Available online at www.sciencedirect.com

SCIENCE DIRECT®

ELSEVIER

Catalysis Today 87 (2003) 123–132

CATALYSIS TODAY

www.elsevier.com/locate/cattod

Deactivation study on nitrided molybdena–alumina during hydrodesulfurization of dibenzothiophene by X-ray photoelectron spectroscopy

Masatoshi Nagai*, Takeshi Arahata

Graduate School of Bio-applications and Systems Engineering, Tokyo University of Agriculture and Technology,
2-24 Nakamachi, Koganei, Tokyo 184-8588, Japan

Abstract

The deactivation of 12.5% Mo/Al_2O_3 catalysts nitrided at various temperatures during the hydrodesulfurization (HDS) of dibenzothiophene at a 10.1 MPa total pressure was studied on the basis of a simulation using the kinetic equation and the behavior of nitrogen release (N/Mo atomic ratio), sulfidation (S/Mo), and carbon deposition (C/Mo) by X-ray photoelectron spectroscopy (XPS). The nitrided catalysts were deactivated in two regions where the activity significantly decreased up to 3 h and then very slowly in the period of 3–14 h. The catalyst deactivation during dibenzothiophene HDS followed the equation: $\Phi = r_1 \exp(-\alpha_1 t) + r_2 \exp(-\alpha_2 t)$, where r and α are constants, subscripts 1 and 2 denote the rapid and slow deactivation species, respectively, and t is the time-on-stream. The rapid initial deactivation (α_1) was mainly attributed to carbon deposition on the surface, while the slow deactivation (α_2) was significantly associated with nitrogen release. The highly nitrided Mo/Al_2O_3 catalyst (nitriding at 973 K) exhibited the least deactivation and longest catalyst lifetime.

Keywords: Deactivation; Hydrodesulfurization; Mo nitride; Simulation; X-ray photoelectron spectroscopy

1. Introduction

In molybdenum-containing catalysts, molybdenum nitrides and carbides effectively eliminate sulfur from the thiophenic compounds [1–5]. In a previous study [1], the nitrided 12.5% Mo/Al_2O_3 catalyst was 1.1–1.2 times more active than the 623 K-sulfided catalyst during dibenzothiophene HDS. However, the nitrided catalyst was rapidly deactivated during the initial stage of the reaction and then slowly deactivated during the steady stage. The nitrogen content of the Mo_2N/Al_2O_3 catalysts decreased after the reaction [4]. A thin layer of molybdenum sulfide covered the surface of the molybdenum nitride particles after the HDS of thiophene. However, the bulk structure of molybdenum nitride was maintained after the reaction [6]. A question arose as to how the decrease in HDS activity was caused by sulfidation and nitrogen release during the reaction. Although carbon deposition was reported to decrease the activity of the sulfided molybdenum catalyst [7–10], it remains as an unanswered question whether or not the molybdenum nitride catalyst was deactivated by carbon deposition during the HDS. There is little or no information on the relationship between the deactivation of the nitrided catalysts during the rapid initial and slow steady stages of the HDS reaction and the deactivation factors calculated by the XPS data. In this study, the deactivation of the nitrided 12.5% Mo/Al_2O_3 catalyst during the initial

---

* Corresponding author. Tel./fax: +81-42-388-7060.
E-mail address: mnagai@cc.tuat.ac.jp (M. Nagai).

0920-5861/$ – see front matter © 2003 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2003.10.020

and steady stages was studied on the basis of the first order deactivation equation established by assuming two types of active species that were easy and difficult to deactivate. The relationship between the catalyst deactivation and the behavior of the nitrogen release, sulfidation, and carbon accumulation measured by XPS was discussed. The surface properties of the nitrided catalyst specific to the anti-deactivation and long catalyst lifetime were also discussed.

2. Experimental

2.1. Catalyst preparation

The 12.5% MoO_3/Al_2O_3 (Nikki Chemicals Co.) catalyst was prepared using a mixture of ammonium paramolybdate with γ-alumina xerogel and calcined in air at 823 K for 3 h. After the oxidic catalyst (granular, 0.85–1.70 mm) was packed on a porous quartz plate in a quartz microreactor, it was oxidized in dry air ($4\,l\,h^{-1}$) at 723 K for 1 h and then cooled from 723 to 573 K in dry air. The catalyst was nitrided from 573 K to the final temperature of 773, 873, 973, 1073, or 1173 K at a rate of $60\,K\,h^{-1}$ with $4\,l\,h^{-1}$ of ammonia, maintained at the final temperature for 3 h, and then cooled to room temperature in a stream of ammonia. The molybdenum content of the catalysts was analyzed using atomic absorption spectroscopy. The catalysts were removed from the quartz reactor in a glovebox filled with argon and subjected to BET surface area, CO adsorption, XPS observations, and catalytic activity measurements for dibenzothiophene HDS.

2.2. Activity measurement

The HDS of dibenzothiophene was carried out using a fixed-bed microreactor in a high-pressure flow system [4]. A 1.0 g quantity of the catalysts was held in place in the middle of the reactor without exposure to air after nitriding of the catalyst in the reactor. The liquid feed consisted of $13.6\,mmol\,l^{-1}$ dibenzothiophene (ultrapure) dissolved in xylene. The hydrogen was dried through a trap of Linde 13X molecular sieves. The feed was introduced into the reactor at the rate of $0.01\,l\,h^{-1}$ with a hydrogen flow of $3\,l\,h^{-1}$ at 573 K and a total pressure of 10.1 MPa after the catalyst was heated from room temperature to 573 K at 10.1 MPa. The reaction products were quantitatively analyzed using an FID gas chromatograph with a 2% silicon OV-17. The HDS rate was calculated based on the moles of dibenzothiophene converted at 573 K. The turnover frequency (TOF) of the nitrided catalysts was expressed as the HDS rate at 0 h extrapolated from the HDS rate versus time-on-stream curve divided by the amount of CO irreversibly adsorbed on the catalysts before the reaction.

2.3. BET surface area and CO chemisorption

The catalyst was packed in the U-shape tubing of the adsorption port in the analysis apparatus with flowing argon, pretreated at 473 K by evacuation at 10^{-3} Pa for 1 h, and then evacuated at 473 K below 10^{-4} Pa for 1 h. The BET surface area of the catalysts was measured using an Omnisorp 100CX (Beckman Coulter Co.) at liquid-nitrogen temperature. The quantity of CO chemisorbed on the surface of the catalysts was determined using the Omnisorp 100CX by conventional volumetric analysis. Before measuring the CO uptake, the catalysts were pretreated in hydrogen at 623 K for 2 h, degassed at 10^{-2} Pa and 653 K for 2 h, and then cooled to room temperature in a vacuum.

2.4. XPS measurement

The behavior of the nitrogen release, sulfidation, and carbon deposition for the nitrided 12.5% Mo/Al_2O_3 catalysts was studied using the XPS measurement during the reaction. The catalysts after nitriding in the microreactor were transferred to the glovebag attached to the XPS prechamber without exposure to air as described in a previous paper [5]. The XPS analysis was carried out using a Shimadzu ESCA 3200 photoelectron spectrometer with Mg Kα radiation (1253.6 eV, 8 kV, 30 mA). No argon etching was done for the analysis. The binding energy of Al 2p 74.6 ± 0.2 eV was taken as a reference to correct the binding energy of the catalysts. The XPS spectra were curve-fitted using the Gaussian distribution function with the Shirley baseline method. In Fig. 1A, the overlapped spectra of N 1s and Mo $3p_{3/2}$ at 394.4–399.4 eV were deconvoluted to the peaks of the N 1s spectra and the Mo $3p_{3/2}$ spectra which were correspondingly distributed to those for the Mo

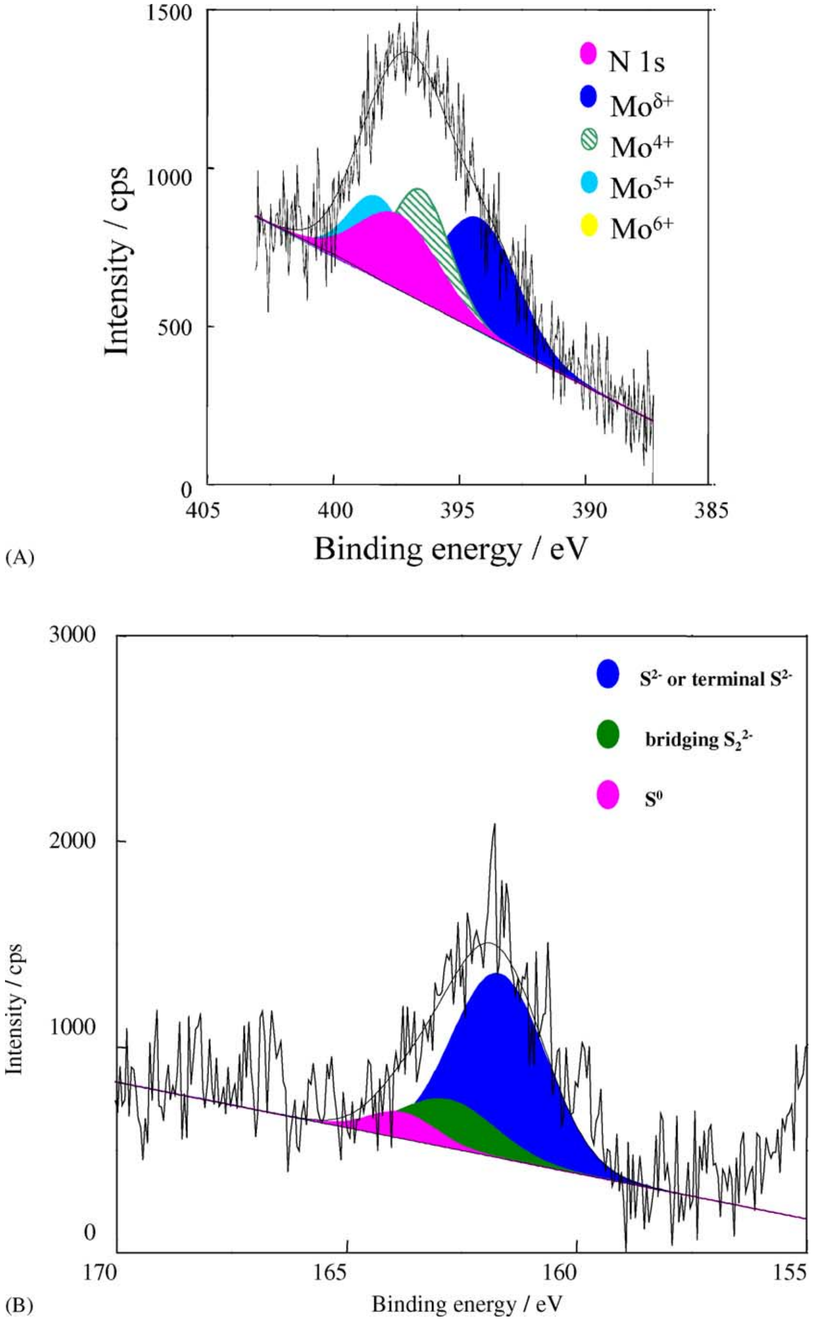

Fig. 1. (A) The deconvolution of N 1s lines from Mo $3p_{3/2}$ ($Mo^{\delta+}$, Mo^{4+}, Mo^{5+}, and Mo^{6+}) for 12.5 wt.% MoO_3/Al_2O_3 nitrided at 873 K before the reaction. (B) The deconvolution of S 2p spectra (terminal S^{2-}, bridging $S_2{}^{2-}$, and S^0) for the 973 K-nitrided catalyst after 14 h.

$3d_{3/2}$ spectra with an intensity ratio of 2/3 and a splitting of 3.2 eV [11–13]. The overlapped spectra were deconvoluted to the peak at 397.6 ± 0.2 eV for the N 1s spectra and to the peaks at 395.0 ± 0.5 ($Mo^{\delta+}$), 396.4 ± 0.2 (Mo^{4+}), 398.2 ± 0.2 (Mo^{5+}), and 399.4 ± 0.2 eV (Mo^{6+}) for the Mo $3p_{3/2}$ spectra. The spectra of the $Mo3p_{3/2}$ envelope were deconvoluted with the individual Mo $3p_{3/2}$ signals based on the same distribution of the Mo 3d electrons of Mo $3p_{3/2}$ as the Mo $3d_{3/2}$ spectra. For the formation of molybdenum sulfide, the S 2p spectra of the catalysts during the reaction were measured at 161–165 eV, i.e. the peaks at 161.8 eV (terminal disulfide and/or sulfide (S^{2-}) ligand) and at 163.1 eV (bridging disulfide ($S_2{}^{2-}$) ligand) with a shoulder peak at 163.8–164.0 eV (sulfur powder) (Fig. 1B) [4,13,14]. The C 1s spectra were also measured in the region of 281–294 eV [15–17].

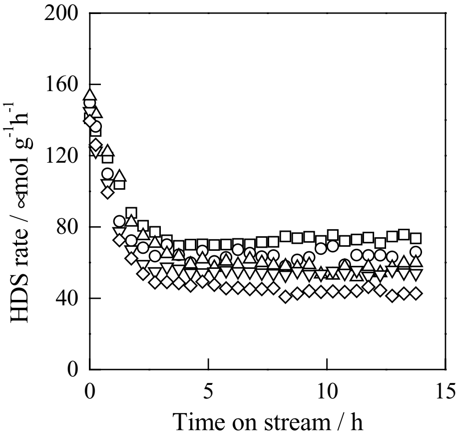

Fig. 2. The rate of the HDS of dibenzothiophene over the nitrided and sulfided 12.5% Mo/Al_2O_3 catalysts with time-on-stream at 573 K and 10.1 MPa: (□) 773 K-nitrided catalyst, (○) 873 K-nitrided catalyst, (△) 973 K-nitrided catalyst, (▽) 1073 K-nitrided catalyst, and (◇) 1173 K-nitrided catalyst.

3. Results and discussion

3.1. Activity for dibenzothiophene HDS

The rates of the HDS of dibenzothiophene on the 12.5% Mo/Al_2O_3 catalysts nitrided at various temperatures are shown in Fig. 2 and Table 1. The HDS rate of the 773 K-nitrided catalyst was the highest of all the catalysts for the entire 14 h. The 12.5% Mo/Al_2O_3 catalysts nitrided at higher temperatures had lower rates of dibenzothiophene HDS. The 973 K-nitrided catalyst had a very slow deactivation during the steady state. Although the 873–1073 K-nitrided catalysts exhibited high HDS rates only for the 0.25 h of a first sampling, they were rapidly deactivated up to 3 h on stream and remained constant thereafter. The deactivation of the nitrided catalysts during the reaction was composed of two periods of rapid deactivation during the initial stage (0–3 h) and very slow deactivation during the steady stage (3–14 h) of the reaction. The

Table 1
HDS activities and surface properties for 12.5% Mo/Al_2O_3 catalysts nitrided at various temperatures

	Nitriding temperature				
	773 K	873 K	973 K	1073 K	1173 K
HDS rate[a] (μmol g^{-1} h^{-1}) at 0 h (14 h)	141.0 (73.6)	149.7 (65.9)	153.4 (66.7)	144.8 (53.9)	139.4 (42.7)
DS selectivity[b]	79.8	49.1	35.2	56.2	25.4
Surface area (m^2 g^{-1})[c]					
Before reaction	141	131	164	128	124
At 3 h	173	n.m.	160	n.m.	114
At 14 h	166	149	135	n.m.	105
Total CO (μmol g^{-1})	39.3	57.6	50.7	26.5	24.8
Irreversible CO[c] (μmol g^{-1})	15.9	20.7	16.6	9.0	8.2
Irreversible CO (molecules nm^{-2})	0.068	0.095	0.061	0.042	0.040
TOF (at 0 h) (h^{-1})	8.9	7.2	9.2	16	17

[a] Reaction temperature of 573 K.

[b] Molar ratio of biphenyl to cyclohexylbenzene (DS: direct desulfurization of DBT at 14 h).

[c] Before the reaction.

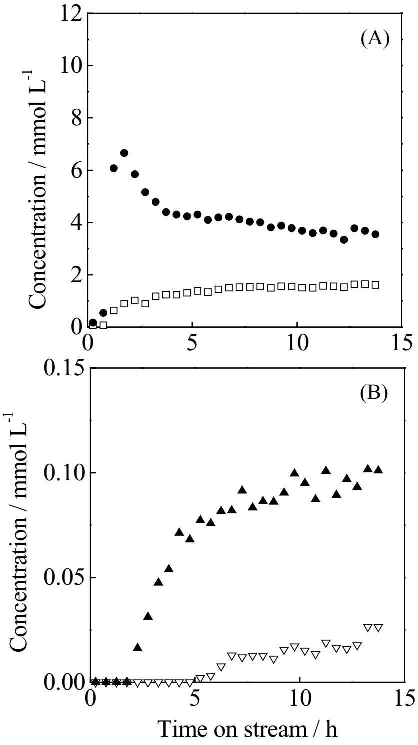

Fig. 3. The products in the HDS of dibenzothiophene over the 973 K-nitrided 12.5% Mo/Al_2O_3 catalyst with time-on-stream at 573 K and 10.1 MPa: (A) (●) Biphenyl, (□) cyclohexylbenzene; (B) (▲) tetrahydrodibenzothiophene, (▽) hexahydrodibenzothiophene.

HDS rate of the 773 K-nitrided catalyst decreased similar to those of the nitrided catalysts but gradually increased after 4 h. The 773 K-nitrided catalyst is ruled out from the deactivation tests. The reaction products for the dibenzothiophene HDS on the 973 K-nitrided catalyst are shown in Fig. 3. Among the reaction products, the biphenyl concentration increased up to 2 h due to the highly active decomposition of dibenzothiophene and then decreased after 2 h. The concentration of cyclohexylbenzene gradually increased after 1 h on stream and reached a steady-state concentration after 5 h. The concentrations of tetrahydrodibenzothiophene and hexahydrodibenzothiophene started to increase after 2.5 and 5.5 h, respectively, and exhibited constant values which were about 35 and 160 times less than the biphenyl concentration. This result indicated the preference to the direct C–S bond breakage of dibenzothiophene rather than hydrogenation. Similar results for the reaction products were observed for the other nitrided catalysts.

As far as the CO adsorption on the nitrides was concerned, the CO uptakes of the 873 and 973 K-nitrided catalysts were greater than those of the other nitrided catalysts. This result showed that the 1173 K-nitrided catalyst had the lowest CO uptake, that is, a small number of active sites. The TOF of the 1173 K-nitrided catalyst (17.0 h^{-1}) was about twice those of the catalysts nitrided at 773–973 K. This result showed that the 1173 K-nitrided catalyst probably had a small number of strongly active sites. The TOFs of the 873–1173 K-nitrided catalysts increased with the increasing nitriding temperature. The 873 and 973 K-nitrided catalysts had a greater CO uptake than the 1073 and 1173 K-nitrided catalysts and also high Mo/Al ratios determined by XPS in Table 2. The 873 and 973 K-nitrided catalysts had greater CO uptakes than the 1073 and 1173 K-nitrided catalysts and also the high Mo/Al ratios determined by XPS. This result indicated that the 873 and 973 K-nitrided catalysts had more Mo atoms exposed on the surface than the other nitrided catalysts. Since the TOFs of the 873 and 973 K-nitrided catalysts were lower than those of the 1073 and 1173 K-nitrided catalysts, the two catalysts probably had more weakly active sites. On the other hand, since the 1073 and 1173 K-nitrided catalysts had about half the CO adsorption sites and 1.7–2.4

Table 2
Surface compositions of the nitrided 12.5% Mo/Al_2O_3 catalyst before reaction (0 h) and after 3 and 14 h on stream

	873 K			973 K			1073 K			1173 K		
	0 h	3 h	14 h	0 h	3 h	14 h	0 h	3 h	14 h	0 h	3 h	14 h
N/Mo	0.121	0.0750	0.0725	0.214	0.137	0.135	0.129	0.100	0.080	0.0802	0.0511	0.0406
S/Mo	0.0	0.333	0.663	0.0	0.340	0.437	0.0	0.300	0.62	0.0	0.128	0.968
C/Mo	0.0	32.6	87.5	0.0	23.0	170	0.0	34.0	117	0.0	25.6	224
Mo/Al	0.080	0.056	0.040	0.075	0.120	0.132	0.059	0.075	0.071	0.050	0.067	0.051

times higher TOFs than the 873 and 973 K-nitrided catalysts, and the 1073 and 1173 K-nitrided catalysts had fewer strongly active sites.

3.2. Catalyst deactivation during HDS

The BET surface area of the catalysts changed during the reaction in Table 1. The BET surface areas of the 973 and 1173 K-nitrided catalysts decreased during the reaction, but for the 873 and 1073 K-nitrided catalysts, they were still unchanged. However, the surface area of the 773 K-nitrided catalyst increased from 141 to 166 $m^2 g^{-1}$ with the increasing reaction time from 0 to 14 h and then gradually decreased, even though the HDS activity decreased. The changes in the surface areas of the nitrided catalysts during the reaction did not correspond to the rapid and slow deactivation of the nitrided catalysts. Thus, the deactivation was not caused by the decrease in the pore mouth.

In order to elucidate the deactivation of the nitrided catalysts during the initial and steady stages, the decreasing rate of the active sites was described to be first order with respect to the decreasing number of active sites by the deactivating and/or releasing species. It is assumed that the diffusion is not affected during the HDS reaction and each active site is independently reacted and deactivated [18–20]. The deactivation of the nitrided catalysts was assumed to be due to coke deposition, sulfur deposition, and nitrogen release. These factors were combined together to describe the deactivation behavior by the equations without the evaluation of each factor. Therefore, the easily deactivated species corresponded to the species for the large deactivation rate during the initial stage of the reaction while the species deactivated with difficulty corresponded to the species for the slow deactivation during the steady stage:

$$\Phi = \frac{r}{r_0} = r_1 \exp(-\alpha_1 t) + r_2 \exp(-\alpha_2 t) \qquad (1)$$

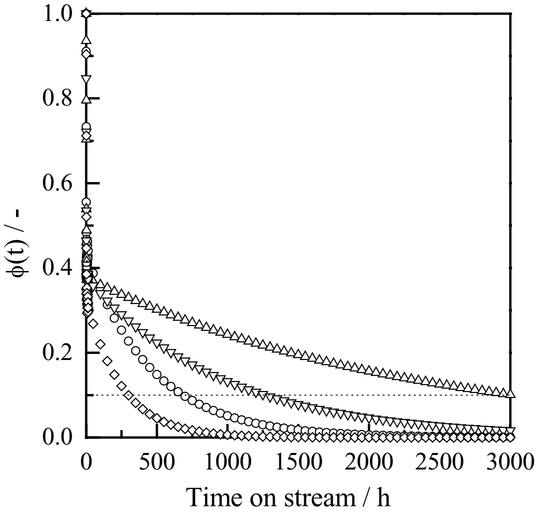

Fig. 4. The simulated Φ in the HDS of dibenzothiophene over the nitrided 12.5% Mo/Al_2O_3 catalysts with time-on-stream. Symbols are the same as those in Fig. 2.

where r_1 and r_2 are constants, α_1 and α_2 are deactivation constants, and t is the time-on-stream. The rate r of the disappearance of dibenzothiophene was proportional to the decreasing number of the two types of active species which were supposed to be present on the surface of the catalysts: the active species rapidly deactivated (r_1, α_1) during the initial stage and the others slowly deactivated (r_2, α_2) during the steady stage. The rate constants (r_1, r_2) and deactivation constants (α_1, α_2) were treated by fitting the reaction rate data for the nitride catalysts to the kinetic expression using a non-linear least-squares fitting. The deactivation Φ of dibenzothiophene HDS over the 12.5% Mo/Al_2O_3 catalysts nitrided at 873, 973, 1073, and 1173 K with time-on-stream was simulated and is shown in Fig. 4. A good fit was observed for Eq. (1) over the HDS reaction. The results for the simulation of the deactivation are summarized in Table 3. The 973 K-nitrided catalyst

Table 3
Parameters for simulated deactivation function

Nitriding temperature (K)	α_1 (h^{-1})	α_2 (h^{-1})	α_2/α_1	r_1	r_2	χ^2 test	Catalyst lifetime[a] (h)
873	1.139	0.00213	0.0187	0.600	0.431	0.00031	672
973	0.694	0.000439	6.33×10^{-4}	0.654	0.376	0.00035	2950
1073	1.056	0.00105	9.94×10^{-4}	0.630	0.377	0.00023	1250
1173	0.947	0.00396	0.0042	0.700	0.327	0.00029	292

[a] Time required for reaching 10% conversion.

had a strong deactivating constant (α_1) of 0.694 but a weak deactivation constant (α_2) of 4.39×10^{-4}. The α_1 value for the 973 K-nitrided catalyst was 1.6 and 1.5 times smaller than for the 873 and 1073 K-nitrided catalysts, respectively, but the α_2 values were 4.9 and 2.4 times higher. The amount of the easily deactivated sites for the nitrided catalysts were 150–1600 times greater than the difficult deactivated sites. Furthermore, the 973 K-nitrided catalyst had the lowest α_2/α_1 value of all of the catalysts and was more slowly deactivated after 3 h during the steady stage than during the initial stage. Therefore, the 973 K-nitrided catalyst is the best anti-deactivating catalyst.

3.3. Deactivation by nitrogen release, sulfidation, and carbon deposition

The changes in the atomic ratios of N/Mo, S/Mo, and C/Mo of the 973 K-nitrided catalyst with time-on-stream are shown in Fig. 5. The ratios of N/Mo, S/Mo, C/Mo, and Mo/Al of the other nitrided catalysts are also listed in Table 2. The 973 K-nitrided catalyst had an N/Mo ratio of 0.214 before reaction and decreased to 0.135 at 14 h, indicating that 36% of the N/Mo ratio of the fresh catalyst was lost after a 14 h run. The 973 K-nitrided catalyst had an N/Mo ratio greater than the other catalysts before the reaction. The nitrogen atoms of the 973 K-nitrided catalyst were removed to a lesser extent than those of the other nitrided catalysts during the HDS reaction. The S/Mo ratio of the 973 K-nitrided catalyst remarkably increased to 0.34 (78% of the final sulfur level) up to 3 h, then slowly increased, and attained 0.437. This trend was observed for the 873 and 1073 K-nitrided catalysts. This result showed that molybdenum nitrides on the catalyst were readily sulfided to form molybdenum sulfide on the surface. Fig. 6 shows the distribution of the sulfur species, S^{2-}, $S_2{}^{2-}$, and S^0 against the Mo species on the 973 K-nitrided catalyst plotted versus time-on-stream. S^{2-} rapidly increased and $S_2{}^{2-}$ decreased with the reaction time, while S^0 was unchanged. This result showed that the deposited sulfur species sulfided molybdenum during the first 3 h. Concerning the carbon deposition, the C/Mo ratio of the 973 K-nitrided catalyst slightly increased up to 5 h, then sharply increased from 5 to 10 h. Diez et al. [7] studied the deactivation of the NiMo/Al_2O_3 by XPS and reported that coke accumulated on alumina more rapidly than on the molybdenum sulfide and that this coke blocks the active MoS_2-crystallite edges. Also, Dadyburjor and Raje [8] reported that the initial deactivation brought about both active site suppression and pore plugging by coke for NiMo/Al_2O_3 during the thiophene HDS. The latter had a more significant contribution than the former for the higher aged catalyst. Panarello and Guanziroli [9] suggested

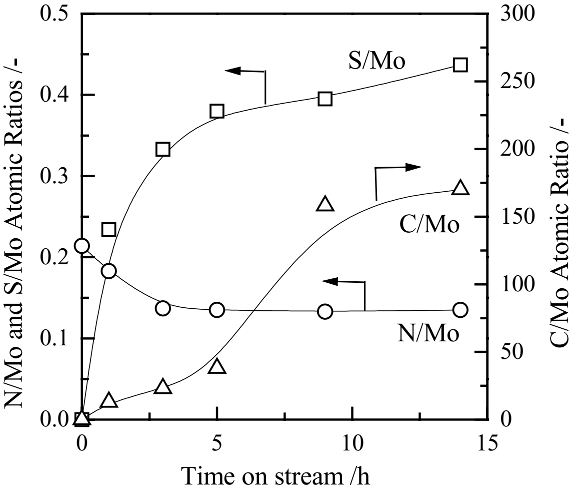

Fig. 5. Change in the atomic ratios of (○) N/Mo, (□) S/Mo, and (△) C/Mo of the 973 K-nitrided catalyst with time-on-stream.

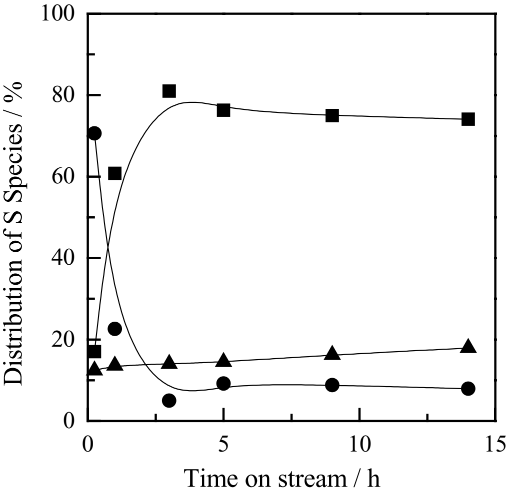

Fig. 6. Change in the XPS S 2p/Mo 3d ((■) S^{2-}, (●) $S_2{}^{2-}$, and (▲) S^0) of 973 K-nitrided catalyst with time-on-stream.

Table 4
Relative coefficients of relationship between atomic ratios of N/Mo, S/Mo, and C/Mo and the values of α_1 and α_2 for the nitrided 12.5% Mo/Al_2O_3 catalysts

	Relative coefficient		
	N/Mo	S/Mo	C/Mo
α_1 (h^{-1})	0.663	0.209	0.869
α_2 (h^{-1})	0.906	0.651	0.489

carbon deposits mainly on the active species for the less stable catalysts (i.e. initial stage) and on alumina for the more stable catalysts (i.e. steady stage). Carbon was deposited on the active molybdenum nitride species and the deposited carbon very quickly deactivated the 973 K-nitrided catalyst before 5 h, and after 5 h, carbon was deposited on the less active sites or alumina support.

The deactivation constants (α_1 and α_2) obtained from the deactivation simulation versus nitrogen release, sulfidation, and carbon deposition were subjected to the relative coefficients given in Table 4. α_1 is plotted versus the C/Mo ratio in Fig. 7. The α_1 value during the initial stage was closely related with carbon deposition (relative coefficient, 0.869). A roughly linear relation (0.663) of the α_1 value versus the N/Mo ratios was observed. This result indicated that the initial deactivation is primarily due to carbon formation on the active sites together with the secondary factor of nitrogen release from Mo nitride during the dibenzothiophene HDS. This result was in agreement with the data obtained by Elst et al. [22]. They reported the deactivation of MoS_2/Al_2O_3 during thiophene HDS and found that a highly aromatic and graphitic type of coke was preferentially deposited and blocked the active sites of MoS_2/Al_2O_3. Although the peaks of the micropore volumes for the 973 K-nitrided catalysts were not changed (0.12–0.16 ml g^{-1} nm^{-1}) before and after the reaction, those of the 1173 K-nitrided catalyst decreased from 0.12–0.15 to 0.08–0.14 ml g^{-1} nm^{-1}. The deposited carbon slightly plugged the pore mouth of the micropores of the catalysts but it mainly covered the active sites.

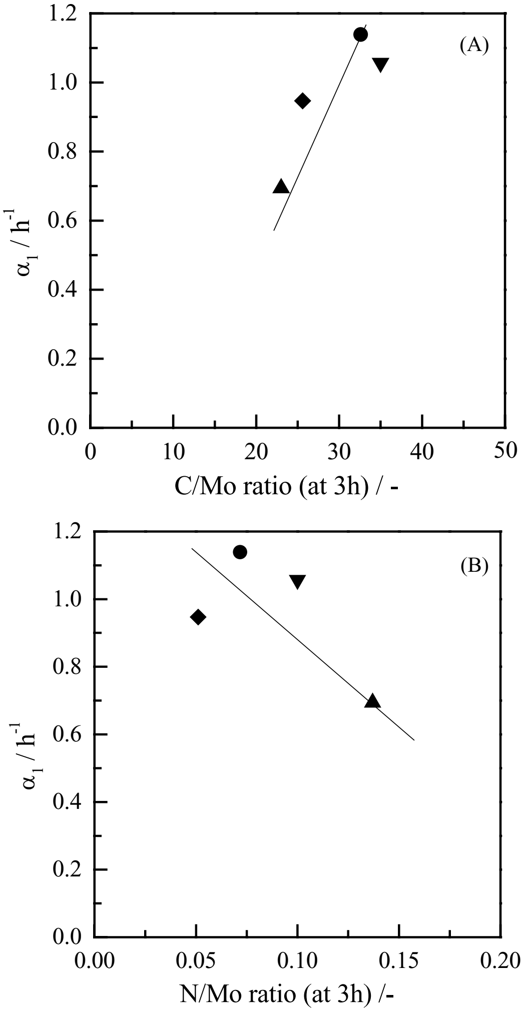

Fig. 7. Relationship between α_1 up to 3 h and the (A) C/Mo and (B) N/Mo atomic ratio of the nitrided 12.5% Mo/Al_2O_3 catalysts at 3 h after the HDS reaction: (●) 873 K-nitrided catalyst, (▲) 973 K-nitrided catalyst, (▼) 1073 K-nitrided catalyst, and (◆) 1173 K-nitrided catalyst.

3.4. Long catalyst lifetime and surface properties

α_2 is plotted versus the N/Mo ratio at 14 h in Fig. 8. The α_2 value was related to the N/Mo ratio (relative coefficient, 0.906), indicating that the nitrogen release was responsible for the deactivation of the nitrided catalysts during the steady stage. The α_2 value varied in the S/Mo ratio range of 0.4–0.7 and was roughly related to the S/Mo ratio (0.651). Sulfidation was slightly related to the deactivation during the steady stage because sulfur replaced nitrogen in the nitrided catalysts during the steady stage. Li and Lee [21] reported that sulfur compounds were deposited

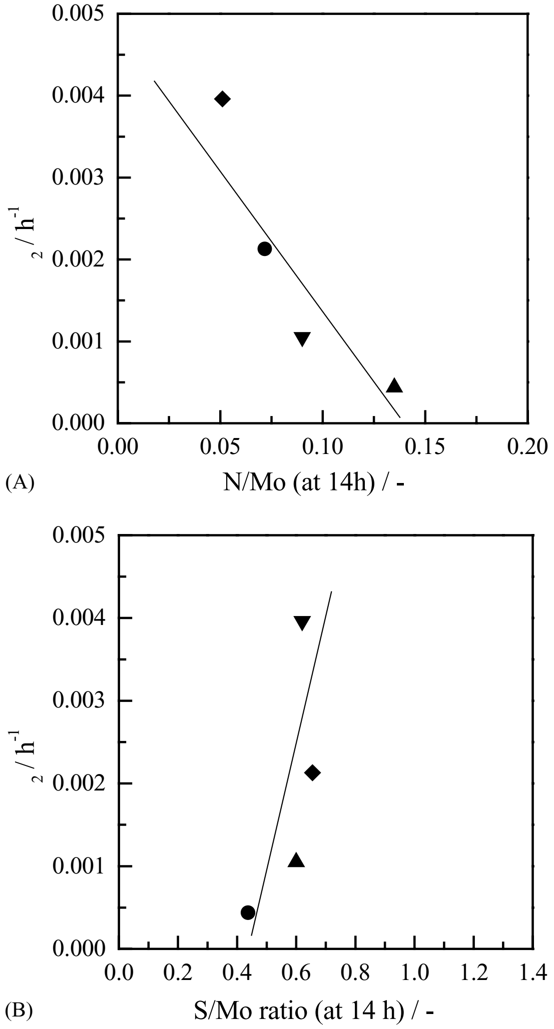

Fig. 8. Relationship between α_2 in the period of 3–14 h and the (A) N/Mo and (B) S/Mo ratios for the nitrided 12.5% Mo/Al_2O_3 catalysts at 14 h after the reaction. Symbols are the same as those in Fig. 7.

on the surface of the unsupported Mo_2N during the benzothiophene HDS and blocked the micropores, thus deactivating the catalyst. The nitrided catalysts were then very slowly deactivated by nitrogen loss together with sulfidation during the steady stage by a factor of 150–1600 compared to the initial deactivation. There is no relationship between α_2 and the C/Mo ratio. Although the 973 K-nitrided catalyst had relatively lower S/Mo and higher C/Mo ratios at 14 h compared to those for the other catalysts in Table 2, it was less deactivated by sulfidation and coke deposits during the steady stage. The 973 K-nitrided catalyst was more resistant to sulfidation and carbon deposition during the steady stage. Furthermore, the catalyst lifetime of the 973 K-nitrided catalyst was the longest of the nitrided catalysts. The 973 K-nitrided catalysts were rapidly deactivated during the initial stage, but were deactivated very slowly after 3 h in the steady state. The N/Mo atomic ratio of the 973 K-nitrided catalyst was higher than those of the other nitrided catalysts before and during the reaction. The nitrogen atoms of the 973 K-nitrided catalyst were removed to a lesser extent than those of the other nitrided catalysts. Therefore, the greater formation of molybdenum nitride (high N/Mo ratio) on the surface, the higher HDS activity and longer catalyst lifetime. Although sulfur and carbon are deposited on the 973 K-nitrided catalyst more than the other catalysts as shown in Table 2, the activity of the 973 K-nitrided catalyst is protected by sulfidation and carbon deposition, i.e. active Mo atoms are likely to be protected by nitrogen atoms on the top surface of the Mo nitride which leads to less sulfiding and coking of the active Mo atoms. Furthermore, hydrogen activated by a Mo atom of Mo nitride attacks sulfur adsorbed on a neighboring Mo atom.

4. Conclusion

The changes in the nitrogen release, sulfidation, and carbon deposition from the XPS analysis for the 773–1073 K-nitrided 12.5% Mo/Al_2O_3 catalysts during dibenzothiophene HDS in a fixed-bed microreactor at 573 K and 10.1 MPa total pressure were studied. The deactivation of the catalysts was described by an equation based on the assumption that two types of deactivated species, i.e. easily deactivated and deactivated with difficulty, were present on the catalyst surface. The former species of the nitrided catalysts were deactivated by a factor of 150–1600 times compared to the latter species. The 973 K-nitrided catalyst is a long-lifetime catalyst for dibenzothiophene HDS. The rapid deactivation of the nitrided catalysts was mainly due to carbon deposition and the slow deactivation due to nitrogen loss as well as due to nitrogen release and sulfidation, respectively.

Acknowledgements

This research was partly supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science, Sports, and Culture, Japan.

References

[1] M. Nagai, T. Miyao, T. Tsuboi, Catal. Lett. 18 (1993) 9.

[2] K.R. McCrea, J.W. Logan, T.L. Tarbuck, J.L. Heiser, M.E. Bussell, J. Catal. 171 (1997) 255.

[3] U.S. Ozkan, L. Zhang, P.A. Clark, J. Catal. 172 (1997) 294.

[4] M. Nagai, A. Irisawa, S. Omi, J. Phys. Chem. 102 (1998) 7619.

[5] K. Hada, J. Tanabe, S. Omi, M. Nagai, J. Catal. 207 (2002) 10.

[6] E.J. Markel, J.W. Van Zee, J. Catal. 126 (1990) 643.

[7] F. Diez, B.C. Gate, J.T. Miller, D.J. Sajkowski, S.G. Kukes, Ind. Eng. Chem. Res. 29 (1990) 1999.

[8] D.B. Dadyburjor, A.P. Raje, J. Catal. 145 (1994) 16.

[9] F. Panarello, S. Guanziroli, Preprints, Div. Petro. Chem. ACS 40 (1995) 542.

[10] G. Gualda, S. Kasztelan, J. Catal. 161 (1996) 319.

[11] R. Fix, R.G. Gordon, D.N. Hoffman, Thin Solid Films 288 (1996) 166.

[12] K. Hada, M. Nagai, S. Omi, J. Phys. Chem. B 105 (2001) 4084.

[13] R.B. Quincy, M. Houalla, A. Proctor, D.M. Hercules, J. Phys. Chem. 93 (1989) 5882.

[14] J.C. Muijsers, Th. Weber, R.M. van Hardeveld, H.W. Zandbergen, J.W. Niemantsverdriet, J. Catal. 157 (1995) 698.

[15] B.J. Tan, Y. Xiao, S.L. Suib, Chem. Mater. 3 (1991) 652.

[16] H. Viswanathan, Y.-Q. Wang, A.A. Audi, P.J. Allen, P.M.A. Sherwood, Chem. Mater. 13 (2001) 1647.

[17] S.A. Evenson, C.A. Fail, J.P.S. Badyal, Chem. Mater. 12 (2000) 3038.

[18] K. Idei, Y. Yamamoto, H. Yamazaki, Kagaku Kogaku Ronbunshiu 21 (1995) 972.

[19] J.B. Butt, E.E. Petersen, Activation, Deactivation, and Poisoning of Catalysts, Academic Press, San Diego, CA, 1988.

[20] M. Nagai, M. Kiyoshi, H. Tominaga, S. Omi, Chem. Lett. (2000) 702.

[21] S. Li, J.S. Lee, J. Catal. 178 (1998) 119.

[22] L.P.A.F. Elst, S. Eijsbouts, A.D. van Langeveld, J.A. Moulijn, J. Catal. 196 (2000) 95.