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Active Site Distribution of Nitrided CoMo/Al₂O₃ Catalyst during Hydrodesulfurization of Dibenzothiophene: A Non-parametric Study

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The distribution of active sites on a nitrided CoMo/Al₂O₃ catalyst was studied based on a non-parametric determination method using the conversion rate of hydrodesulfurization of dibenzothiophene. This method makes use of a Fredholm integral equation of the first kind and provides the activity distribution of the catalytic active sites. These active sites were discussed based on the reaction products during the reaction, the surface properties by CO adsorption and X-ray photoelectron spectroscopy. The distribution function revealed two active sites of the nitrided catalyst with different rate constants for the hydrogenation of dibenzothiophene on Site I and for the C–S hydrogenolysis on Site II. Site II had a 58.3 times higher rate and 1.27 times the population than Site I for the 973 K-nitrided catalyst.

Keywords

Hydrodesulfurization, Nitrided cobalt molybdenum, Fredholm equation, Non-parametric determination, Active site distribution

1. Introduction

The catalytic active sites on the surface of CoMo catalysts for hydrodesulfurization (HDS) and hydrodenitrogenation have been extensively studied based on characterization of the catalyst surfaces, such as temperature-programmed desorption, infrared and X-ray photoelectron spectroscopies and extended X-ray absorption fine structure. Another method is to determine the active sites on the surface during the reaction by a parametric or non-parametric method using reaction data. In previous papers^{1),2)}, the deactivation behavior of the nitrided Mo/Al₂O₃ catalyst during dibenzothiophene HDS was studied based on a simulation using a first-order reaction represented by two exponentials, $\Phi = \beta_1 \exp(-\alpha_1 t) + \beta_2 \exp(-\alpha_2 t)$, where β_1 and β_2 are constants (the number of active sites), α_1 and α_2 are deactivation rate constants, and t is the time on stream. This kinetic model presented an appropriate assumption of two active sites on the surface for catalyst deactivation during the HDS reaction. This result supported the idea that the direct desulfurization of dibenzothiophene occurred to form biphenyl on one active site and the desulfurization to form cyclohexylbenzene on another site after the hydrogenation on the nitrided Mo/Al₂O₃ catalyst^{1)–3)}, the same reaction scheme

as proposed in earlier studies on sulfided Mo/Al₂O₃^{4)–6)}. In this paper, the catalytic active sites on the nitrided CoMo/Al₂O₃ catalyst during dibenzothiophene HDS are investigated by the non-parametric method instead of using simulated equations.

Zeldovich and Roginsky originally studied the heterogeneity of a catalyst surface concerning adsorption and developed a general analysis of an isotherm equation for adsorption on nonuniform surfaces using the distribution of heat adsorption^{7)–10)}. The adsorption equation with the coverage was adopted in terms of the proportion of sites of adsorption energy (Q_i) covered with molecules and is given by

$$\sigma_i(P, Q_i) = b_0 \exp\{Q_i/RT\}P/[1 + b_0 \exp\{Q_i/RT\}P] \quad (1)$$

where P is the pressure and b_0 is a quantity which is independent of Q ⁹⁾. The adsorption isotherm $\sigma(P, Q)$ on a nonuniform surface was expressed as a function of the pressure P in the formula and described to Eq. (2)

$$\sigma = \int_{Q_1}^{Q_2} \sigma(P, Q) \rho(Q) dQ \quad (2)$$

where $\rho(Q)$ is the distribution function of the heat of adsorption Q , and Q_1 and Q_2 are the lower and upper limits of the heats of adsorption on the surface, respectively. Their efforts toward elucidation of a general adsorption on a heterogeneous surface encouraged us to find the solution to the adsorption of molecules and the distribution of activity and population of reactive species on the active sites during reaction. The heat of

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adsorption on the surface sites during the reaction is related to the interaction energy of each adsorbed molecule with the catalytic sites upon the surface. Thus, the distribution of catalytic sites is related to the reactivities (reaction rate constant) of adsorbed reacting species on the active sites. Equation (2) is transformed into Eq. (3) which becomes the Fredholm integral equation of the first kind.

$$\phi(t) = \int h(t, k) \times f(k) dk \quad (3)$$

where $\phi(t)$ is relative conversion of the HDS rate at a time (t) and $h(t, k)$ is a nondegenerate kernel, in our case, $\phi(t)$ is the change in the strength of adsorbed reactive species on the catalyst surface with time. $f(k)$ is the distribution of reactivity of the adsorbed species on the catalytic sites. This model equation contains the simplification of assumption that individual species react in a first-order manner and that the subsequent adsorbed reactive species have rate constants which depend on the activity of the catalytic sites. Therefore, $f(k)$ represents the distribution of active sites with activity given by the rate constant of k . The site distribution analysis for $h(t, k) = k \exp(-kt)$ was applied to the reactivity of the adsorbed species during CO hydrogenation^{11)~14)} as well as the analysis for $h(t, k) = \exp(-kt)$ during dibenzothiophene HDS on Mo sulfide catalyst¹⁵⁾. In this study, the distribution of activity and selectivity of the active sites on the nitrided CoMo/Al₂O₃ catalyst during dibenzothiophene HDS was investigated based on the non-parametric determination using Eq. (3) with a kernel of $\exp(-kt)$. The distribution was related to the reaction products in the reaction, with the surface properties determined by CO adsorption and X-ray photoelectron spectroscopy (XPS).

2. Experimental

A CoMo/Al₂O₃ catalyst (Ketjenefine 124-1.5, 4 wt% CoO, 12 wt% MoO₃) was calcined in air at 823 K for 3 h. The CoMoO₃/Al₂O₃ was packed on a porous quartz plate in a quartz microreactor, oxidized in dry air at 723 K for 1 h and then cooled to 573 K. The catalyst was nitrided from 573 K to a final temperature of 773, 873 or 973 K in flowing ammonia at 4 L h⁻¹ at a rate of 60 K h⁻¹, held at the final temperature for 3 h, and then cooled to room temperature in a stream of ammonia. The nitrided catalyst was removed from the quartz reactor in a glove box filled with argon and transferred to the microreactor for HDS activity measurement.

The HDS of dibenzothiophene on the nitrided CoMo/Al₂O₃ catalyst (1.0 g) was carried out using a fixed-bed microreactor in a high-pressure flow system. The liquid feed, consisting of 13.6 mmol L⁻¹ (0.25 wt% dibenzothiophene) dibenzothiophene dissolved in xylene, was introduced into the reactor at 10 mL h⁻¹, at a

hydrogen flow of 3 L h⁻¹ at 573 K and at a total pressure of 10.1 MPa. The reaction products were separated from gaseous products by a separator, collected at the bottom of the separator and quantitatively analyzed using a Shimadzu FID gas chromatograph with 2 % silicone OV-17. The reaction rates (conversion) of the formed compounds were calculated based on the moles of the formed compounds. The equation was programmed in C using a PC station, according to the algorithm for the implementation of the computational procedure¹⁶⁾.

The numerical problem to be solved is given by Eq. (3). The optimal $f(k)$ is given by the dot product of the kernel $h(t, k)$ in Eq. (3) and a vector, $\mathbf{V}$, which should satisfy Eq. (4)

$$q = (\mathbf{U} + \alpha \mathbf{I}) \mathbf{V} \quad (4)$$

In Eq. (4) q is experimentally measured conversion ($t_i, f(t_i)$) ($i = 1, 2, 3, \dots, N$) of the each time, and $\mathbf{I}$ represents the identity matrix. α is varied systematically and for each fixed α an optimal vector $f(k)$ is found. In our study, the kernel, $h(t, k)$ is given by

$$h(t, k) = \exp(-kt) \quad (5)$$

The matrix $\mathbf{U}$ has $N \times N$ entries which are given by Eq. (6),

$$U_{ij} = \int \exp(-kt_i) \exp(-kt_j) dk \quad (6)$$

The algorithm to find the optimal $\mathbf{V}$ proceeds on the basis of a pure Newton search. Using the obtained $\mathbf{V}$, $f(k)$ is given by Eq. (7)

$$f(k) = \max\{0, \exp(-kt) \mathbf{V}\} \quad (7)$$

In order to find the optimal smoothing parameter, the function $H(\alpha)$ (given by Eq. (8)) is calculated, and the optimum value of α is determined at the minimum of the function $H(\alpha)$.

$$H(\alpha) = \mathbf{q}' \mathbf{T} \mathbf{U} \mathbf{T} \mathbf{q} - 2 \mathbf{q}' \mathbf{T} \mathbf{q} + 2 \|\mathbf{V}\| N \left(\sum_{i=1}^N \frac{1}{\varepsilon_i^2} \right)^{-1/2} \quad (8)$$

$$\mathbf{T} = (\mathbf{U} + \alpha \mathbf{I})^{-1} \quad (9)$$

ε_i in Eq. (8) is an indeterminate error and set to 0.05 in this study. Finally, the curve is obtained in the forms of $f(k)$ and k . This study shows two peaks at k_1 for Site I and k_2 for Site II. The former peak k_1 has population (x_1) calculated for the relative peak area and the latter has a population (x_2).

The CO adsorption of the catalysts was measured using the Omnisorp 100CX analyzer. Irreversible CO chemisorption was determined using the Omnisorp 100CX analyzer. Before measuring the CO adsorption, the catalysts were first heated from room temperature to 673 K at 10 K min⁻¹ in a stream of He, purged at 673 K for 2 h, subsequently pretreated in a stream of H₂ at 623 K for 1 h, and then cooled to 303 K in a vacuum.

Fig. 1 (A) Relative Conversion, $\phi(t)$, of the HDS Rate at a Time (t) for HDS of Dibenzothiophene on 973 K-nitrided Catalyst and (B) Surface Site Distribution by a Plot of $h(t,k)$ of $\exp(-kt)$ for the Nitrided Catalyst at 573 K and 10.1 MPa

Table 1 Comparison of Peak Characteristics of Non-parametric Estimation for Dibenzothiophene HDS

Nitriding temperature [K]	Mo nitride	Site I		Site II		x_2/x_1 [x_2 percent, %]	k_2/k_1
		$k_1^{a)}$ [h^{-1}]	$x_1^{b)}$	$k_2^{c)}$ (h^{-1})	$x_2^{b)}$		
773		0.045	0.831	1.32 (0.560) ^{c)}	0.547	0.658 (39.7)	29.3
873		0.030	0.470	1.76 (0.896) ^{c)}	0.956	2.03 (70.1)	58.7
973		0.036	0.583	2.10 (1.08) ^{c)}	0.741	1.27 (56.0)	58.3

a) Value at one-half of $f(0)$. For Site I, the value k of the peak of $f(k_1)$ is zero.

b) x_1 and x_2 are the population (relative peak areas) of Site I and Site II, respectively.

c) Higher k_2 value at half-maximum of $f(k_2)$ for Site II. (blanket): the value k_2 of the highest peak of $f(k_2)$.

The surface composition of the catalysts were analyzed by X-ray photoelectron spectroscopy using a Shimadzu ESCA 3200 photoelectron spectrometer with Mg K α radiation. The sample, removed from the reactor with xylene solvent, was put into a glovebag dipped in xylene, dried in the glovebag and mounted on a holder with carbon tape without exposure to air. Al 2p (74.6 eV) was taken as a reference to correct the binding energy of the samples. The peaks of the XPS binding energies were deconvoluted using the Origin package software after the analysis data were transferred from the Shimadzu ESCA 3200 to a PC data station. Curve fitting of the Mo 3d peaks was accomplished using an intensity ratio of 2/3 and a splitting of 3.2 eV^{1),17)~20)}. The peaks of Co 2p_{3/2} of CoMo/Al₂O₃ were also deconvoluted at 778.0 to 782.2 eV for Co⁰ to Co³⁺^{19),20)}.

3. Results and Discussion

3.1. Non-parametric Analysis

The HDS of dibenzothiophene on the nitrided CoMo/Al₂O₃ catalyst was carried out in order to obtain the activity distribution of the catalytic sites. The curve of $f(k)$ was calculated from the data for the conversion, $\phi(t)$, for dibenzothiophene HDS on the 973 K-nitrided CoMo/Al₂O₃ (Fig. 1A), and was plotted versus k , as

shown in Fig. 1B. In this study, two active sites are obtained and presented as Site I (rate constant, k_1 and population, x_1) and Site II (k_2 , x_2). The activities of the sites are evaluated by comparing the k_1 value at one-half of $f(0)$ for Site I and k_2 for Site II. k_2 (open value) is the higher k_2 value at half-maximum of $f(k_2)$ and (k_2) the k_2 value at the highest peak of $f(k_2)$ for Site II. x_1 and x_2 are the population (relative peak areas) of Site I and Site II, respectively. One monotonous peak at the low k_1 value was observed, with a small peak at the higher k_2 value for the catalyst. The 973 K-nitrided Mo/Al₂O₃ catalyst exhibited a good curve fitting of the data and had two groups of activity distribution of the catalytic sites. One located below the value of 0.036 h^{-1} (Site I) and the value at 2.10 h^{-1} (Site II) in Table 1. Site II was 58.3 times more active than Site I. Among the parameters, x_1 and x_2 were the populations of the active sites. Site I had a lower activity and a population of 44.0 %, and Site II had a population of 56.0 %.

Figure 2 shows the curves of $f(k)$ for the 773 K-nitrided catalysts during the dibenzothiophene HDS. The 773 K-nitrided catalyst had a Site II with a high k_2 of (0.045 h^{-1}) and a population of 39.7 %. The 773 K-nitrided catalyst exhibited the highest k_1 , the lowest k_2 values for Sites I and II, respectively, and the

Fig. 2 Relative Conversion, $\phi(t)$, of the HDS Rate at a Time (t) for HDS of Dibenzothiophene on (A) 773 K-nitrided Catalyst and Surface Site Distribution of (B) 773 K-nitrided Catalysts by a Plot of $h(t,k)$ of $\exp(-kt)$ during Dibenzothiophene HDS at 573 K and 10.1 MPa

Fig. 3 Relative Conversion, $\phi(t)$, of the HDS Rate at a Time (t) for HDS of Dibenzothiophene on (A) 873 K-nitrided Catalyst and Surface Site Distribution of (B) 873 K-nitrided Catalysts by a Plot of $h(t,k)$ of $\exp(-kt)$ during Dibenzothiophene HDS at 573 K and 10.1 MPa

lowest k_2/k_1 ratio compared to all of the other catalysts. In Fig. 3, the 873 K-nitrided catalyst had Site II with a high population (70.1 %) and a k_2 value of 1.76 h^{-1} , and Site I with a low population, 29.9 %, at the k_1 value of 0.030 h^{-1} . The three catalysts had the curves with two peaks indicating Site I and Site II. The 773 K-nitrided catalyst had Site I with the largest k_1 and the x_1/x_2 ratio, showing more hydrogenation activity and higher site distribution. The activity of Site II of the nitrided catalysts decreased in the following order: 973 K-nitrided > 873 K-nitrided > 773 K-nitrided catalyst. Thus, the two activity distributions support the fact that one active site (Site II) with relative factors of 29.3–58.7 is present at populations of 39.7–70.1 % on the nitrided CoMo catalysts in dibenzothiophene HDS. In a previous paper²¹⁾, the 973 K-nitrided 12.5 % Mo/Al₂O₃ catalyst had Site I of k_1 (0.03 h^{-1}) and x_1 (39.4 %) while Site II had k_2 (1.08 h^{-1}) and x_2 (60.6 %). These values are similar to those of the 973 K-nitrided CoMo/Al₂O₃. These results suggested little effect of the cobalt con-

tent on the activity of the nitrided CoMo/Al₂O₃ catalyst which was different from the sulfided CoMo/Al₂O₃ catalyst.

3.2. Reaction Rate, Active Sites and Product Selectivity

The CO chemisorption and BET surface area of the nitrided CoMo/Al₂O₃ catalyst are shown in Table 2. The irreversible CO adsorption and surface area of the CoMo/Al₂O₃ nitrided at 973 K were $0.0343 \text{ mmol g}^{-1}$ and $321 \text{ m}^2 \text{ g}^{-1}$, respectively. The 973 K-nitrided catalyst had the highest site density of 0.064 nm^{-2} , which did not correspond to the most C–S hydrogenolysis and hydrogenation of dibenzothiophene among the three catalysts. However, the distribution on different sites could not be estimated by characterization. Furthermore, the k value did not correspond to the turnover frequency (TOF) value, although the k value (h^{-1}) is compared to the experimental TOF value (h^{-1}) calculated from the product formation (Table 3). Although the 773 K-nitrided catalyst had the highest TOF for C–S

Table 2 Surface Properties of the Oxidized and Nitrided CoMo/Al₂O₃ Catalysts

Surface property		Oxide	CoMo/Al ₂ O ₃ nitrided at		
			773 K	873 K	973 K
BET surface area	[m ² g ⁻¹]	304	276	329	321
CO uptake	[mmol g ⁻¹]	0.0464	0.0996	0.0957	0.0997
CO irreversible chemisorption	[mmol g ⁻¹]	0.0113	0.0227	0.0277	0.0343
Site density for CO adsorption	[nm ⁻²]	0.092	0.197	0.175	0.186
Site density for irreversible CO adsorption	[nm ⁻²]	0.022	0.049	0.051	0.064

Table 3 Reaction Rate and Product Selectivity of Dibenzothiophene HDS on the Nitrided CoMo/Al₂O₃ Catalyst

Nitriding temperature [K]	Reaction rate [mmol h ⁻¹ g ⁻¹]		TOF [h ⁻¹]		Selectivity BPN/CHB at 14 h
	C-S hydrogenolysis ^{a)}	HY ^{b)}	C-S hydrogenolysis ^{c)}	HY ^{c)}	
773	64	1.1	2.87	0.048	2.5
873	50	1.26	1.855	0.045	3.5
973	59	0.88	1.746	0.026	4.0

a) Formation rate of biphenyl (BPN) and cyclohexylbenzene (CHB).

b) Formation rates of tetrahydrodibenzothiophene (4HDBT) and hexahydrodibenzothiophene (6HDBT).

c) TOF = C-S hydrogenolysis (or HY)/CO irreversible adsorption.

Fig. 4 Reaction Scheme for the HDS of Dibenzothiophene on the Nitrided CoMo/Al₂O₃

hydrogenolysis and hydrogenation in the dibenzothiophene HDS based on the product production, k for C-S hydrogenolysis was the lowest and hydrogenation was the highest. This discrepancy would be caused by reaction product formations in the regime of diffusion control at high reaction temperatures. Thus, the non-parametric determination can estimate each formation of reaction products during the HDS reaction.

The main reaction product was biphenyl with the small amounts of cyclohexylbenzene, tetrahydro- and hexahydrodibenzothiophene for three catalysts as shown in **Table 3**. The 773 K-nitrided catalyst had the higher TOF for hydrogenation and the highest cyclohexylbenzene/biphenyl selectivity, showing the catalyst more hydrogenation activity. The high C-S hydrogenolysis of the 773 K-nitrided catalyst was probably due to the direct sulfur removal from dibenzothiophene by incompletely nitrided CoMo oxides (shown

later in **3.3**). On the other hand, the 973 K-nitrided catalyst had the least hydrogenation activity and the highest biphenyl/cyclohexylbenzene selectivity due to a direct C-S bond cleavage. The distribution and selectivity of the reaction products indicated a network of two reaction routes (**Fig. 4**) as shown in the experimental results obtained with the sulfided⁵⁾ and nitrided^{22)~24)} Mo/Al₂O₃ catalysts. According to previous papers^{4)~6),25)}, the C-S hydrogenolysis occurs on one site of the nitrided catalyst together with the hydrogenation of dibenzothiophene on another site; dibenzothiophene was adsorbed on one active site (Site II) and desulfurized to form biphenyl, and cyclohexylbenzene was formed *via* the hydrogenated dibenzothiophenes on another site (Site I) of the nitrided catalysts. Tetrahydro- and hexahydrodibenzothiophene on Site I were slightly observed. The selectivity of biphenyl formation relative to cyclohexylbenzene for the de-

Table 4 Distribution of Mo Oxidation States of the Oxidized and Nitrided CoMo/Al₂O₃ Catalysts before Reaction

Mo oxidation state	Oxide	CoMo/Al ₂ O ₃ nitrided at		
		773 K	873 K	973 K
Mo ⁰	0	2.2	1.5	3.7
Mo ²⁺	0	0	3.5	21.6
Mo ³⁺	0	8.7	3.5	11.4
Mo ⁴⁺	0	44.7	42.4	34.5
Mo ⁵⁺	36.0	32.8	36.2	18.0
Mo ⁶⁺	64.0	11.6	12.9	10.8

Table 5 Surface Properties of the Oxidized and Nitrided CoMo/Al₂O₃ Catalysts

Element ratio ^{a)}	Oxide	CoMo/Al ₂ O ₃ nitrided at		
		773 K	873 K	973 K
Mo/Al	0.047	0.067	0.087	0.075
Co/Al	0.063	0.072	0.087	0.056
S/Al ^{c)}	-	0.023	0.003	0.007
N/Mo ^{d)}	-	0.200	0.345	0.242
		(0.123) ^{b)}	(0.117) ^{b)}	(0.068) ^{b)}
Co/Mo	1.34	1.08	0.999	0.757
		(1.16) ^{b)}	(0.675) ^{b)}	(0.864) ^{b)}
N/Co ^{e)}	-	0.216	0.345	0.183
		(0.143) ^{b)}	(0.079) ^{b)}	(0.058) ^{b)}

a) Before reaction. b) (blanket) After reaction. c) S/Al ratio after reaction.
d) (N_{1s} + Mo_{2p})/Mo_{3d}. e) (N/Mo)^{d)}/(Co/Mo).

sulfurization on the 973 K-nitrided CoMo/Al₂O₃ catalyst was the highest k_2 value (Site II) in the estimation. The reaction rate and TOF of C-S hydrogenolysis including cyclohexylbenzene formation for the 973 K-nitrided catalyst were close to those of the 873 K-nitrided catalyst. This results from the product selectivity back up a similar k_2/k_1 ratio and the high value for each k_2 and k_1 . As shown in **Table 1**, Site II of the 973 K-nitrided catalyst was 58.3 times more active than Site I. This result suggested that the product distribution in the HDS reaction did not correspond to the HDS activity obtained from the non-parametric calculation. Thus, the non-parametric determination using the Fredholm integral of the first kind provides two types of active sites, of which Site II differs in activity by 29.3-59.7 times more than Site I on the nitrided CoMo/Al₂O₃ catalyst in dibenzothiophene HDS.

3.3. Surface Co and Mo Species by XPS

The active species of the nitrided CoMo/Al₂O₃ catalyst are discussed based on the XPS analysis of the surface Co and Mo species. The valence distributions of the XPS Mo spectrum of the catalyst before reaction are shown in **Table 4**. The Mo⁵⁺ and Mo⁶⁺ ions of the catalysts decreased with increasing nitriding temperature and were distributed at 18.0 % and 10.8 %, respectively, for the 973 K-nitrided catalyst. The Mo⁰ and Mo²⁺ reached 3.7 % and 21.6 %, respectively, at the maximum nitridation temperature of 973 K. The Mo²⁺ ion was observed the most for the 973 K-nitrided

CoMo/Al₂O₃ catalyst, indicating the formation of Mo nitride. In previous papers^{18),19)}, the total distribution of Mo⁰ and Mo²⁺ was reported to be 70 % for bulk Co(30 %)/Mo(65 %) nitrided at 973 K. As a result, the nitridation hardly reduced Mo oxides of alumina-supported Co(4 %)/Mo(12 %) catalyst to metals or nitrides.

In **Table 5**, the 973 K-nitrided catalyst had the lowest Co/Mo ratio and it was the most active for the desulfurization, suggesting that much more molybdenum atoms contained in the catalyst were active for the desulfurization. The nitridation at 873 K increased the N/Mo ratio before reaction, but after reaction decreased from 0.345 to 0.117 lower than the ratio (0.242) of the 973 K-nitrided catalyst before reaction. On the other hand, the 773 K-nitrided catalyst had the lowest ratios of Mo/Al and Co/N and the highest Co/Mo and (after reaction) S/Al among the nitrided catalysts. This 773 K-nitrided catalyst was the least active for the desulfurization and the highest for hydrogenation. As a result, this is probably due to the faster hydrogenation on the formed sulfide because of sulfidation of reduced Mo and Mo oxide, because it contained much more sulfur after reaction (3-8 times higher than the two catalysts). For the nitridation in catalyst preparation, Mo nitride was not fully formed in the 773 K-nitrided catalyst. The 773 K-nitrided catalyst exhibited the highest k_1 for Site I (hydrogenation) and the lowest k_2/k_1 and x_2/x_1 ratios as shown in **Table 1**. This estimation result

was supported by the S/Al ratio after the reaction from the XPS analysis, which the 773 K-nitrided catalyst was sulfurized during the reaction because of incomplete nitridation during catalyst preparation. Furthermore, the 973 K-nitrided catalyst had a lower Mo/N ratio, leading to enough nitridation as the composition of $\text{Co}_{5.5}\text{Mo}_{7.3}\text{N}$ before reaction based on the XPS data (but the nitrogen composition decreased to $\text{Co}_{17}\text{Mo}_{20}\text{N}$ after reaction). This CoMo nitride formation facilitated the selectivity of the direct C-S bond cleavage of dibenzothiophene to biphenyl due to the highest k_2 and higher x_2 values. The Co atom of the nitrided CoMo/ Al_2O_3 catalyst might not play an important role in dibenzothiophene HDS. In a previous paper¹⁹⁾, cobalt species penetrated into the bulk and increased the surface area of $\gamma\text{-Mo}_2\text{N}$. Also, the highly active 973 K-nitrided bulk CoMo catalyst had a slightly reduced Mo nitride containing Mo^0 and Mo^{2+} . As a result, Mo nitride contained appropriately two active sites, probably $\text{Mo}^{\delta+}$ of $\gamma\text{-Mo}_2\text{N}_{0.78}$ as Site II and metallic Mo as Site I. The alumina-supported CoMo nitride would contain bifunctional catalytic sites, characterizing the metallic molybdenum sites for the hydrogenation and $\text{Mo}^{\delta+}$ for the desulfurization. Consequently, the non-parametric determination can elucidate the activity distribution of catalytic sites on the catalyst using the Fredholm integral of the first kind, even though the characterization by various methods could not fully clarify them.

4. Conclusions

The non-parametric determination of the activity distribution of the catalytic sites on nitrided CoMo/ Al_2O_3 catalyst was studied based on the Fredholm integral of the first kind. The general form of dibenzothiophene HDS was described as $\phi(t) = \int h(t,k)f(k)dk$, where $h(t,k) = \exp(-kt)$. The 973 K-nitrided CoMo/ Al_2O_3 catalyst contained two types of active sites with different activity distributions; one of the active sites had a 58.3 times higher activity at a population of 56.0 % for desulfurization than the other sites for hydrogenation. Thus, the two activity distributions of the nitrided Mo/ Al_2O_3 catalyst support the fact that one active site with

a relative factor of 29.3-58.7 was present at populations of 39.7-70.1 % in the dibenzothiophene HDS.

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要 旨

コバルト・モリブデン窒化触媒のジベンゾチオフェンの水素化脱硫反応における触媒活性点分布
—ノンパラメトリック研究—

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ジベンゾチオフェンの水素化脱硫反応時の経時時間における活性変化から, $\text{CoMo}/\text{Al}_2\text{O}_3$ 窒化処理触媒の活性点の分布をノンパラメトリックな方法により研究した。この方法は Fredholm 第1積分方程式を用い, 触媒の活性点の活性分布を与える。CO 吸着, XPS 測定による表面特性と反応時の生成物分布に基づいて, これらの活性点を議論した。この分布関数は, 活性点

Site I 上で進行するジベンゾチオフェンの水素化反応と活性点 Site II 上での C-S 結合の水素化分解に対する異なる反応速度を有する二つの活性点を明らかにした。973 K 窒化処理 $\text{CoMo}/\text{Al}_2\text{O}_3$ 触媒の Site II は Site I より 58.3 倍の反応速度定数を持ち, 1.27 倍の活性点数を有する。

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