XPS Study of the Deactivation and Sulfiding of Nitrided Molybdena−Alumina Catalyst during the Hydrodesulfurization of Dibenzothiophene

Masatoshi Nagai,* Atsushi Irisawa, and Shinzo Omi

Department of Advanced Materials, Graduate School of Bio-applications and Systems Engineering, Tokyo University of Agriculture and Technology, 2-24 Nakamachi, Koganei, Tokyo 184, Japan

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The deactivation and sulfidation processes of nitrided 12.5% Mo/Al_2O_3 catalysts at the initial stage were studied on the basis of the behavior of sulfur and nitrogen using XPS spectroscopy. The hydrodesulfurization (HDS) of dibenzothiophene was carried out in a fixed-bed microreactor at 573 K and 10.1 MPa of total pressure. The Mo/Al_2O_3 catalyst was nitrided by a temperature-programmed reaction with pure ammonia at 4 L h^{-1} at various temperatures. From XPS measurement, the sulfur atoms removed from dibenzothiophene were not exchanged with nitrogen atoms in the nitride catalyst during the first hour but molybdenum was sulfided by 71% of the total sulfur accumulated during the 14-h run. The sulfur deposition followed the Elovich equation. The decreased HDS activity and increased hydrogenation selectivity of the nitride Mo/Al_2O_3 catalyst were caused by the accumulation of sulfur on the nitride catalyst. At steady state achieved after 14 h, however, the nitrogen achieved after the Mo/Al_2O_3 catalysts were nitrided at high temperatures was difficult to exchange by deposition of sulfur and the release of nitrogen from the nitride catalyst was hampered. The regeneration of the aged nitride catalysts with NH_3 after the 14 h-run increased the activity and decreased the hydrogenation selectivity. The mechanism of the regeneration of the aged nitride catalyst by NH_3 retreatment and the exchange of oxygen or nitrogen atoms with sulfur atoms in the HDS of dibenzothiophene on the nitrided Mo/Al_2O_3 catalyst are also discussed.

Introduction

Hydrodesulfurization (HDS) on molybdenum-containing catalysts has received considerable attention during the past decades. Environmental regulation can be expected soon to be the driving force for even deeper HDS's so as to desulfurize the more stable sulfur-containing molecules. The types of catalysts possessing high hydrogenation activities are typically not as efficient at removing sulfur from heavy oils. Therefore, new hydrotreatment catalysts are being developed that can effectively eliminate undesirable heteroatoms while consuming a minimum amount of hydrogen. A number of investigations have been published in the literature that suggest that molybdenum nitride and carbide catalysts have strong potential for use in the HDS process.[1−14] The majority of these studies have found bulk and supported molybdenum nitride catalysts to have HDS activities similar to or higher than conventional molybdenum sulfide catalysts. Sajkowski and Oyama[1] found unsupported Mo_2N to be nearly twice as active as the commercial NiMo/Al_2O_3 catalyst per active site for the HDS of a coal-derived gas oil and residuum at 633 K and 13.7 MPa. Thompson et al.[2] reported that the activities of the alumina-supported molybdenum nitrides were more active than that of the sulfided commercial CoMo/Al_2O_3 catalyst for the HDS's of benzothiophene and dibenzothiophene based on oxygen chemisorption. Furthermore, we reported the nitrided catalyst to be 1.1−1.2 times more active than a 623 K sulfided 12.5% Mo/Al_2O_3 catalyst on a surface area basis and also to be extremely selective for the C−S bond breakage of dibenzothiophene to form biphenyl.[3−6] Recently, Bussell et al.[7,8] found a significantly higher activity for a 10% γ-Mo_2N/Al_2O_3 catalyst than for a sulfided Mo catalyst for the HDS of thiophene. In addition, they pointed out that the activities of the γ-Mo_2N/Al_2O_3 catalyst, based on CO or O_2 chemisorption measured after sulfiding, were quite similar since a thin layer of molybdenum sulfide is present on the surfaces of molybdenum nitride particles during the reaction.[7−9] However, no attention has been paid to the behavior of nitrogen atoms in the nitride catalysts and the sulfur removed from thiophene or dibenzothiophene during the reaction. Furthermore, few studies have been reported concerning the deactivation mechanism of nitrided molybdenum−alumina during the HDS reaction and the behavior of nitrogen and sulfur in relation to the structure compositions and activities of the nitride catalysts.

Sulfidation of molybdenum oxide is an essential step in the activation of hydrotreating catalysts to be converted into the catalytically active sulfide phase, typically in H_2S/H_2 atmospheres at temperatures between 570 and 670 K.[15−21] Several studies have been devoted to the mechanism of sulfidation of molybdenum oxides and the possible structures of intermediates by temperature-programmed sulfidation (TPS[15−17]), XPS,[18−21] EXAFS,[17,22,23] IR spectroscopy,[24] and Raman spectroscopy.[25] Sulfidation initially takes place via an oxygen−sulfur exchange reaction on Mo^{6+}, followed by reduction of Mo^{6+} to less than Mo^{5+} and subsequent formation and growth of MoS_2 slabs upon sulfidation of Mo/Al_2O_3. Although Markel and Van Zee[10] reported that the bulk structure of the unsupported molybdenum nitrides was preserved despite the sulfiding conditions in the catalytic reactor, for all supported molybdenum nitride catalysts, the activities in the HDS's of thiophene and dibenzothiophene were decreased gradually with the formation of molybdenum sulfides during the reaction.[6,7,9] This result may be inconsistent with the sulfidation of the HDS catalyst to create active sites. In this work, the deactivation and sulfidation processes of the

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* To whom correspondence should be addressed.

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nitrided molybdena−alumina catalyst at the initial stage of the HDS of dibenzothiophene were studied on the basis of the behavior of sulfur and nitrogen using XPS spectroscopy. The mechanism of the exchange of oxygen and nitrogen atoms of the catalysts with sulfur atoms during the HDS of dibenzothiophene on the 773, 973, and 1173 K nitrided Mo/Al_2O_3 catalysts is also discussed. The active molybdenum and sulfur species for dibenzothiophene HDS are also discussed, along with the generation of sulfur species on the catalyst by NH_3 retreatment at steady state to become active.

Experimental Section

Catalyst Preparation. MoO_3/Al_2O_3 (12.5%) was prepared using a mixture of ammonium paramolybdate and γ-alumina and calcined in air at 823 K for 3 h (Nikki Chemicals Co.). The oxidic sample was packed on a fritted plate in a quartz microreactor, which consisted of 20-mm-long tubing of 10-mm o.d., attached at both sides with 50-mm-long tubing of 6-mm o.d. Nitriding of the oxidic precursor was carried out by a temperature-programmed reaction with ammonia.[26,27] Ammonia (99.999%) was used without further purification. The sample was first oxidized in dry air at 723 K and then treated in flowing ammonia at 49.6 μmol s^{-1} at a rate of 0.0167 K s^{-1} from 573 K to the desired temperature (773−1173 K) and held at the nitriding temperature for 3 h. The 773 K nitrided catalyst was sulfided in flowing 10% H_2S/H_2 at 573 K for 3 h (nitride/sulfide catalyst), to compare the HDS activity and sulfur content of the nitride catalyst with that of the nitride/sulfide catalyst. The molybdenum and carbon contents of the catalysts were analyzed using atomic absorption spectroscopy and a CHN analyzer (Perkin-Elmer, 2400II), respectively, as well as XPS spectroscopy. The specific surface area of the nitride catalysts was measured by nitrogen adsorption using a standard BET volumetric apparatus (Shibata Co., P-700) after the catalysts were evacuated at 473 K and 10^{-2} Pa for 2 h.

Activity Measurement. The HDS of dibenzothiophene was carried out using a fixed-bed microreactor in a high-pressure flow system described elsewhere.[28] The microreactor used was a 325-mm-long stainless steel tube of 17.3-mm o.d. and 3.2-mm thickness. The reactor was placed in a vertical position and externally heated, using an oven with a programmable temperature controller. The reactor was connected upward to a hydrogen gas cylinder and high-pressure feeder pump and downward to a high-pressure separator. A chromel−alumel thermocouple, positioned near the catalyst bed, outside of the reactor, was used to control the catalyst temperature. Another thermocouple was placed in the center of the catalyst bed for separately measuring the catalyst temperature. A quantity of 2.0 g of the granular catalyst (0.85−1.70 mm) was held in place, in the middle of the reactor, by interposing it between stainless steel bars, engraved with spiral grooves in the stainless steel reactor. The liquid feed, consisting of 13.6 mmol L^{-1} dibenzothiophene in xylene, was introduced into the reactor at 5.56 μL s^{-1} with a hydrogen flow of 74.4 μmol s^{-1} at 573 K and a total pressure of 10.1 MPa. Dibenzothiophene (ultrapure) and xylene (guaranteed, mixed *o*-, *m*-, *p*-xylene, specific gravity 0.85) were used without further purification. Hydrogen was dried by passing it through a Linde 13X molecular sieve trap. The reaction products were quantitatively analyzed using a FID gas chromatograph with a 2% silicon OV-17 column. The HDS rate was calculated, based on the moles of dibenzothiophene converted at 573 and 533 K. The turnover frequency (TOF) was expressed as moles of dibenzothiophene converted per moles of irreversible CO adsorbed at room temperature.

CO Chemisorption. The quantity of CO chemisorbed on the surface of the nitride catalysts was determined by conventional volumetric analysis (Coulter Co., Omnisorp 100CX). Before measuring the CO uptake, the sample was first evacuated at 10^{-2} Pa at 653 K and pretreated in hydrogen (26 kPa) at 653 K for 2 h and 673 K for 1 h. After pretreatment, the catalyst was degassed at 10^{-2} Pa and at 673 K for 2 h and then slowly cooled to room temperature in a vacuum.

XPS Measurement. To understand the deactivation of the nitrided 12.5% catalysts during the HDS of dibenzothiophene, the behavior of nitrogen and sulfur in the nitrided Mo/Al_2O_3 catalysts was studied using XPS measurement by interrupting the reaction at different reaction times (1, 4, 8, and 14 h). The surface compositions of the sulfur, nitrogen, and molybdenum atoms in the catalysts as a function of nitriding temperature were measured using a Shimadzu ESCA 850 spectrometer with monochromatic Mg Kα exciting radiation (8 kV, 30 mA). Analyses were carried out at a pressure of 5×10^{-4} Pa. The values of the binding energy for the catalysts were referenced to Al 2p at 74.7 ± 0.2 eV, which was checked against the Ag $3d_{5/2}$ line at 368.0 eV. The XPS spectra obtained were fitted using a nonlinear square method with a Gaussian−Lorentzian function after an FFT filter smoothing of the raw spectra. Curve fitting of Mo 3d peaks was accomplished using linked doublets of equal fwhm, 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.[29] The release of nitrogen from the nitride catalysts was evaluated by the difference in the atomic ratio of N 1s/Al 2p before and after the reaction. The experimental procedure consisted of cooling the catalysts after reaction to room temperature in flowing xylene, removing the catalysts from the reactor mixed in xylene solvent, and transferring them in a glovebag without exposure to air. The glovebag was pumped and backfilled with purified helium three times before the catalysts were transferred to a stainless steel prechamber, where the catalysts were mounted on a stainless steel probe with 10-mm o.d. and 1-mm depth. The catalysts were then moved from the prechamber into the analyzing chamber of the electron spectrometer.

Results and Discussion

Catalyst Deactivation during HDS. The HDS of dibenzothiophene on the 12.5% Mo/Al_2O_3 nitrided at 773 K as a function of time on stream at 573 K is shown in Figure 1. The nitride catalyst deactivated rapidly during the first stage of the reaction. The concentration of biphenyl formed for the nitride catalyst was 13 mmol L^{-1} 0.5 h after the start of the run and decreased to 53% of this initial concentration after 8 h (almost the same concentration at 14 h). The concentrations of dibenzothiophene, cyclohexylbenzene, and tetrahydro- and hexahydrodibenzothiophene increased and also reached steady state after 8 h. The formation of biphenyl, one of the desulfurized compounds, decreased with time on stream at the initial stage, whereas that of the other desulfurized compound, cyclohexylbenzene, increased. This observation is analogous to the results obtained for the sulfided Mo/Al_2O_3[30] and $NiMo/Al_2O_3$[31] catalysts. The HDS of dibenzothiophene is reported to proceed via parallel reactions involving the selective C−S hydrogenolysis of dibenzothiophene to form biphenyl and the C−S bond scission of hexahydrodibenzothiophene through the hydrogenation of dibenzothiophene to form tetrahydrodibenzothiophene, as shown in Figure 2. The molar ratio of biphenyl to tetrahydrodibenzothiophene and the selectivity of the direct C−S hydrogenolysis for the 773, 973, and 1173 K nitrided catalysts are shown in Figure 3. The effect of sulfiding on the

TABLE 1: Surface Area and CO Uptake on Nitrided Catalysts

	nitriding temp/K				
catalyst	773	873	973	1073	1173
surface area[a]/$m^2\ g^{-1}$	226	162	195	151	138
CO total/μmol g^{-1}	38.9	28.0	18.2	15.0	10.5
CO irreversible/μmol g^{-1}	7.0	4.1	3.2	2.0	1.3
HDS rate[b]/μmol $g^{-1}\ h^{-1}$ at 14 h	84.8(53.6)[d]	73.4(56.6)[d]	66.7	60.7	58.7
C−S hydrogenolysis selectivity[b]	33.3(102)[d]	30.1(51.6)[d]	28.6	40.5	48.3
TOF[e]/s^{-1}	0.00337(0.00213)[c]	0.00497(0.00383)[c]	0.00579	0.00843	0.0125

[a] Volumetric titration method using Shibata P-700. [b] Reaction temperature of 573 K at 14 h. [c] Biphenyl/tetrahydrodibenzothiophene at 573 K and 14 h. [d] Reaction temperature of 533 K at 14 h. [e] μmol $g^{-1}\ s^{-1}$/CO μmol g^{-1}.

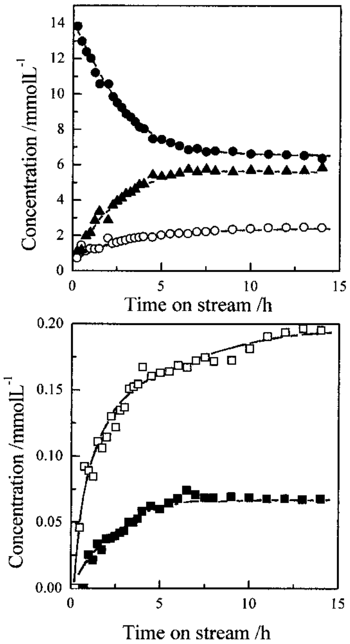

Figure 1. Reaction products in the HDS of dibenzothiophene on the 12.5% Mo/Al_2O_3 catalyst nitrided at 773 K with time on stream at 573 K and total pressure of 10.1 MPa. (●) Biphenyl, (○) cyclohexylbenzene, (▲) dibenzothiophene, (□) tetrahydrodibenzothiophene, and (■) hexahydrodibenzothiophene.

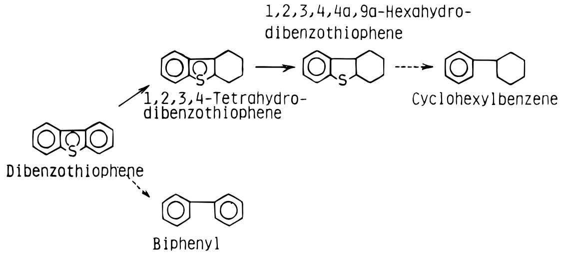

Figure 2. Reaction scheme of the HDS of dibenzothiophene on the nitrided Mo/Al_2O_3 catalyst.

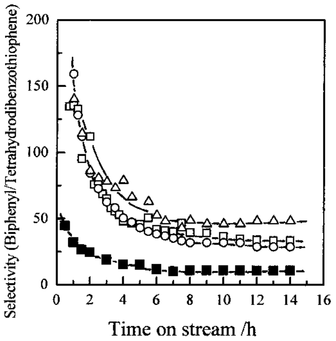

Figure 3. Selectivity of biphenyl to tetrahydrodibenzothiophene in the HDS of dibenzothiophene on the 12.5% Mo/Al_2O_3 nitrided at (□) 773, (○) 973, and (△) 1173 K and nitrided at (■) 773 K and subsequently sulfided at 623 K.

C−S hydrogenolysis selectivity of the nitride/sulfide catalyst is also shown. The C−S hydrogenolysis selectivity for the catalysts decreased with time on stream as well as the deactivation. The molar ratio for the nitride catalysts was about 130 at 1 h after the start of a run, decreased to 40 at 8 h, and nearly reached a constant value after 8 h. The selectivities for all the nitride catalysts at 14 h are shown in Table 1. The 773 and 1173 K nitrided catalysts had a superior selectivity over the 973 K nitrided catalyst for the C−S hydrogenolysis. Furthermore, the selectivity for the 1173 K nitrided catalysts was higher than for the other catalysts. When the nitride catalyst was sulfided at 573 K, the selectivity of the nitride/sulfide catalyst (10.7 at 14 h) decreased to about one-fourth that of the original nitride catalyst. As a result, sulfiding of the nitride catalyst decreased the selectivity for C−S hydrogenolysis but increased the hydrogenation selectivity. The nitride catalyst carried out the predominantly selective C−S hydrogenolysis with a minimum amount of hydrogen, compared to the sulfide catalyst. The TOF of the nitride catalyst increased with increasing nitriding temperature. The TOF of the 1173 K nitrided catalyst, 0.0125 s^{-1}, was 3.7 and 2.2 times more active than the 773 and 973 K nitrided catalysts, respectively. Bussell et al.[7,8] reported a TOF of 0.0136 s^{-1}, based upon titration of sites with CO for thiophene HDS at 693 K after 24 h of reaction time. The TOF obtained by their result is slightly greater than that in our experiment of dibenzothiophene HDS at 573 K after the 14-h run. Thompson et al.[2] also obtained a TOF value 5 times greater than our TOF for benzothiophene HDS at 593 K and 1.56 MPa. This is probably due to the lower reactivity of the three-ring thiophenic compound compared to the single and double ring.

X-ray Photoelectron Spectroscopy of the Nitrided Catalyst. The results of the XPS spectra in the S 2p and N 1s region (overlapping the Mo 3p) are shown in Figure 4. The weak binding energies of the XPS S 2p spectra were observed at 161.7 and 162.8 eV, with a shoulder peak at 163.8 eV for the nitrided Mo/Al_2O_3 catalysts, as shown in Figure 4A. The three S 2p peaks (a, b, and c) were very weak but were likely to be related to the distinguished peaks (d and e) of molybdenum sulfide and disulfide, while the intensities varied with the reaction time and conversion in the HDS. For d, the sulfided 12.5% Mo/Al_2O_3, and e, the nitride/sulfide catalyst, the XPS S 2p spectrum consisted of a single doublet with a S $2p_{3/2}$ binding energy of 161.7 eV, consistent with sulfide (S^{2-}) (161.5[32] and 161.8 eV[18,20,21,33]). The peak at 162.8 eV was reported to be that assigned to disulfide (S_2^{2-}) (163.1[18] and 162.9 eV[21]). As for the disulfide, Muijsers et al.[20] reported that all S spectra can be fitted with two S 2p doublets, having binding energy values for the S $2p_{3/2}$ peak at 161.8 eV (terminal S_2^{2-}), together with that at 162.8 eV (bridging S_2^{2-}) on the MoO_3/Si(100) catalyst sulfided at room temperature. The terminal S_2^{2-} would appear at the same value (161.8 eV[20,21]) as the S $2p_{3/2}$ binding energy

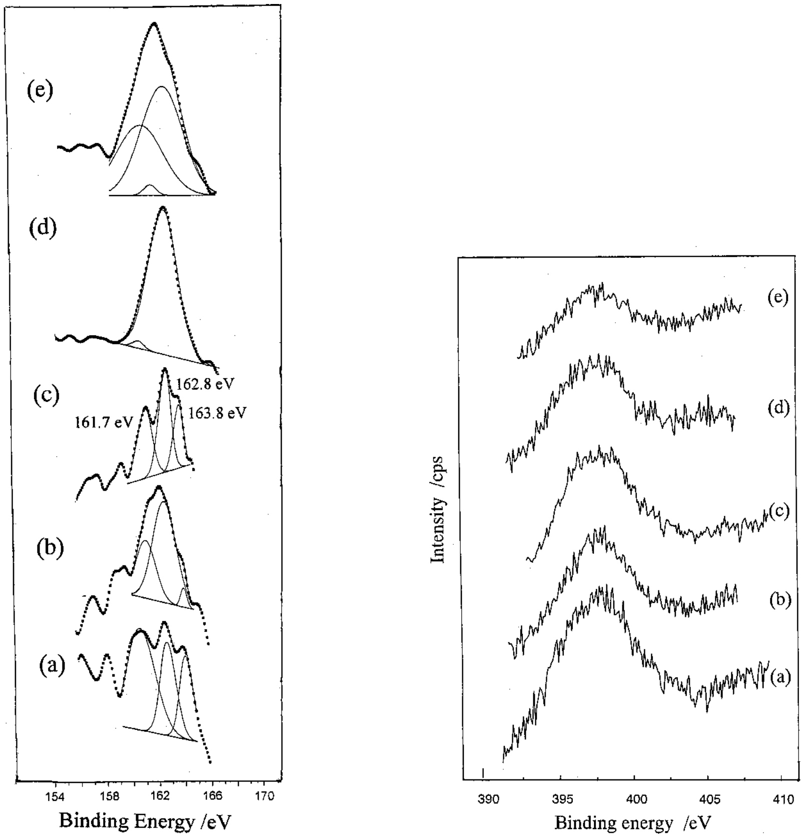

Figure 4. (A) XPS S 2p spectra for the spent 12.5% Mo/Al_2O_3 catalysts nitrided at 773 K (a) 8 and (b) 14 h after reaction, (c) the Mo/Al_2O_3 catalyst nitrided at 973 K 14 h after reaction, (d) the Mo/Al_2O_3 catalyst nitrided at 773 K and subsequently sulfided at 573 K in a 10% H_2S/H_2 flow, and (e) the Mo/Al_2O_3 catalyst sulfided at 573 K in a 10% H_2S/H_2 flow. (B) Region of XPS N 1s and Mo 3p spectra for the 12.5% Mo/Al_2O_3 catalysts nitrided at 773 K (a) before reaction and (b) 1, (c) 4, (d) 8, and (e) 14 h after the reaction.

of 161.8 eV[20] (S^{2-}), consistent with the S^{2-}-type ligands present in MoS_2. Although XPS did not distinguish between terminal $S_2{}^{2-}$ and S^{2-} species, the presence of the terminal $S_2{}^{2-}$ ligands is unlikely because if present on the edge of the metal centers of the MoS_2 particles, the ligands are expected to undergo reductive elimination reactions.[19−21] Binding $S_2{}^{2-}$ species are clearly present after sulfidation at low temperatures but disappear almost completely above 473−523 K.[20] The formation of S^{2-} and bridge $S_2{}^{2-}$ indicated that the sulfur ions of molybdenum covered the surface of the nitrided Mo/Al_2O_3 catalyst, leading to the decrease in the C−S hydrogenolysis activity and the increase in hydrogenation selectivity on the nitride catalyst during the HDS reaction, as shown in Figure 3. Furthermore, the shoulder peak at 163.8 eV was possibly due to S^0 (164.0[19] and 163.9 eV[35]). Also, the higher binding energy portion, such as the region of S^0 in 163.8−164.5 eV, matches in part the adsorbed dibenzothiophene or hydrogenated sulfur compounds.[34]

The regions of XPS N 1s for the nitrided 12.5% Mo/Al_2O_3 catalysts before reaction are shown in Figure 4B. The region of the N 1s spectra contained several peaks of N 1s and Mo 3p binding energies in the nitride catalysts. The peak of the XPS N 1s is reported to be the binding energies at 397.4[5] and 398.1 eV[9] (N 1s binding energy for Mo−N). Furthermore, weak and broad N 1s binding energies at more than 398.8 eV were reported to be observed for NH_3 adsorbed on acid sites.[36−38] The Mo $3p_{3/2}$ spectral envelope overlapped with the N 1s spectra and contained the spectra of several molybdenum states: Mo^{6+} (399.4 eV), Mo^{5+} (398.3 eV), Mo^{4+} (396.3 eV), and Mo^0 (393.6 eV).[34,39] Although the N 1s spectra were overlapped with the Mo $3p_{3/2}$ spectra for the nitrided Mo/Al_2O_3 catalysts, the loss of nitrogen from the nitride catalysts can be estimated from the difference in the total peak areas of the N 1s and Mo 3p spectra before and after the reaction. The atomic ratio of XPS C 1s/Al 2p was measured to determine the effect of carbon deposition on the activity for dibenzothiophene HDS as shown in Table 2. The C/Al ratios of the 773 and 1173 K nitrided catalysts were greater than that of the 973 K nitrided catalyst. This result showed that the drop in activity of the nitride catalysts during reaction was not related to carbon deposition on the surface of the nitride catalysts. Moreover, alumina in the catalysts was not nitrided under the pretreatment conditions, since the Al 1s XPS spectra were indistinguishable for the nitrided Mo/Al_2O_3 catalysts before and after the reaction.

TABLE 2: Surface Compositions of the Nitrided 12.5% MoO_3/Al_2O_3 Catalyst at a Reaction Temperature of 573 K

		10^2XPS			
catalyst	N/Mo ratio[a]	C/Al	S/Al	N[b]/Al	S/Mo[c]
773[d]	0.24	1.4[e]	3.76 (1.61)[f]	2.5 (1.61)[f]	53.9
973[g]	0.46	1.7	1.70	1.7	14.9
1173[h]	0.35	2.8	0.81	2.8	9.2

[a] Nitrogen content of N was measured using CHN analyzer, and the Mo loading was 12.5% in the sample measured by atomic absorption spectroscopy. The reaction took place at 573 K. [b] XPS N/Al before reaction minus XPS N/Al after reaction at 573 K for 14 h. [c] Atomic ratio of S 2p/Mo 3d after reaction. [d] Conversion of 0.66 at 573 K. [e] The C/Al ratios are (1h) 1.16, (4h) 1.28, (8h) 1.18, (14h) 1.43. [f] Conversion of 0.279 at 533 K. [g] Conversion of 0.463 at 573 K. [h] Conversion of 0.283 at 573 K.

Behavior of Sulfur and Nitrogen in the Nitride Catalysts during Reaction. The atomic ratio of S 2p/Al 2p and the difference in N 1s/Al 2p of the 773, 973, 1173 K nitrided catalysts with time on stream are shown in Figure 5. The S 2p/Al 2p ratio of the 773 K nitrided catalyst at the first hour

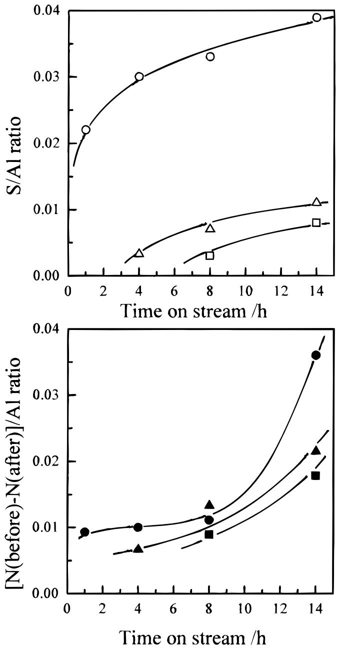

Figure 5. (a, top) Atomic ratios of XPS S 2p/Al 2p and (b, bottom) the differences in N 1s/Al 2p of the 12.5% Mo/Al_2O_3 catalysts nitrided at (○,●) 773, (△,▲) 973, and (□,■) 1173 K with time on stream.

increased significantly by 57% of the ratio of 0.0376 at the 14-h run and then gradually increased. This ratio is equivalent to 40% of all sulfur atoms of the nitride/sulfide catalyst before reaction (S 2p/Al 2p: 0.0552). On the other hand, the difference in the N 1s/Al 2p ratio for the 773 K nitrided catalyst increased slightly at the first hour and became constant up to 8 h and then increased extremely after 8 h. The nitrogen lost from the 773 K nitrided catalyst did not correspond to the sulfur accumulated on the nitride catalyst at the initial stage of the reaction. Sulfur atoms removed from dibenzothiophene at the initial stage were not exchanged with nitrogen atoms but were exchanged with the oxygen atoms of molybdenum oxides on the catalyst. Furthermore, little change in the distribution of the Mo oxidation state of the 773 K nitrided catalyst with reaction time was observed in the abundance of 28−37% of each Mo oxidation state of Mo^{4+}, Mo^{5+}, and Mo^{6+}, except for the decrease in the Mo oxidation state of Mo^{4+} (from 28% to 21%) and the increase in that of Mo^{5+} (from 37% to 42%) in 4 h after the run started at 573 K. The small change in Mo oxidation state was probably due to a mixture of nitrides[9,40] and sulfides[29,34] during reaction.

For the 973 and 1173 K nitrided catalysts, the S/Al ratio and the difference in N/Al increased with increasing reaction time. The S 2p/Al 2p ratio for the 1173 K nitrided catalyst was extremely lower than that for the 773 K nitrided catalyst at the 14-h run at a reaction temperature of 573 K. For the 773 K nitrided catalyst, a S/Al ratio of 0.0161 was obtained at a reaction temperature of 533 K when a conversion of 0.279 occurred in a similar conversion for the 1173 K nitrided catalyst. The value of 0.0161 was twice greater than that of 0.0081 for the 1173 K nitrided catalyst. The S/Mo ratio for the 773 K nitrided catalyst was considerably greater than those for the 973 and 1173 K nitrided catalysts in Table 2. This result indicated that the 1173 K nitrided catalyst was sulfided much less than the 773 K nitrided catalyst. The nitrogen difference for the 1173 K nitrided catalyst was one-half of that of the 773 K nitrided catalyst, although the 1173 K nitrided catalyst had a greater N/Mo ratio than the 773 K nitrided catalyst. For the Mo/Al_2O_3 catalyst nitrided at high temperatures, sulfur was difficult to exchange with nitrogen. Hence, the 1173 K nitrided catalyst was more difficult to sulfide and to release nitrogen atoms, compared to the 773 K nitrided catalyst. Our result is in agreement with the result obtained by Markel and Van Zee[10] that a fully nitrided molybdenum prevented sulfiding, preserving the bulk structure during the reaction. In contrast, not fully nitrided molybdenums, such as 773 K nitrided 12.5% Mo/Al_2O_3 in this study and the 973 K nitrided 10% Mo/Al_2O_3 catalysts (Bussell et al.[8] and this study), were readily sulfided during HDS.

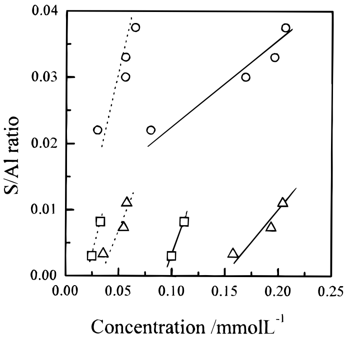

Figure 6. Relationship between the atomic ratio of the XPS S 2p/Al 2p and the formation of (—) tetrahydro- and (···) hexahydrodibenzothiophene in the HDS of dibenzothiophene on the (○) 773, (△) 973, and (□) 1173 K nitrided 12.5% Mo/Al_2O_3 catalysts at 573 K, respectively.

The atomic ratios of S 2p/Al 2p as a function of the concentrations of tetrahydro- and hexahydrodibenzothiophene on the nitride catalyst at 573 K are shown in Figure 6. The atomic ratio of S 2p/Al 2p was clearly proportional to the formation of two hydrogenated dibenzothiophene compounds in dibenzothiophene HDS on the 773 K nitrided catalyst at 573 K. Also, a linear relationship was observed for the 973 and 1173 K nitrided catalysts. This result showed that the hydrogenation of dibenzothiophene was related to the accumulation of sulfur on the nitride catalysts. Therefore, the hydrogenation of dibenzothiophene occurred predominantly on molybdenum sulfides formed on the nitrided Mo/Al_2O_3 catalysts.

Elovich Kinetics of Sulfur Accumulation. We now attempt to relate the effect of sulfur on the activity for dibenzothiophene HDS on the 773, 973, and 1173 K nitrided catalysts, assuming chemisorption of sulfur (ν_S) deposited from sulfur removal of dibenzothiophene. ν_S is estimated with the S 2p/Al 2p atomic ratio for the nitride catalysts. The Elovich equation is,[41−43] viz.,

$$d\nu_S/dt = a \exp(-\alpha\nu_S) \quad (1)$$

Integrating, then,

$$\nu_S = a \ln(t + t_0) \quad (2)$$

where a, α, and t_0 are constants, shows a reasonably good linear fit to the data as seen in Figure 7. A good fit over the entire range is observed for the 773 K nitrided catalyst. The adsorption data were correlated with eq 1 by a nonlinear regression analysis. The good correlation of the sulfur adsorption data with the Elovich equation implies a distribution of strengths of adsorption sites on the catalysts, such as molybdenum nitride and coordinatively unsaturated molybdenum sites. Slow chemisorption processes proceed by an initial rapid uptake of the adsorbate. The 973 and 1173 K nitrided catalysts should have obeyed the Elovich kinetics, but the S/Al ratios were too small to determine whether molybdenum sulfide was formed. Gas chromatography can detect the small amount of reaction products better than

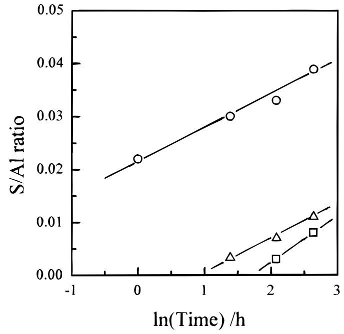

Figure 7. Elovich plots representing the growth of sulfur (S 2p/Al 2p atomic ratio) during the HDS of dibenzothiophene on the (○) 773 K, (△) 973 K, and (□) 1173 K nitrided catalyst.

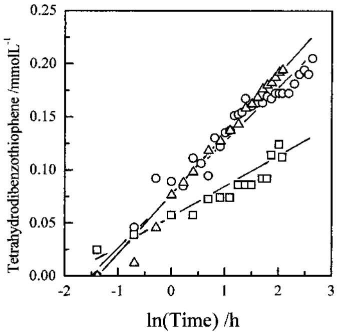

Figure 8. Elovich plots representing desorbing of tetrahydrodibenzothiophene in dibenzothiophene HDS at 573 K for the (○) 773, (△) 973, and (□) 1173 K nitrided Mo/Al_2O_3 catalysts.

the XPS analysis detects the sulfur species of the sulfides. Figure 8 shows a good relationship between the concentrations of tetrahydrodibenzothiophene for the three nitrided catalysts and the logarithm of time on stream. The formation of tetrahydrodibenzothiophene on the 773 K nitrided catalyst depended on the formation of molybdenum sulfides as shown in Figure 6. Consequently, the accumulation of sulfur on the surface of the 973 and 1173 K nitrided catalysts obeyed the Elovich kinetics, as it also did on the 773 K nitrided catalyst. Thus, the HDS reaction was poisoned by sulfur accumulated on the surface to form molybdenum sulfide for the effective hydrogenation at the initial stage, while the reaction takes place on a nearly sulfide-covered molybdenum catalyst at steady state after 8 h.

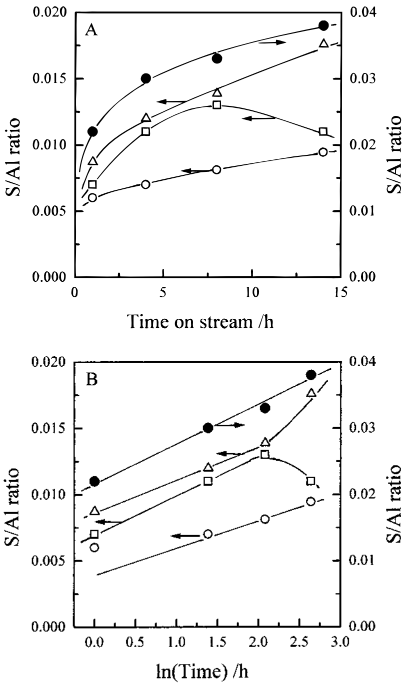

Figure 9. (A) (○) XPS S^{2-}/Al, (△) S_2^{2-}/Al, (□) S^0/Al, and (●) total S/Al atomic ratios for the 773 K nitrided catalyst with time on stream and (B) the Elovich plots representing the growth of the sulfur species on the catalyst.

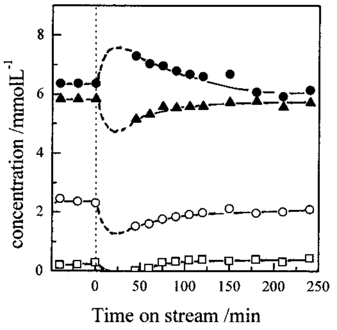

Figure 10. Regeneration of the aged 773 K nitrided Mo/Al_2O_3 catalyst with NH_3 at 773 K. (▲) Dibenzothiophene, (●) biphenyl, (○) cyclohexylbenzene, (□) tetrahydrodibenzothiophene. The reaction was interrupted 14 h after the reaction started. After the reaction feed was stopped and hydrogen gas was changed to ammonia gas, the catalyst was heated to 773 K in flowing ammonia and kept in ammonia at 773 K for 3 h.

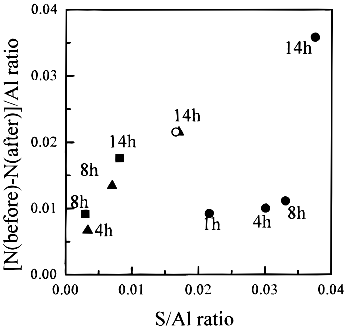

Figure 11. Relationship between the atomic ratio of XPS S 2p/Al 2p and the difference in N 1s/ Al 2p of the 12.5% Mo/Al_2O_3 nitrided at several conditions. The HDS was carried out using the 12.5% Mo/Al_2O_3 nitrided at (●) 773, and (▲) 973 K and (■) 1173 K at a reaction temperature of 573 K. For (○) the catalyst nitrided at 773 K, the HDS was carried out at a reaction temperature of 533 K.

Sulfidation and Hydrogenation Sites Formed during Reaction. The XPS S 2p/Al 2p of the sulfur species, S^{2-}, S_2^{2-}, and S^0, on the 773 K nitrided catalyst are plotted with reaction time in Figure 9A. S^{2-} and S_2^{2-} gradually increased with reaction time, but S^0 had a maximum value at 4 h and then decreased. The chemisorption of the S^{2-} and S_2^{2-} species was adjustable with the Elovich equation. Figure 9B shows the Elovich plots relevant to the growth of the peaks of the sulfur species adsorbing on the nitride catalysts. Excess S^0 and adsorbed sulfur compounds would be highly reactive toward hydrogen during HDS reaction at 573 K. At the initial stage, an irreversible, slow adsorption of sulfur poisons the molybdenum active sites and changes the surface structure to form molybdenum sulfides. Moulijn and co-workers[15,16] studied the temperature-programmed sulfidation of molybdenum oxide on alumina and reported that sulfidation initially takes place via an oxygen−sulfur exchange reaction on Mo^{6+} ions to form oxysulfides. This exchange is followed by reduction of Mo^{6+} by means of sulfur elimination from the formed MoO_xS_y compounds. Additionally, EXAFS studies[17,22,23] on the sulfidation of Mo/Al_2O_3 indicated the subsequent formation and growth of MoS_2 slabs between 573 and 673 K. XPS studies on $MoO_3/SiO_2/Si(100)$ model catalysts by Niemantsverdriet and

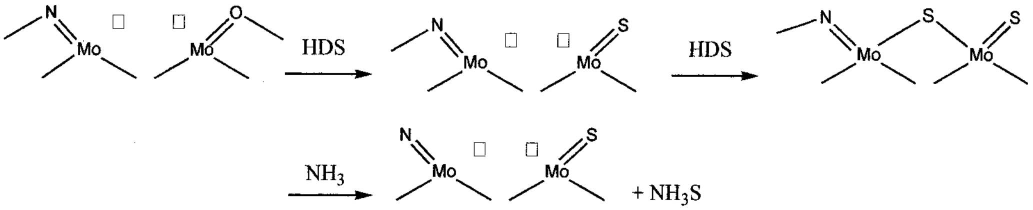

Figure 12. Sulfiding, deactivation, and NH_3 regeneration of the nitrided Mo/Al_2O_3 catalyst during the HDS of dibenzothiophene.

co-workers[19,20] showed the formation of $Mo^{4+}OS_x$ at the surface and oxides of Mo^{4+} ($H_{1.6}MoO_3$ or MoO_2) in the interior of the particle as well as the presence of two forms, as S^{2-} and S_2^{2-} or SH^-, during sulfidation in an early stage of sulfidation. The oxidation of the S^{2-} ligand of the MoS_4^{2-} anion ($2S^{2-} \rightarrow S_2^{2-} + 2e$) and the reduction of the metal ($Mo^{6+} + 2e \rightarrow Mo^{4+}$) occur. The terminal S_2^{2-} groups can undergo reductive elimination to elemental sulfur with reduced Mo centers, while simultaneously the bridging S_2^{2-} groups are reduced to S^{2-} ligands. As a result, S^{2-} in the sulfides mainly increased for the catalysts with high sulfur content.

We proposed, therefore, that the oxygen−sulfur exchange takes place on a pair of molybdenum and oxygen of the 773 K nitrided catalyst at the initial stage as shown in Figure 9A. Dibenzothiophene first adsorbs, on active sites of a molybdenum atom, a combination of molybdenum and oxygen of the catalyst surface. The carbon−sulfur bond scission of dibenzothiophene takes place to form biphenyl, and then a molybdenum is readily sulfided with accumulated sulfur. A molybdenum−sulfur bond is generated at the initial stage. After 8 h, the exchange reaction of nitrogen of the nitride catalyst with sulfur occurred greatly. The HDS of dibenzothiophene on the nitride catalyst was responsible for pair sites of molybdenum and oxygen on the surface at the initial stage, while at steady state it is responsible for two pair sites of molybdenum−nitrogen and molybdenum−sulfur of the catalyst. For the 973 and 1173 K nitrided catalysts, which rarely contained molybdenum oxides, as shown in Table 2, sulfur adsorbed on molybdenum nitride or coordinatively unsaturated Mo sites and the direct exchange reaction of nitrogen with sulfur occurred, as shown in Figure 9B.

Regeneration of the Catalysts with NH_3. The change in the activity of the aged catalyst before and after regeneration with NH_3 is shown in Figure 10. After the reaction started again in 25 min after the NH_3 treatment, the concentrations of dibenzothiophene converted and biphenyl formation increased 1.1 and 2.5 times more than those for the aged catalysts before the retreatment, respectively. However, the HDS activity of the regenerated catalyst was rapidly decreased to less than the activity before the NH_3 retreatment in 2 h. The difference in N 1s/Al 2p for the various nitrided catalysts and the NH_3-regenerated catalyst plotted against that of S 2p/Al 2p is shown in Figure 11. The difference in N 1s/Al 2p was proportional to the S 2p/Al 2p ratio of the nitride catalysts at steady state. This result showed that nitrogen atoms of the nitride catalysts were replaced with sulfur atoms deposited on the catalyst surface for 14 h of the run. In contrast, the deviation from the straight line for the 773 K nitrided catalyst at the initial stage (1−8 h) indicated that sulfur atoms removed from dibenzothiophene were predominantly exchanged with oxygen atoms of molybdenum oxides on the surface since the catalyst was not fully nitrided at 773 K. In Table 3, the XPS analysis showed that the NH_3 retreatment of the 773 K nitrided catalyst lowered by 44% the ratio S 2p/Al 2p before the retreatment and shrunk by 60% the difference in the N 1s/Al 2p ratio; i.e., nitrogen increased. The S/Al ratio of 0.0166 and the difference in N/Al of 0.0215 were similar to those of the 973 K nitrided catalyst. This result suggested that the renitriding of the aged catalyst with ammonia eliminated sulfur species adsorbed on the catalyst surface incompletely and added nitrogen atoms on the surface. The presence of noneliminated sulfurs on the aged catalyst with the NH_3 retreatment at 773 K suggested the presence of a exchangeable and unexhangeable sulfur. From the deconvolution of XPS, sulfur spectra S_2^{2-} and sulfur species (S^0 and adsorbed sulfur compounds) were extremely reduced but S^{2-} ions remained, suggesting that S_2^{2-} and the sulfur species are more exchangeable but S^{2-} is not. The sulfide ions (S^{2-}) of molybdenum sulfides were probably hard to eliminate but the disulfide ions (S_2^{2-}) were readily removed by renitriding with NH_3. Therefore, we proposed the scheme for the renitriding treatment of the aged nitride catalyst as shown in Figure 12. The renitriding treatment regenerated the surface-active species such as coordinatively unsaturated molybdenum species of the nitride catalyst by removing S_2^{2-} ions and the sulfur species on the surface of the catalysts.

TABLE 3: Presence of Sulfur Species of the 773 K Nitrided 12.5% Mo/Al_2O_3 Catalyst before and after NH_3 Treatment

		atomic ratio[b]	
a		before	after
S 2p/Al 2p	S^{2-}	0.009	0.0152
	S_2^{2-}	0.0162	4.3×10^{-4}
	S^0	0.0122	9.5×10^{-4}
	total S	0.0376	0.0166
N 1s/Al 2p		0.0358	0.0215

[a] XPS S 2p/Al 2p and difference in N 1s/Al 2p. [b] NH_3 treatment, before or after.

Conclusions

The release of nitrogen atoms in the nitrided 12.5% Mo/Al_2O_3 catalysts and the deposition of sulfur atoms during the HDS of dibenzothiophene were studied using XPS measurement. Sulfur deposition brought about the initial deactivation in dibenzothiophene HDS to cover the active sites of the nitride catalysts. The exchange of nitrogen in molybdenum nitride with sulfur occurred at all reaction stages for the catalysts nitrided at various temperatures, except for the exchange of oxygen in molybdenum oxide with sulfur at the initial stage for the 773 K nitrided catalyst. The 1173 K nitrided catalyst exhibited the highest activity for the HDS of dibenzothiophene, the 973 K nitrided catalyst the second highest. Molybdenum sulfide formed on the surface preceded the hydrogenation of dibenzothiophene. The renitriding of the aged catalyst regenerated more coordinatively unsaturated molybdenum species and reduced disulfide and the sulfur species on the only near-surface of the catalyst.

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