New approach to active sites analysis of molybdenum-containing catalysts for hydrodesulfurization and hydrodenitrogenation based on inverse problem, fractal and site-type analyses

Masatoshi Nagai *, Nguyen Thanh Tung, Yasutaka Adachi, Kentaro Kobayashi

Tokyo University of Agriculture and Technology, BASE, Koganei, Tokyo, Japan

ABSTRACT

A new approach to the active sites of Mo-containing catalysts for hydrodesulfurization and hydrodenitrogenation was studied by three methods, i.e., the inverse problem, fractal and site-type analyses. The distribution of the active sites of the sulfided and nitrided Mo/Al$_2$O$_3$ catalysts was studied based on the inverse problem using the Fredholm integral equation. The two active sites of the nitrided Mo/Al$_2$O$_3$ catalyst have a distribution involving the reaction rate and population; one site for a fast rate and large population and the other site for a slow rate and small population. The fractal analysis was applied to the morphology of the Mo nitride and the reactivity for the carbazole hydrodenitrogenation and related to the Mo^0 or Mo$^{\delta+}$ species. The fractal dimension of the Mo nitride surfaces was calculated to be from 2.02 to 2.60 and estimated the two active sites for the hydrogenation and denitrogenation. These sites were related to the Mo^{3+} of γ-Mo$_2$N from the XPS analysis. The active sites for the hydrodesulfurization of 4,6-dimethyldibenzothiophene on a sulfided NiMo/Al$_2$O$_3$ catalyst were discussed based on the site-type analysis. A third active site of the sulfided NiMo/Al$_2$O$_3$ catalyst was proposed for the simultaneous desulfurization and hydrogenation from 4,6-dimethyldibenzothiophene to 3,3-dimethylbicyclohexyl as well as the two active sites for the hydrogenation to 3-methylcyclohexyltoluene and the desulfurization to 3,3-dimethylbiphenyl.

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1. Introduction

Many studies have focused on the deep hydrodesulfurization (HDS) process in response to environmental and clean fuel legislation [1–3]. The current increase in energy demands has raised a lot of interest in the hydrotreatment of low-rank oils [4,5] which contain various three-ringed sulfur and nitrogen compounds, such as dibenzothiophene (DBT), 4,6-dimethyldibenzothiophene (DMDBT) and carbazole, to reduce the effectiveness of the heavy-oil desulfurization by blocking the access of sulfur compounds to the catalysts' active sites. Moreover, the nitrogen compounds are known to inhibit the HDS catalysts and degrade the petroleum feedstock properties [6–8].

In our earlier studies of the selective poisoning on HDS [9–11] over sulfided Mo/Al$_2$O$_3$ catalysts, it was shown that the best kinetic

equations for the formation of biphenyl (BPN) and cyclohexylbenzene (CHB) were proposed as follows:

$$r_{BPN} = k_{BPN} K_D P_D K_H P_H / \left(1 + K_D P_D + K_H P_H + \sum K_{HD} P_{HD}\right)^2$$

$$r_{CHB} = k_{CHB} K_{HHD} P_{HHD} K_H P_H / \left(1 + K_D P_D + K_H P_H + \sum K_{HD} P_{HD}\right)^2$$

where k_i is the reaction rate constant, K_i the equilibrium constant of adsorption, P_i the partial pressure, and D, HHD, H and HD of i are DBT, hexahydrodibenzothiophene, and the hydrogen and hydrogenated DBT compounds adsorbed on the desulfurization site, respectively. The BPN was formed from the direct desulfurization of DBT and the CHB from the desulfurization of hexahydrodibenzothiophene on one active site, while the hydrogenated DBT was formed from the successive hydrogenation of DBT on the other site. For the hydrodenitrogenation (HDN) of carbazole and acridine [12,13] over the sulfided Mo/Al$_2$O$_3$ catalysts, the reaction proceeded via similar pathways. The duality of the C–S (and C–N) bond scission and hydrogenation was found for the two active

sites of the sulfided Mo/Al_2O_3 catalyst for the HDS and HDN. These described methods are a direct problem.

1.1. Inversion problem

The active sites have a distribution involving the reaction rate and population of individual sites on the catalyst surfaces. An inverse problem analysis that can distinguish the different active sites during the reaction for the elucidation of the heterogeneity of a surface is available. The heterogeneity of a catalyst surface undergoing adsorption was studied and developed into a general analysis of an isotherm equation using the distribution of heat adsorption by Zeldowitch and Roginsky [14–17]. The generalized Langmuir adsorption equation is given by

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

where P is the pressure and b_0 is a quantity which is independent of Q. The adsorption isotherm $\sigma(P, Q)$ is described by Eq. (2)

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

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 heat of adsorption on the surface, respectively [17]. The distribution of heat adsorption is converted into the distribution, $f(k)$, of the rate coefficient (k) of the reactive species on the active sites on which the adsorbed species were individually converted using the rate coefficient. Eq. (2) is then transformed into Eq. (3) of the Fredholm integral equation of the first kind.

$$\phi(t) = \int h(t, k) \cdot f(k)dk \qquad (3)$$

where $\phi(t)$ is the relative conversion of the HDS rate at time (t) and $h(t,k)$ is a kernel. The inverse problem method estimates the distribution of active sites from the measured conversion results. In this study, the active sites with the distribution of rate and population on the sulfided and nitrided Mo/Al_2O_3 catalysts were analyzed based on the inverse problem using the Fredholm integral equation of the first kind [18–21]. Furthermore, the active sites were characterized based on the temperature-programmed reduction (TPR) and XPS analyses.

1.2. Fractal analysis

The fractal concept describes the heterogeneous surfaces and the morphology of porous materials [22]. Mandelbrot is a pioneer in this field and defined that a fractal object had the dimension which was greater than the topological dimension, but less than or equal to the dimension of the Euclidean space. He reported that the length of the coastline of England was measured by different compass steps and obtained a power law of the scale [23]. The surface fractal dimension (D) of porous surfaces was given by $V_m = k\sigma^{-D/2}$ [24,25]. Here, V_m is the monolayer adsorption of various molecules, k the constant and σ is the cross-sectional area of the adsorbents. Thus, the D value is determined from the monolayer capacities of molecules of different molecular sizes, and can provide valuable information about the catalyst surface morphology.

For application of the fractal analysis to the catalysis field, the reaction rate was related to the radii of the catalyst particles during the benzene hydrogenation, hydrogenolysis, oxidation and isomerization on the catalysts including Fe, Ni, noble metals and bimetallic catalysts dispersed on various supports [24–26]. Furthermore, the fractal dimension reported the relation to the surface morphologies during the hydrogenation synthesis of a pharmaceutical compound [27] and the linear relation to the catalytic activity of MoP for the HDS of DBT [28]. However, the surface morphology of the catalysts from the fractal dimension was neither compared to the BET surface area nor related to the catalytic active sites. In this study, the fractal dimension from the adsorption measurement of a series of molecules with various sizes was determined, and compared to the BET surface area and related to the activity of the Mo nitride for the C–N bond scission and hydrogenation during the carbazole HDN [29]. The active sites were discussed based on the fractal dimension along with the XRD, TPR and XPS analyses.

1.3. Type-site analysis

The active sites for the HDS of DBT have been studied and reported two active sites for the desulfurization and hydrogenation [9,11,12]. The HDS of more refractory sulfur-containing molecules, such as DMDBT, has received increased attention in recent years and has been studied. It reports that DMDBT can occur through two different pathways; in a successive pathway, 3,3-dimethylbicyclohexyl (DMBCH) was formed from the hydrogenation of 3-methylcyclohexyltoluene (MCHT) through DMDBT [30–32] via DMBP [33–35], while in the parallel pathway, DMBCH, was formed from the desulfurization of the undetected 4,6-dimethylperhydrodibenzothiophene through DMthDBT [36–39]. These active sites for the simultaneous hydrogenation and desulfurization (or denitrogenation) are still debated. There is a further point which needs to be clarified as to whether the formation of propylcyclohexene during the HDN reactions of o-propylaniline and quinoline [40–42] occurs, and those of BCH during the HDS of DBT [9,11] and the carbazole HDN [43]. The molar ratio of the feed to the nitrogen compounds should be selected and controlled in order to elucidate the active sites on the catalyst surface. The catalytic sites including vacant sites would not be fully lost at all with a small amount of nitrogen compounds [44], but they were controlled with large amounts of nitrogen compounds due to the strong adsorption of the nitrogen compounds and their products on the vacant sites and other sites. In this study, the site-type analysis shed light on the simultaneous hydrogenation/desulfurization reaction for the HDS of DMDBT on a sulfided phosphorus-doped $NiMo/Al_2O_3$ catalyst. This is based on the Langmuir adsorption and the behaviors of the reaction products in a competitive reaction of DMDBT with large amounts of nitrogen compounds (carbazole, acridine or quinoline) with the molar ratios of the nitrogen compound to DMDBT of 1:1 and 1:2. This study involves an understanding of the active sites of the sulfided $NiMo/Al_2O_3$ for the simultaneous reaction. Furthermore, the active sites of the catalyst were discussed based on the XPS and TEM measurements. In these three studies, new angles of the inverse problem, fractal analysis and site-type analysis offer a new understanding of the active sites for the HDS and HDN reactions.

2. Experimental

2.1. Inverse problem and calculations

The 12.5% Mo/Al_2O_3 catalyst was prepared from a mixture of ammonium paramolybdate with γ-Al_2O_3 powder, which was calcined in air at 823 K for 3 h. The catalyst was packed in a quartz microreactor, oxidized in dry air at 723 K, cooled to 573 K, nitrided from 573 K to a final temperature of 773 K (or 973 K and 1173 K) in flowing NH_3 at 4 L h^{-1} at the rate of 60 K h^{-1}, held at the final temperature for 3 h, then cooled to room temperature (nitrided catalyst). The 12.5% Mo/Al_2O_3 catalyst was reduced at 773 K in flowing hydrogen at 4 L h^{-1} for 3 h after the oxidation (reduced catalyst). A 97.1% Mo/Al_2O_3 catalyst was prepared using a mixture of 97.1% MoO_3 and γ-Al_2O_3 hydrogel (2.9%) (Nikki Chemical Co.) [18–21] as