most active for the HDS of dibenzothiophene.

Introduction

An increasing interest has developed in exploring the catalytic properties of molybdenum nitrides and carbides. Unsupported molybdenum nitride has been reported to exhibit high activities for hydrodesulfurization (HDS),^{1–4} compared to the catalytic properties of Co–Mo and Ni–Mo catalysts. Recently, Sajkowski and Oyama¹ found unsupported Mo₂N to be nearly twice as active as the commercial Ni–Mo/Al₂O₃ catalyst on the basis of Mo atoms measured by CO chemisorption for the HDS of coal-derived feed. Recently, the nitrided molybdena/alumina has been applied to the HDS of thiophene and dibenzothiophene as a catalyst.^{5–8} Nagai and co-workers^{7,8} reported the nitrided Mo/Al₂O₃ catalyst to be 1.1–1.2 times more active than a sulfided Mo/Al₂O₃ catalyst in the HDS of dibenzothiophene and to be extremely selective in the C–S hydrogenolysis of dibenzothiophene to form biphenyl. Furthermore, the alumina-supported molybdenum nitrided catalyst was more active than the sulfided CoMo/Al₂O₃ catalyst for the HDS's of thiophene and benzothiophene on the basis of an oxygen chemisorption. Bussell and co-workers^{5,6} found that turnover frequency (TOF) of the nitrided Mo/Al₂O₃ catalysts was essentially identical to that of the sulfided Mo/Al₂O₃ catalysts during the reaction based on adsorbed CO and O₂, since a thin layer of highly dispersed molybdenum sulfide was present on the surface of the nitride particles. With respect to the effect of support on the HDS activity of molybdenum sulfides, titania-supported molybdenum sulfide catalysts are reported to be more active than alumina-supported catalysts in the HDS's of thiophene and dibenzothiophene by many researchers.^{9–14} For characterization, the XPS analysis provides the distribution of molybdenum oxidation

states of the reduced and sulfided Mo/TiO₂¹⁵ and Mo/Al₂O₃^{16–19} and results in the correlation between the HDS activity and the molybdenum species on the surface of the catalysts. The molybdenum ions with an oxidation state of 2+ are reported to be the most active species in benzene hydrogenation on reduced Mo/TiO₂¹⁵ and Mo/Al₂O₃¹⁶ catalysts and in thiophene HDS on sulfided Mo/SiO₂ catalysts.¹⁷ However, for titania-supported molybdenum nitrides, there are few reports on catalytic activity of nitrided catalysts for HDS reactions. It has not yet been understood what molybdenum species of molybdenum nitrides generated by the nitriding temperature is the oxidation state responsible for the HDS reaction. The objectives of this paper were to produce molybdenum species on the surface of the 10.3% Mo/TiO₂ catalysts with molybdenum oxidation states between 6+ and 0, to treat the oxide forms with ammonia at various temperatures to quantitatively determine the distribution of these oxidation states, and to correlate the results with dibenzothiophene HDS measurement.

Experimental Section

Materials and Preparation of Nitrided Catalyst. Hydrogen (99.999%) was dried by passing it through a Deoxo unit (SUPELCO Co. Oxsorb) and a Linde 13X molecular sieve trap prior to use. Ammonia (99.999%) and dibenzothiophene (99.9%) were used without further purification. Xylene (mixed o-, m-, and p-xylene, extra pure; specific gravity 0.86) was used as a solvent for activity measurement. TiO₂ was provided by the Catalysis Society of Japan (JRC-TIO-1): powder, TiO₂, 95.0%, SiO₂, 3.64%, surface area 72.6 m² g⁻¹. A 10.3% MoO₃/TiO₂ was prepared by addition of ammonium heptamolybdate dissolved in aqueous ammonia solution into titania by an incipient wetness method. The solid product was molded to granules of 0.85–1.70 mm for activity measurement, then dried at 473 K for 3 h, calcined at 773 K for 12 h in air, and ground below 200 mesh to a powder consistency for characterization

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of the catalysts. The microreactor was constructed of a quartz tube (11 mm i.d.) having a total volume of 2.4 mL. The catalyst was held in place with a fretted ceramic disk. The microreactor was externally heated, using an oven connected to a variable temperature programmer with a chromel–alumel thermocouple, positioned outside the reactor near the catalyst bed to monitor the temperature and provide feedback to the PID temperature programmer. A separate thermocouple was placed in the center of the catalyst bed for measuring the catalyst temperature. The 10.3% MoO₃/TiO₂ catalyst was treated with ammonia at 49.6 $\mu\text{mol s}^{-1}$ from 573 K to the desired temperature at a rate of 0.0167 K s⁻¹ and held at this temperature for 3 h. After the NH₃ treatment, the catalyst was cooled to room temperature in flowing ammonia. The space velocity of ammonia was 5096 h⁻¹ with a flow rate of 49.6 $\mu\text{mol s}^{-1}$. The nitrided catalysts were removed from the pretreatment reactor using a glovebag filled in argon without exposure to air for the measurements of XPS, CO adsorption, and the catalyst activity for dibenzothiophene HDS.

Characterization. The surface compositions of the molybdenum atoms in the catalysts were measured using a Shimadzu ESCA3200 spectrometer with monochromatic Mg K α exciting radiation (8 kV, 30 mA) at a pressure of 5×10^{-4} Pa. The values of the binding energy for the catalysts were referenced to C 1s at 284.6 ± 0.2 eV, which was checked against the Ag 3d_{5/2} line at 368.0 eV. The peaks of the XPS binding energy of Mo 3d_{3/2} and Mo 3d_{5/2} were deconvoluted to check the validity of various distributions with the χ^2 test using Kratos software installed in Shimadzu EA3200, with an intensity ratio of ²/₃ and a splitting of 3.2 eV for the Mo 3d_{3/2} and Mo 3d_{5/2} lines.^{4,15–18} The Mo 3d spectra were fitted into five sets of Mo doublets (Mo 3d_{3/2} and 3d_{5/2}) corresponding to five different molybdenum species (Mo⁶⁺, Mo⁵⁺, Mo⁴⁺, Mo²⁺, and Mo⁰). The experimental procedure consisted of removing the catalysts from the reactor after nitriding and transferring them in a glovebag without exposure to air. The glovebag was pumped and backfilled with purified argon three times before the catalysts were transferred to the ESCA prechamber. No argon etching was done in the XPS measurement. Powder X-ray diffraction analysis was performed with Ni-filtered Cu K α radiation ($\lambda = 0.15418$ nm) with a Rigaku X-ray diffractometer operating at a scanning speed of 2° min⁻¹ from $2\theta = 5^\circ$ to 120°. Patterns were identified by comparison to the following JCPD standards: anatase, rutile, and TiN. The quantity of CO chemisorbed on the surface of the catalysts was determined by a volumetric analyzer in evacuation (Beckman Coulter Co., Omnisorp 100CX). The nitrided catalyst (0.2 g) was packed into a BET measurement cell in a glovebag in argon atmosphere. Before measuring the CO uptake, the catalyst (0.2 g) was first pretreated in flowing helium at 723 K for 2 h and reduced in hydrogen at 653 K for 2 h. After the reduction, the catalyst was degassed at 10⁻² Pa and at 673 K for 1 h and then slowly cooled to room temperature in a vacuum. The amount of irreversible CO uptake was obtained from the difference between the two CO isotherms which were extrapolated to zero pressure. The specific BET surface area of the catalysts was measured by nitrogen adsorption using a standard volumetric BET apparatus (Omnisorp 100CX) after the catalysts were evacuated at 473 K and 0.1 Pa for 2 h. The molybdenum content for the prepared catalysts was measured by atomic absorption spectroscopy (Shimadzu AA-630-1). The catalysts were dissolved in aqua regia (HCl/HNO₃ = 3:1) before use in the spectrometer.

Activity Measurement. The activity of the nitrided catalyst for the HDS of dibenzothiophene was measured using a

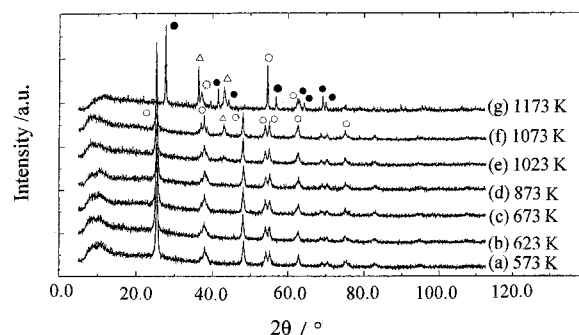


Figure 1. XRD analysis of 10.3% Mo/TiO₂ nitrided at (a) 573, (b) 623, (c) 673, (d) 873, (e) 1023, (f) 1073, and (g) 1173 K in a flow of ammonia: (○) anatase; (●) rutile; (Δ) TiN.

microreactor in a high-pressure flow system described elsewhere.²⁰ The reactor, a 325 mm long stainless steel tube of 17.3 mm o.d. and 3.2 mm thickness, was connected upward to a hydrogen gas cylinder and high-pressure feeder pump and downward to a gas–liquid separator. Without exposure to air, 1.0 g of the granular catalyst was packed in the reactor, heated at 773 K with hydrogen for 1 h, and then cooled to the reaction temperature before the reaction. The liquid feed, consisting of 13.6 mmol L⁻¹ dibenzothiophene in xylene, was introduced into the reactor at 5.56 $\mu\text{L s}^{-1}$ with a hydrogen flow of 48.2 $\mu\text{mol s}^{-1}$ and a total pressure of 10.1 MPa. The hourly liquid space velocity was 10 h⁻¹, and the molar ratio of hydrogen to dibenzothiophene was 986. The liquid products were separated from gaseous products such as hydrogen, ammonia, and other reaction products having boiling points lower than the xylene solvent in a high-pressure gas–liquid separator. The liquid reaction products were quantitatively analyzed using an FID gas chromatograph with a 2% silicone OV-17 column. The HDS rate was calculated based on moles of dibenzothiophene converted in dibenzothiophene HDS on the catalysts at 573 K. The turnover frequency was expressed as moles of dibenzothiophene converted per second and per moles of irreversible CO adsorbed at room temperature.

Results and Discussion

X-ray Diffraction and BET Surface Area. The effect of various nitriding temperatures on the crystal structure of the compounds obtained from the XRD data is shown in Figure 1. The formation of TiN is confirmed above 1023 K, but TiN begins to form at 1073 K. At 1173 K the predominant crystal structure is rutile, but no transformation of anatase to rutile was observed at temperatures lower than 1073 K. However, for the 5% Mo/TiO₂ reduced with hydrogen at 725 K,¹⁵ the composition of anatase(200)/rutile(111), measured by reflections at 48.1° and 41.2°, respectively, was about 73%, and at reducing temperature of 873 K, the composition was still about 20%. Thus, it is evident that nitriding of molybdenum compounds with ammonia inhibits the transformation of anatase to rutile compared to reducing with hydrogen. Furthermore, no molybdenum compounds were observed by XRD analysis under the nitriding conditions in this study.²¹ Figure 2 shows a plot of BET surface area versus nitriding temperature for the 10.3% Mo/TiO₂. The surface area of the nitride catalysts was constant below 873 K but slightly decreased above 973 K without observation of the transformation of anatase to rutile. When TiO₂ without molybdenum was nitrided with ammonia, TiN (200) was detected for TiO₂ nitrided above 973 K but was not observed below 873 K. Thus, the TiO₂ support of 10.3% Mo/TiO₂ catalyst was nitrided above 973 K together with formation of molybdenum nitride

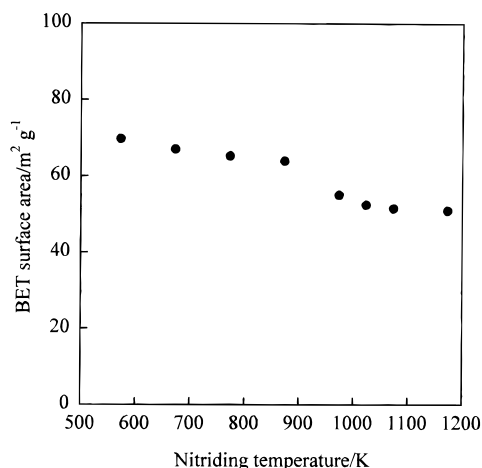


Figure 2. BET surface area as a function of nitriding temperature.

TABLE 1: XPS Atomic Ratios of 10.3% Mo/TiO₂ Catalysts Nitrided at Various Temperatures

catalyst nitriding temp/K	Mo/Ti ^a	N/Ti ^b	N/Ti ^c	S/Mo ^d	S/Ti ^d	C/Ti ^d
773	0.362	1.70	0.273	0.305	0.120	1.13
873	0.384	1.55	0.201	0.146	0.078	1.72
973	0.287	2.42	0.860	0.183	0.064	2.93
1023	0.317	3.13	1.09	0.108	0.041	4.78
1073	0.292	3.24	1.17	0	0	2.29

^a XPS Mo 3d and Ti 2p spectra were determined before reaction.

^b XPS N 1s and Ti 2p spectra were determined before reaction. ^c The difference in the atomic ratios of (N 1s + Mo 3p)/Mo 3d and (N 1s + Mo 3p)/Ti 2p before and after the HDS reaction, since N 1s was overlapped with Mo 3p spectra. ^d XPS S 2p, Mo 3d, Ti 2p, and C 1s spectra were determined after reaction at 12 h.

crystalline detected by XRD, and therefore the surface area slightly decreased above the nitriding temperature of 973 K. Since anatase was transformed to rutile at nitriding temperature of 1173 K, the XPS and activity measurements were performed for the 10.3% Mo/TiO₂ nitrided below 1073 K.

Surface Species by XPS. The XPS Mo 3d/Ti 2p atomic ratio for various nitriding temperature is shown in Table 1. A decrease in Mo/Ti atomic ratio is observed roughly with increasing nitriding temperature from 773 to 1073 K but not with a rapid increase. This can be attributed to particle growth of molybdenum nitride and not to changes in morphology of the surface molybdenum species upon nitridation. This is in disagreement with the decrease of the TiO₂ surface area of Mo/TiO₂ catalyst with a sharp increase in Mo/Ti ratio observed in the range 873–923 K in hydrogen reduction.¹⁵ Therefore, nitriding of Mo/TiO₂ with ammonia caused less sintering of TiO₂ than hydrogen reduction even at nitriding temperature of 1073 K. Figure 3 shows the binding energies of the XPS Ti 2p_{3/2} spectra for the 10.3% Mo/TiO₂ catalysts nitrided at various temperatures. The Ti 2p_{3/2} peak for TiO₂ in the oxidic form is characteristic of Ti⁴⁺.^{15,25–27} The shape of the Ti 2p_{3/2} peak for the 10.3% Mo/TiO₂ after nitriding is centered at 458.7 eV and identical with that of 100% oxidic TiO₂ at nitriding temperatures of 773 and 873 K. Furthermore, the Ti 2p_{3/2} peak position for the TiO₂ species of the Mo/TiO₂ catalysts nitrided at 773 and 873 K is centered sharply at 458.7 eV (Ti⁴⁺, 458.7 eV)^{15,27} (Table 2). Furthermore, for the 973–1073 K nitrided 10.3% Mo/TiO₂, the binding energies of the Ti 2p_{3/2} line were determined to be 456.7 and 454.8 eV, in good agreement with the number obtained in an extensive XPS study of Ti³⁺ species (456.7 eV)^{15,27} and TiN (454.8 eV;²⁵ Ti²⁺, 454.5 eV^{26,27}). Therefore, titania was nitrided to some degree at temperatures above 973 K, in agreement with

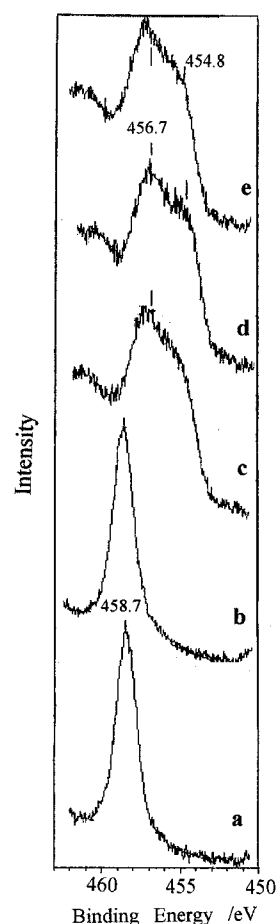


Figure 3. XPS Ti 2p spectra for 10.3% Mo/TiO₂ nitrided at (a) 773, (b) 873, (c) 973, (d) 1023, and (e) 1073 K.

TABLE 2: XPS Binding Energies of Mo 3d_{5/2}, Mo 3p_{3/2}, N 1s, and Ti 2p_{3/2} Derived from Other Literatures

Mo, Ni, Ti species binding energy/eV						literature
Ti 2p _{3/2}	Ti ⁴⁺ 458.7	Ti ³⁺ 456.7	TiN 454.8	Ti ²⁺ 454.5		15, 27, this work 25, this work 26, 27
N 1s	Ti–N		396.7 396.9			26 25
	Mo–N		398.1 397.4			29, 31 24
Mo 3d _{5/2}	Mo ²⁺ 228.2 228.5		Mo ^{δ+} 228.5 228.5	Mo ⁰ 227.6 227.6 227.8		15, this work 33 34 4
Mo 3p _{3/2}	Mo ⁶⁺ 399.4	Mo ⁵⁺ 398.3 398.3	Mo ⁴⁺ 396.3 396.3 365.8	Mo ²⁺ 393.6	Mo ⁰ 393.6	22, 28–30 8 this work

the result obtained by XRD analysis described before. The region of XPS N 1s for the nitrided 10.3% Mo/TiO₂ catalysts before the reaction contained several peaks of N 1s and Mo 3p binding energies at 398.1, 396.7, and 394.4 eV for the 773 and 873 K nitrided catalysts and 397.8 and 395.8 eV for the 973–1073 K nitrided catalysts as shown in Figure 4. The Mo 3p_{3/2} spectra in the range 399–394 eV overlapped with the N 1s spectra of several molybdenum states (Table 2): Mo⁶⁺ (399.4 eV); Mo⁵⁺ (398.3 eV); Mo⁴⁺ (396.3 eV); Mo⁰ (393.6 eV).^{22,28–30} For the 773 and 873 K nitrided catalysts, the XPS N 1s spectra are reported to have binding energies of 396.7²⁶ and 396.9 eV²⁵

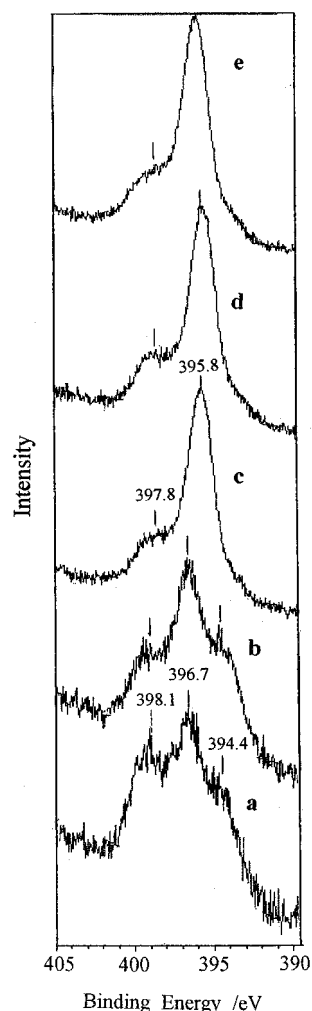


Figure 4. XPS N 1s and Mo 3p spectra for the 10.3% Mo/TiO₂ catalysts nitrided with ammonia at (a) 773, (b) 873, (c) 973, (d) 1023, and (e) 1073 K.

for Ti–N and 398.1^{29,31} and 397.4 eV²⁴ for Mo–N. The peak at 398.1 eV is reported to be assigned to nitrogen atoms trapped in the grain boundary of molybdenum nitride.³¹ Also, the peaks at 398.3 and 396.3 eV are due to Mo 3p_{3/2} (Mo⁵⁺ and Mo⁴⁺).²⁸ The peaks higher than 398.8 eV were also assigned to the N 1s levels of NH₃ adsorbed on the surface Lewis sites of an Al–ZSM-5 zeolite.³² The strong XPS peak at 395.8 eV for the 973–1073 K nitrided catalysts and the shoulder peak at 394.4 eV for the 773 and 873 K nitrided catalysts were probably due to Mo^{δ+} ions (Mo³⁺ and Mo²⁺) of Mo 3p_{3/2}. Therefore, molybdenum trioxide was reduced to the reduced ions such as Mo⁴⁺, Mo²⁺, and Mo⁰ ions by nitriding pretreatment higher than 973 K. Furthermore, the atomic ratio of N 1s/Ti 2p before the reaction increased with increasing nitriding temperature as shown in Table 1, although the N 1s peak overlapped with the Mo 3p peak. This suggested that the 1073 K nitrided catalyst contained much more nitrogen than the catalysts nitrided at lower temperatures.

The binding energies of the XPS Mo 3d_{5/2} and 3d_{3/2} lines for the 10.3% Mo/TiO₂ catalysts nitrided at various temperatures before the reaction are shown in Figure 5. These molybdenum species on titania and alumina were assigned to the binding energies in the references.^{4,15,16,19,33,34} The spectra for the 10.3% Mo/TiO₂ catalysts were fitted into five doublets, with Mo 3d_{5/2} binding energies values lower than 232.7 eV for Mo⁶⁺ and values higher than 227.6 eV for Mo⁰ on the reduced Mo/TiO₂

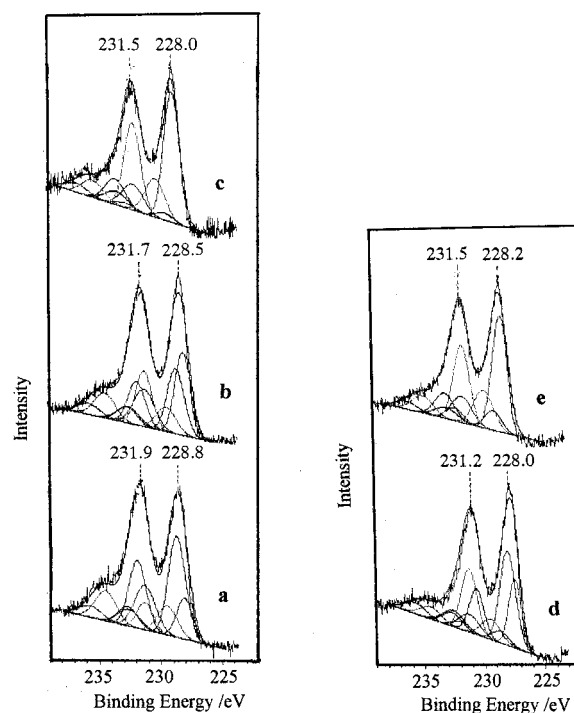


Figure 5. XPS Mo 3d spectra for the 10.3% Mo/TiO₂ catalysts nitrided with ammonia at (a) 773, (b) 873, (c) 973, (d) 1023, and (e) 1073 K.

TABLE 3: XPS Parameters Derived from Curve Fitting the Mo 3d Envelope for the Series of Nitrided 10.3% Mo/TiO₂ Catalysts

Mo species	binding energy/eV		fwhm ^a /eV	
	Mo 3d _{3/2}	Mo 3d _{5/2}	Mo 3d _{3/2}	Mo 3d _{5/2}
Mo ⁶⁺	235.9	232.7	2.07	2.07
Mo ⁵⁺	234.6	231.4	1.98	1.98
Mo ⁴⁺	232.8	229.6	1.87	1.87
Mo ³⁺	232.0	228.8	1.63	1.63
Mo ²⁺	231.4	228.2	1.53	1.53
Mo ⁰⁺	230.8	227.6	1.41	1.23

^a Full width at half-maximum.

catalysts. The molybdenum oxidation states of the molybdenum species were assigned to the binding energies for Mo⁶⁺ (Mo 3d_{5/2} binding energy, 232.7 eV; full width at half-maximum (fwhm), 2.07 eV), Mo⁵⁺ (231.4, 1.98 eV), Mo⁴⁺ (229.6, 1.87 eV), Mo³⁺ (228.8, 1.63 eV), Mo²⁺ (228.2, 1.53 eV), and Mo⁰ (227.6, 1.23 eV) (Table 2), according to the XPS data obtained by Quincy et al.¹⁵ for 5% Mo/TiO₂ reduced in hydrogen. Yamada et al.¹⁶ also reported the same assignment of the XPS binding energies of Mo 3d_{3/2,5/2} line with slightly different fwhms. Table 3 lists the parameters derived from curve fitting the Mo 3d envelope for all treatments. The Mo 3d_{5/2} spectra of 227.6 and 228.2 eV need to be identified (Table 2). Thompson and co-workers³⁴ assigned the Mo 3d_{5/2} binding energies of 227.8 and 228.5 eV levels that they observed in the XPS spectra of the molybdenum nitrides to molybdenum metal and nitride (δ⁺), respectively, indicating that Mo^{δ+} is a molybdenum atom of molybdenum nitride (δ⁺, probably 2+). Ozkan et al.⁴ assigned the peak at 228.5 eV to Mo^{δ+} with δ < 4, corresponding to a molybdenum phase with a lower nitrogen coordination for the nitrided Mo/Al₂O₃. They suggested that the binding energy of Mo 3d_{5/2} of 227.6 eV would be added as Mo⁰ to the binding energies of the molybdenum species for a good curve-fitting of the XPS Mo 3d spectra. McGarvey and Kasztelan¹⁹ reported that the additional peak found in their work was viewed as an indication of the presence of reduced molybdenum species

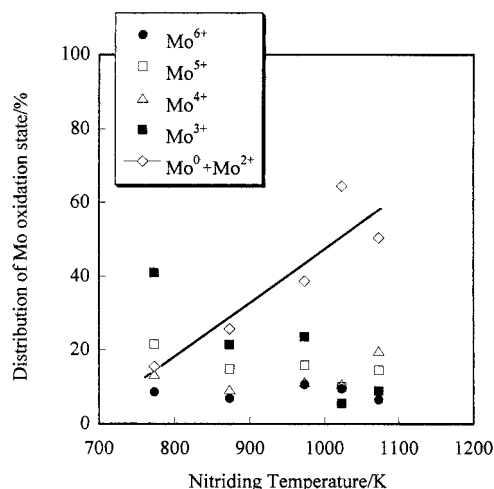


Figure 6. Distribution of the molybdenum oxidation state of the 10.3% Mo/TiO₂ catalysts generated by NH₃ treatment at various temperatures.

with oxidation numbers lower than 4+, symbolized by Mo^{δ+}. Goldwasser et al.³³ reported that the XPS binding energies of Mo 3d_{5/2} at 227.6 and 228.5 (or 228.9) eV were assigned to Mo⁰ and Mo²⁺, respectively, for Mo(CO)₆ on alumina dehydrogenated at 773 and 1173 K in flowing helium. Thus, although the Mo 3d_{5/2} molybdenum signals at 227.6 and 228.5 eV were attributed to Mo⁰ and Mo²⁺, respectively, the total abundance of Mo⁰ and Mo²⁺ ions would be represented instead of the individual Mo⁰ and Mo²⁺ ions in the relationship between the activity and molybdenum oxidation state as mentioned later. The distribution of the molybdenum oxidation state of the catalysts as a function of nitriding temperature is shown in Figure 6. The relative abundance of each molybdenum oxidation state was calculated by dividing the Mo 3d/Ti 2p atomic ratio for a given molybdenum oxidation state by the total area of the Mo 3d/Ti 2p atomic ratio. The percentage of Mo⁶⁺ was low at 773 K but was still detected at 1073 K. The relative abundance of Mo⁴⁺ and Mo⁵⁺ gradually decreased with increasing nitriding temperature. There was a significant decrease of Mo³⁺ with increasing nitriding temperature. The abundance of Mo²⁺ plus Mo⁰ appeared at 773 and increased proportionally with nitriding temperature, reaching a maximum of ca. 60% at 1073 K. For the 5% Mo/TiO₂ catalyst,¹⁵ 50% of the catalyst was reported to be Mo⁰ and Mo²⁺ in the hydrogen reduction at 823 K and Mo⁰ was 90% at 923 K. Thus, the Mo/TiO₂ reduced with hydrogen held lower valence molybdenum atoms than the Mo/TiO₂ nitrided with ammonia at the same treatment temperature. This is probably due to nitridation with ammonia of the titania-supported molybdenum oxides. This does not exceed reduction of molybdenum species but to stabilize the reduced and nitrided molybdenum species on the surface of the catalysts. Moreover, Nakamura and Redey and co-workers^{35,36} reported the distribution of the Mo oxidation state of the Mo/Al₂O₃ in the reduction with hydrogen, in measurement of the average oxidation numbers of molybdenum by titration with oxygen at 773 K. The average molybdenum oxidation state for the Mo/Al₂O₃ catalysts prepared by impregnating Mo(CO)₆ onto alumina decreased to only 2+ in the reduction with hydrogen at 923 K and reached zero at 1073–1223 K.³⁵ Also, the average molybdenum oxidation state was 1.3 after reduction in hydrogen at 1073 K and 0.9 after reduction in hydrogen at 1173 K for the 8% Mo/Al₂O₃ catalysts with metallic molybdenum evidently present.³⁶ Thus, nitriding of the 10.3 Mo/TiO₂ catalyst with ammonia gently reduced molybdenum species from Mo⁶⁺ to Mo²⁺ and Mo⁰ even at 1073 K and stabilized low valence states

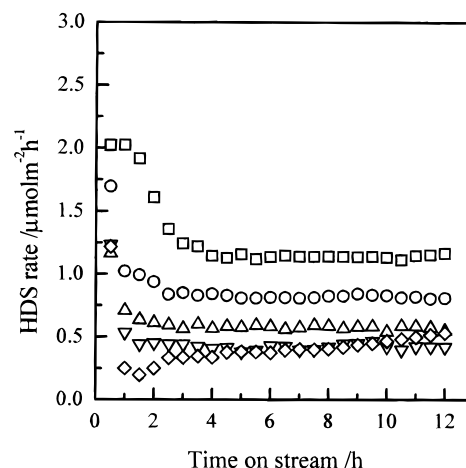


Figure 7. Hydrodesulfurization of dibenzothiophene over the catalysts nitrided at various temperatures with time on stream at 573 K and a total pressure of 10.1 MPa: (□) 773; (○) 873; (△) 973; (▽) 1023; (◇) 1073 K.

on the surface of the catalyst compared to the Mo/TiO₂ catalysts reduced with hydrogen.

Sulfur accumulation on the aged catalyst after the HDS reaction was analyzed by the XPS spectra of S 2p.^{17,22,37,38} The weak binding energies of the XPS S 2p spectra were observed at 162.8 and 162.0 eV for the 773 K nitrided 10.3% Mo/TiO₂ catalysts. The peaks at 162.8 and 162.0 eV are reported to be assigned to disulfide (S₂²⁻) (163.1 and 162.9 eV³⁷) and sulfide (S²⁻) (161.5¹⁷ and 161.8 eV^{37,38}), respectively. Molybdenum sulfide and disulfide are formed on the nitrided catalysts after the 12 h run in dibenzothiophene HDS. From Table 1, the atomic ratio of S 2p/Mo 3d for the nitrided catalysts decreased with increasing nitriding temperature. The 1023 K nitrided catalyst had less sulfur accumulation than the 773 K nitrided catalyst. This result showed that it was difficult to sulfide the catalyst in nitriding treatment at higher temperatures.

HDS of Dibenzothiophene. The rate of the HDS of dibenzothiophene over the 10.3% Mo/TiO₂ nitrided at various temperatures with time on stream at 573 K and a total pressure of 10.1 MPa is shown in Figure 7. The HDS rate for the 773 K nitrided catalyst was 1.94 μmol m⁻² h⁻¹ at 0.5 h (Table 4) after the start of a run, decreased to 1.23 μmol m⁻² h⁻¹ after 3 h, and reached the HDS rate of 1.13 μmol m⁻² h⁻¹ after 4 h (almost the same rate at 12 h). The other nitrided catalysts have the same deactivation trend during the reaction. The 773 K nitrided catalyst had the highest rate for dibenzothiophene HDS based on catalyst surface area and also had the greatest S 2p/Mo 3d atomic ratio of the spent catalyst in Table 1. Consequently, more sulfur species were removed and accumulated on the nitrided catalyst. The distribution of the reaction products in dibenzothiophene HDS on the 773 K nitrided catalyst is shown in Figure 8. The major products desulfurized during the reaction were biphenyl and cyclohexylbenzene. The hydrogenated compounds, tetrahydro- and hexahydrodibenzothiophene, were produced in small amounts. The concentration of biphenyl formed over the nitride catalyst was 8.4 mmol L⁻¹ 2 h after the start of the run and decreased to 63% of this initial concentration after 12 h. Dibenzothiophene disappeared up to 1.5 h, but the concentration of dibenzothiophene gradually increased and reached steady state value after 4 h. The hydrogenated compounds were observed below 1% of all the reaction products for the 773 K nitrided catalyst after 2 and 6 h, respectively. This is because the hydrogenated compounds from the hydrogenation of dibenzothiophene was strongly adsorbed and

TABLE 4: CO Adsorption and Catalytic Activity of the Mo/TiO₂ Catalysts for the HDS of Dibenzothiophene at 573 K

catalyst nitriding temp K	surface area ^a m ² g ⁻¹	HDS rate ^b μmol h ⁻¹ m ⁻²	desulfurization selectivity ^c	CO total μmol g ⁻¹	CO irreversible		TOF ^d h ⁻¹
					μmol g ⁻¹	10 ¹² atoms cm ⁻²	
773	65	1.94	85.1	59.3	15.2	14.1	8.3
873	64	1.69	34.6	45.8	6.14	5.78	17.6
973	55	1.18	16.1	38.0	3.32	3.63	19.5
1023	53	1.22	10.1	13.8	1.33	1.51	48.5
1073	52	1.22	1.8	37.6	2.45	2.84	25.9

^a Evacuated at 473 K and at 1 Pa. ^b HDS rate was calculated based on moles of dibenzothiophene converted in dibenzothiophene HDS on the catalysts at 573 K and at 0.5 h. ^c Molar ratio of biphenyl to tetrahydrodibenzothiophene at 12 h after time on stream. ^d TOF was expressed as moles of dibenzothiophene converted per hour and per moles of irreversible CO adsorbed at room temperature.

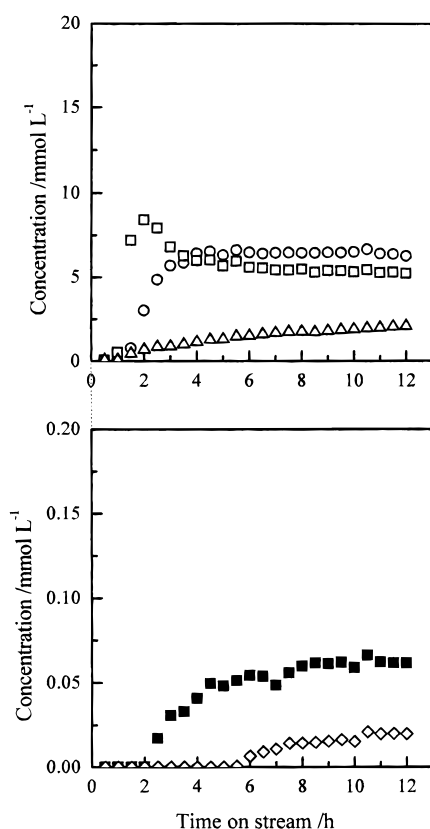


Figure 8. Reaction products in the HDS of dibenzothiophene on the 10.3% Mo/TiO₂ catalyst nitrided at 773 K with time on stream at 573 K and total pressure of 10.1 MPa: (□) biphenyl; (Δ) cyclohexylbenzene; (○) dibenzothiophene; (■) tetrahydrodibenzothiophene; (◇) hexahydrodibenzothiophene.

desulfurized to form cyclohexylbenzene without desorption into the gas phase.

The effect of biphenyl addition on dibenzothiophene HDS on the 773 K nitrided Mo/TiO₂ catalyst was studied to determine whether biphenyl was hydrogenated to form cyclohexylbenzene in the presence of dibenzothiophene at the initial stage of the reaction (Figure 9). When 5.3 mmol L⁻¹ of biphenyl was added to the xylene solution of 14.2 mmol L⁻¹ dibenzothiophene at 573 K, the amount of biphenyl increased by the same amount added. No cyclohexylbenzene increased during the period of biphenyl addition. From the result, biphenyl is not hydrogenated to form cyclohexylbenzene at 573 K during the HDS of dibenzothiophene. Furthermore, there was no increase in tetrahydro- and hexahydrodibenzothiophene during the reaction. The concentration of biphenyl was at maximum at 1–2 h after the start of the reaction, but the material balance was significantly low. It suggested that the reaction products were decomposed to lightweight compounds at a boiling point lower

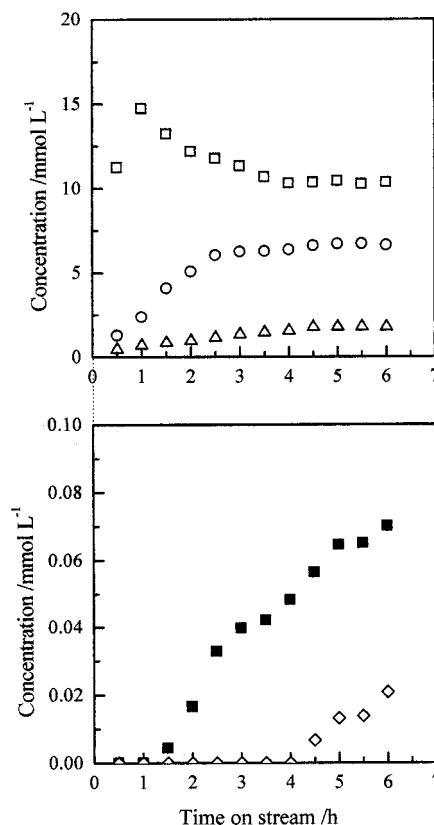


Figure 9. Addition of biphenyl to dibenzothiophene HDS and the hydrogenation of biphenyl in the absence of dibenzothiophene on the 773 K nitrided Mo/TiO₂ catalyst at 573 K: (□) biphenyl; (Δ) cyclohexylbenzene; (○) dibenzothiophene; (■) tetrahydrodibenzothiophene; (◇) hexahydrodibenzothiophene.

than that of xylene solvent in the initial stage of the reaction. In previous papers,^{7,8} the additive effect of biphenyl on the HDS of dibenzothiophene on the nitrided Mo/Al₂O₃ catalysts showed the same observation that biphenyl was not hydrogenated to form cyclohexylbenzene in the presence of dibenzothiophene. The nitrided catalysts have a high C–S hydrogenolysis selectivity of dibenzothiophene rather than the hydrogenation. The reaction scheme for the HDS of dibenzothiophene on the nitrided Mo/TiO₂ catalyst is shown in Figure 10. The HDS of dibenzothiophene (A) proceeds via a parallel reaction involving the selective C–S hydrogenolysis of dibenzothiophene to form biphenyl (B) and the C–S bond scission of hexahydrodibenzothiophene (D) to form cyclohexylbenzene (E) through a successive hydrogenation of dibenzothiophene to tetrahydrodibenzothiophene (C). The molar ratio of biphenyl to tetrahydrodibenzothiophene and the selectivity of the direct C–S hydrogenolysis for the nitrided 10.3% Mo/TiO₂ catalysts with time on stream are shown in Figure 11. The C–S hydrogenolysis

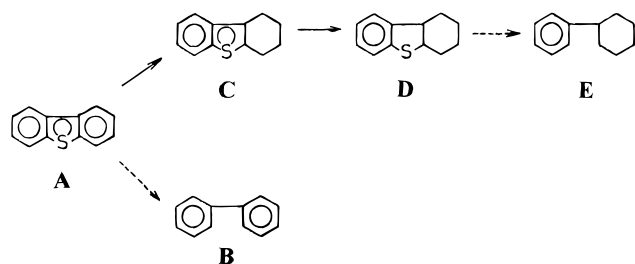


Figure 10. Reaction scheme of the HDS of dibenzothiophene on the nitrided Mo/TiO₂ catalyst.

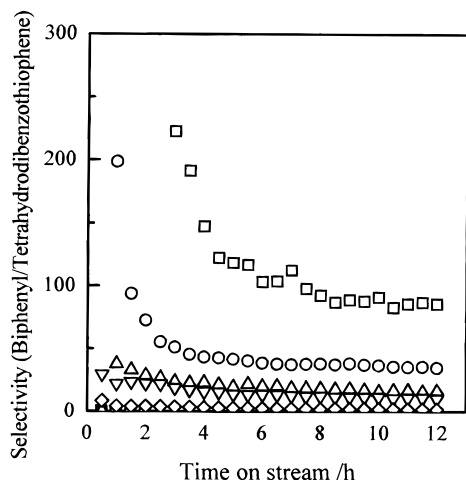


Figure 11. Selectivity of biphenyl to tetrahydrodibenzothiophene in the HDS of dibenzothiophene on the 10.3% Mo/TiO₂ nitrided at (□) 773, (○) 873, (△) 973, (▽) 1023, and (◇) 1073 K.

selectivity for the catalysts decreased with time on stream as well as the decreased conversion. The C–S hydrogenolysis selectivity for the 873 K nitrided catalysts was about 200 at 1 h after the start of a run, decreased to 35 at 6 h, and then reached the constant value. The selectivity of the 773 K nitrided 10.3% Mo/TiO₂ catalyst decreased to 38% of the 3 h run nitride catalyst (1 h) at 12 h. The 773 K nitrided catalysts had a superior selectivity over the other nitrided catalysts for the C–S hydrogenolysis. Furthermore, the 1073 K nitrided catalyst had extremely low selectivity in the C–S bond breakage (high hydrogenation selectivity), compared to the other nitrided catalysts. Since the 1073 K nitrided catalyst contained less Mo²⁺ and Mo⁰ than the 1023 K nitrided catalyst, the high selectivity for hydrogenation was not likely to relate to reduced molybdenum and molybdenum metal on the catalysts. However, from the XRD data, the formation of titanium nitrides of the 1073 K nitrided catalyst suggested that titanium nitrides with molybdenum would be more active in hydrogenation. The relationship between the atomic ratio of (N 1s + Mo 3p)/Ti 2p for the nitrided catalysts before the reaction and that of S 2p/Ti 2p after the 12 h run in dibenzothiophene HDS at 573 K is shown in Figure 12. Sulfur was less accumulated on the nitrided catalysts with much nitrogen consisting of adsorbed NH_x ($x = 1-3$) and molybdenum and titanium nitrides. This suggested that molybdenum nitride catalysts containing more nitrogen were tolerant of sulfur accumulation and sulfidation. Furthermore, the difference in N 1s/Ti 2p before and after the reaction as shown in Table 1 lost much nitrogen from the Mo/TiO₂ nitrided at high temperature. The catalysts nitrided at high-temperature held much more nitrogen before and after the reaction than the Mo/TiO₂ nitrided at low temperatures. Since no change in the structure of the nitrides was observed from XRD and XPS data,

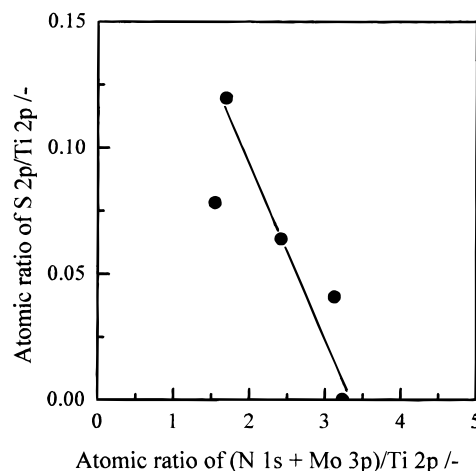


Figure 12. Relationship between the atomic ratio of S 2p/Ti 2p of the spent Mo/TiO₂ catalysts after the reaction and the atomic ratio of (N 1s + Mo 3p)/Ti 2p of the fresh Mo/TiO₂ catalyst before the reaction.

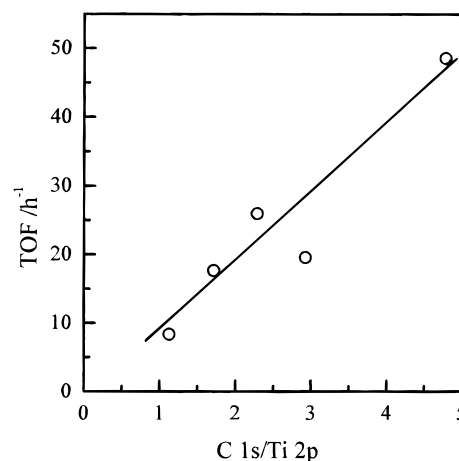


Figure 13. Relationship between the atomic ratio of C 1s/Ti 2p of the spent catalysts and the TOF at 0.5 h of the nitrided catalysts.

loss of nitrogen is probably due to NH_x adsorbed on the surface and dissolved nitrogen in the catalyst. Park et al.³⁹ reported that the catalyst with resistance to H₂S adsorption and/or the easiness of H₂S desorption from the catalyst surface had much higher catalytic activity for dibenzothiophene HDS over molybdenum nitride catalysts. Thus, the highly active nitrided Mo/TiO₂ catalyst became resistant by sulfiding during the HDS reaction.

Furthermore, the atomic ratio of XPS C 1s/Ti 2p was measured to determine the effect of carbon deposition on the activity for dibenzothiophene HDS as shown in Table 1. The atomic ratio of C 1s/Ti 2p showed that the 1023 K nitrided catalyst had the highest C/Ti ratio of the catalysts but the 773 K nitrided catalyst had the least. This result showed that the drop in the reaction rate on the nitride catalysts was not related to carbon deposition on the surface. In Figure 13, however, the TOF of the nitrided catalyst was correlated to the C 1s/Ti 2p atomic ratio. This result suggested that carbons accumulated for every HDS reaction per catalytic site per hour at 573 K and 10.1 MPa. In a previous paper,²² the TOF of the nitrided 12.5% Mo/Al₂O₃ catalysts was also correlated to the XPS C 1s/Al 2p atomic ratio during dibenzothiophene HDS at 573 K. Therefore, one step of the HDS reaction per active site forms carbons on the surface of the nitrided Mo/TiO₂ and Mo/Al₂O₃ catalysts. Another possibility might be that carbons formed during the reaction participate in the HDS reaction.

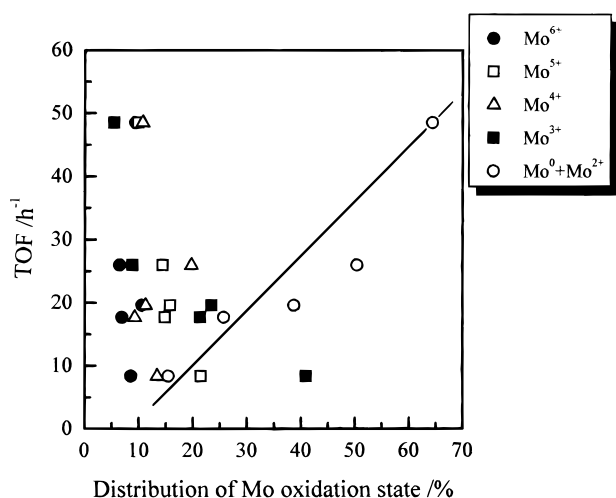


Figure 14. Relationship between the TOF and molybdenum species of the nitrided catalysts.

Active Sites for Dibenzothiophene HDS. The CO adsorption for the nitrided 10.3% Mo/TiO₂ catalysts is shown in Table 4. The irreversible CO uptake for the 973 K nitrided catalyst was $3.63 \times 10^{12} \text{ cm}^{-2}$, which was 0.26 and 2.4 times greater than the 773 and 1023 K nitrided catalysts, respectively. Bussell and co-workers⁵ prepared 10% Mo₂N/Al₂O₃ using the temperature-programmed reaction with ammonia from 673 to 950 K which was cooled to room temperature in flowing helium. They reported that the CO adsorption ($2.39 \times 10^{13} \text{ cm}^{-2}$) on the 10% Mo₂N/Al₂O₃ catalyst measured by a pulse technique of CO adsorption at 273 K was about 0.6 times greater than the total CO uptake of $4.15 \times 10^{13} \text{ cm}^{-2}$ for the 973 K nitrided catalyst in our study. Thompson et al.⁴⁰ also reported the O₂ uptake was $33.2 \mu\text{mol O}_2 \text{ g}^{-1}$ for 11.2% Mo₂N/Al₂O₃ nitrided at 973 K in the pulse method at atmospheric pressure, which was approximately 0.9 times greater than the total CO uptake of $38.0 \mu\text{mol g}^{-1}$ for the 973 K nitrided catalyst in our study. Thus, the large amounts of chemisorbed O₂ and CO reported roughly correspond to the total CO chemisorption in our study, despite the different method of the pulse technique from our volumetric technique in evacuation. The TOF of the nitrided 10.3% Mo/TiO₂ catalysts is shown in Table 4, calculated from the initial HDS rate at 0.5 h for irreversible CO uptake. The TOF of the catalysts roughly increased with increasing nitriding temperature. The 1073 K nitrided catalyst, 25.9 h^{-1} at 573 K, had a TOF value 3 times greater than the 773 K nitrided catalyst. The HDS rate for the 773 K nitrided catalyst was the highest among the nitrided catalysts, but the 1023 K nitrided catalyst had the greatest for TOF activity. Since the 1073 K nitrided catalyst was remarkably active for the hydrogenation of dibenzothiophene, the TOF of the 1073 K nitrided catalyst for overall HDS reaction would be less than that of the 1023 K nitrided catalyst. Bussell et al.⁵ reported a TOF of 49 h^{-1} for the 10% Mo₂N/Al₂O₃ catalysts in thiophene HDS at 693 K. Thompson et al.⁴⁰ also obtained a TOF value of 216 h^{-1} for the Mo₂N/Al₂O₃ catalyst in benzothiophene HDS at 593 K. The TOF's obtained by their results are greater than those in our experiment of dibenzothiophene HDS at 573 K. This is probably due to the lower reactivity of the three-ring thiophenic compound, compared to the single- and double-ring. The TOF for dibenzothiophene HDS is plotted against the abundance of the molybdenum oxidation state of the nitrided catalysts obtained from the XPS analysis in Figure 14. The TOF for dibenzothiophene HDS was linearly correlated with the abundance of Mo²⁺ and Mo⁰ of the nitrided Mo/TiO₂ catalysts. The TOF

value increases with decreasing the abundance in the fractions of Mo⁵⁺ and Mo³⁺ and is constant for Mo⁶⁺ and Mo⁴⁺ ions. The 1023 K nitrided catalyst held Mo²⁺ and Mo⁰ more than the catalysts nitrided at the lower temperatures in Figure 6. This result indicates that Mo²⁺ and Mo⁰ are the active centers for dibenzothiophene HDS on the nitrided Mo/TiO₂ catalyst. Bussell et al.⁶ studied the infrared spectroscopy of adsorbed CO on molybdenum nitride catalyst and deduced that Mo²⁺ site was present on the surface of the sulfided molybdenum nitride during the HDS reaction. Furthermore, Quincy et al.¹⁵ studied the hydrogenation of benzene on a 5% MoO₃/TiO₂ reduced in hydrogen and reported that Mo²⁺ ion is the most active species on a MoO₃ gram basis. Yamada et al.¹⁶ also reported that Mo metal is the most active species of reduced 8% MoO₃/Al₂O₃ catalyst for benzene hydrogenation, adding that Mo metal and (to a lesser extent) Mo²⁺ ion are the active centers. Sullivan and Ekerdt¹⁷ studied a correlation between the molybdenum oxidation state and thiophene HDS activity and reported that Mo²⁺ ion was the most active molybdenum species of sulfided silica-supported molybdenum catalysts. Therefore, molybdenum metal and Mo²⁺ ion are the most active species in the HDS of dibenzothiophene on the nitrided Mo/TiO₂ catalyst as well as being resistant for sulfur accumulation.

Conclusions

The TiO₂ support of the 10.3% Mo/TiO₂ catalyst did not sinter even at a nitriding temperature of 1073 K. Many more nitrogen containing catalysts were tolerant of sulfur accumulation and sulfidation of molybdenum nitrides. The TOF of the 10.3% Mo/TiO₂ catalysts increased with increasing nitriding temperature. The 1023 K nitrided catalyst showed the highest TOF activity for the HDS of dibenzothiophene. From the XPS analysis, the molybdenum oxidation states decreased from Mo⁶⁺ to Mo⁰ with increasing nitriding temperature, with Mo²⁺ and Mo⁰ predominant for the 1023 K nitrided catalyst. The distribution of molybdenum oxidation states of the nitrided Mo/TiO₂ catalysts was related to the HDS activity. Therefore, Mo²⁺ and Mo⁰ species were the most active in the HDS of dibenzothiophene on the nitrided Mo/TiO₂ catalysts.

Acknowledgment. This work has been carried out as a research project of the Grant-In-Aid for Scientific Research from the Ministry of Education (Grant 09555244).

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