JOURNAL OF CATALYSIS **66**, 93–100 (1980)

Surface Structure and Catalytic Activity of Sulfided MoO_3/Al_2O_3 Catalysts: Hydrodesulfurization and Hydrogenation Activities

YASUAKI OKAMOTO, HIROYUKI TOMIOKA, TOSHINOBU IMANAKA, AND
SHIICHIRO TERANISHI

Department of Chemical Engineering, Faculty of Engineering Science, Osaka University, Toyonaka, Osaka 560, Japan

Received February 13, 1980

The hydrogenation activities of sulfided MoO_3/Al_2O_3 catalysts for the butenes produced in the hydrodesulfurization of thiophene were studied in connection with the surface structure of the catalysts. The hydrodesulfurization of thiophene was carried out at 400°C and atmospheric pressure. It was found that the catalytic activity for the hydrogenation depended simply on the sulfidation degree of molybdenum (S/Mo by XPS) regardless of the molybdenum content, calcination temperature, and sulfidation conditions as well as for the hydrodesulfurization. In the low-sulfur-content catalysts ($S/Mo < 1$), the relative activity for the hydrogenation to the hydrodesulfurization was constant, implying that only one kind of molybdenum species, which is active for both reactions, is present. On the basis of the relationships between the relative activity and the sulfidation degree of molybdenum, it is suggested that two-dimensional MoS_2 (monolayer structure) is initially formed at the expense of the above species and subsequently transformed to three-dimensional MoS_2 microcrystals by further sulfidation of the catalysts, accompanying the sintering of molybdenum.

INTRODUCTION

In our previous papers (*1*) on MoO_3/Al_2O_3 catalysts, it was found that the intrinsic activity of molybdenum (conversion per gram of MoO_3) for the hydrodesulfurization (HDS) of thiophene depended on the sulfidation degree of molybdenum regardless of the MoO_3 content (2.4–23.1 wt%), calcination temperature (550 and 700°C), and pretreatment conditions (prereduction, presulfidation, and nonpretreatment). The intrinsic activity of molybdenum increased linearly with increasing the S/Mo atomic ratio up to $S/Mo = 1$ and subsequently decreased with further sulfidation of molybdenum, showing a good volcano-type curve. Combining these results with the observations on the changes in the surface structure induced by sulfidation and pyridine adsorption experiments, it has been proposed (*1*) that a molybdenum species (**1**) with $S/Mo(IV) = 1$ composition is present on partially sulfided MoO_3/Al_2O_3 catalysts and that species (**1**) has higher intrinsic activity for the HDS of thiophene than MoS_2 which is progressively formed with increasing the S/Mo ratio in the $S/Mo > 1$ region. To reveal the surface structure in more detail, it will be fruitful to examine the relationships between the selectivity in the HDS of thiophene and the sulfidation degree of molybdenum.

According to Boudart (*2*), catalytic reactions can be classified into two groups: structure sensitive or demanding and structure insensitive or facile reactions. Siegel (*3*) proposed a relationship between the degree of coordinative unsaturation and the set of elementary reactions involving hydrogen and simple olefins which may occur at a particular site on the surface of a transition metal oxide. With the relationships between the activity and the configuration of a molybdenum atom in MoS_2, Tanaka and Okuhara (*4*) pointed out the importance of the number of coordinative unsaturation of the molybdenum atom for the hydrogenations of olefins and dienes

0021-9517/80/110093-08$02.00/0

and the isomerization of olefins. On the other hand, Stevens and Edmonds (*5*) have shown by using MoS_2 catalysts that the butane/C_4 products ratio in the HDS of thiophene is much higher on the MoS_2 catalysts comprised preferentially of edge planes than on the basal-plane-rich MoS_2 catalysts, while the thiophene HDS activities of these catalysts are comparable. Therefore, the hydrogenation of butenes is a highly structure-sensitive reaction, whereas the HDS of thiophene would be a facile reaction. The surface structure of sulfided MoO_3/Al_2O_3 catalysts would be clarified more by applying the above concepts to selectivity in the HDS of thiophene.

In this study, the catalytic activity for the hydrogenation of butenes produced in the HDS of thiophene was investigated in connection with the activity for the HDS of thiophene to examine our proposals (*1*) and to obtain more detailed information about the surface structure of sulfided MoO_3/Al_2O_3 catalysts. The relative activity of the catalyst for the hydrogenation to the HDS was found to be a function of the sulfidation degree of molybdenum. On the basis of the relationships between them, surface models of the sulfided catalysts were suggested, including the morphology of MoS_2 formed on the MoO_3/Al_2O_3 catalysts during the sulfidation.

EXPERIMENTAL METHODS

Catalysts

MoO_3/Al_2O_3 catalysts were prepared as follows. Aqueous solutions of ammonium paramolybdate were used to impregnate γ-Al_2O_3 (Nishio Industry Co. Ltd., Type AE-11). The water was evaporated to dryness at 90°C under stirring, followed by drying at 100°C for 16 h and calcining at 550°C for 5 h in air. Some parts of the catalysts calcined at 550°C were recalcined at 700°C for 5 h. The catalysts were used in powders as prepared. The surface areas of these catalysts have been shown in the previous paper (*1*).

Procedures

The HDS of thiophene was carried out over the MoO_3/Al_2O_3 catalysts (usually 0.154 g) at 400°C and atmospheric pressure using a conventional fixed-bed flow reactor in a differential mode. The reaction was undertaken after one of the three kinds of pretreatment at 400°C for 1 h: (a) prereduction with H_2 (50 ml/min), (b) presulfidation with CS_2/H_2 (1/9, H_2; 27 ml/min), and (c) nonpretreatment in which the catalyst was contacted with a reaction mixture, thiophene/benzene/H_2 (1/0.8/18, H_2; 50 ml/min), immediately after a N_2 treatment at 400°C. Hydrogen and nitrogen were purified by passage through copper turnings at 350°C and a zeolite trap at −78°C. The reaction reached steady state after ca. 3 h for the prereduced and oxidic catalysts and after ca. 2 h for the presulfided catalysts. The reaction gas was analyzed by gas chromatography. The conversion of thiophene was determined by using benzene as an internal standard, since no hydrogenation of benzene was detected under our reaction conditions.

The sulfidation degree of molybdenum was elucidated by means of X-ray photoelectron spectroscopy (Hitachi 507, Al$K\alpha_{1,2}$ radiation) without exposing the catalyst sample, which had reached steady-state activity, to air or moisture using a N_2-filled glove box attached to the spectrometer (*1*). In these procedures, no oxidized sulfur was detected by XPS. The S_{2p}/Mo_{3d} peak area intensity ratios (S_{2p} binding energy, 162.0 eV, referenced to Al_{2s}, 119.1 eV) were converted to S/Mo atomic ratios by using the atomic sensitivities obtained from MoS_2 and $CoSO_4$ powders as standards, which were ground in N_2 atmosphere. The detailed procedures have been described in the previous papers (*1*).

RESULTS AND DISCUSSIONS

The C_4 products in the HDS of thiophene were 1,3-butadiene, three *n*-butene isomers, and *n*-butane. The product distribu-

TABLE 1

Conversion Data for the Hydrodesulfurization of Thiophene at 400°C and Atmospheric Pressure over MoO_3/Al_2O_3 Catalysts and Sulfidation Degree of Molybdenum

wt% MoO_3	Calcination temperatures (°C)	Pretreatment[a]	Raw conversion[b] (%)	Intrinsic activity[c]	S/Mo[d]	Product distribution[e]					k_{HG}/k_{HDS}[f]
						Butane/C_4 (%)	Butene			Butadiene/C_4 (%)	
							1 − b	t − 2 (%)	c − 2		
2.4	550	H	1.4	3.6	0.29	1.5	37.5	39.1	23.4	2.2	1.10
4.8	550	H	3.0	4.1	0.41	3.4	36.3	38.8	24.9	1.0	1.12
		N	4.1	5.5	0.50	4.6	34.7	39.6	25.7	1.1	1.15
		S	5.9	8.0	1.60	7.8	33.0	41.3	25.7	1.1	1.36
	700	H	5.2	7.1	0.69	5.6	33.3	40.7	26.0	0.5	1.08
6.5	550	H	7.7	7.7	0.81	8.0	33.1	41.0	25.9	0.2	1.04
9.1	550	H	17.2	12.3	1.12	17.1	33.7	40.2	26.1	0.3	0.99
13.0	550	H	20.6	10.2	1.25	19.1	32.5	40.9	26.4	0.2	0.91
		S	6.7	3.4	1.72	10.5	30.9	42.6	26.5	0.4	1.63
16.7	550	H	19.6	7.7	1.31	20.4	32.5	41.1	26.4	0.2	1.05
		N	23.6	9.2	1.42	28.6	32.0	41.4	26.5	0.1	1.30
23.1	550	H	23.8	6.7	1.45	30.5	33.5	40.2	23.6	0.2	1.41
		S	8.8	2.5	1.84	15.4	33.3	40.6	26.0	0.6	1.90

[a] Pretreatment conditions: H, prereduction with H_2 at 400°C for 1 h; N, nonpretreatment; S, presulfidation with CS_2/H_2 at 400°C for 1 h.

[b] Reaction conditions: reaction temperature, 400°C; thiophene/benzene/H_2, 1/0.8/18 (mol/mol/mol); H_2 flow rate, 50 ml/min; catalyst weight, 0.154 g.

[c] (Raw conversion(%)/g MoO_3) × 10^{-2}.

[d] Atomic ratio obtained by XPS.

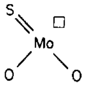
[e] Butane and butadiene, percentage fraction in the C_4 products; butene, percentage fraction in the butenes (1 − b, but-1-ene; t − 2, *trans*-but-2-ene; c − 2, *cis*-but-2-ene).

[f] Defined by Eq. (5).

tions are summarized in Table 1, together with the raw conversion of thiophene and the sulfidation degree of molybdenum (S/Mo, atomic ratio). The effect of the pretreatment conditions on the S/Mo ratio has been discussed in the previous papers (*1*). The concentration of butadiene was very low and the *cis-/trans*-but-2-ene ratio was almost equilibrated in all cases. However, but-1-ene was in excess of the equilibrium proportion with respect to the but-2-enes. These observations are in good agreement with those of other workers (*6, 7*).

It is evident that butane is produced by the hydrogenation of butenes, since the proportion of butane approached zero with decreasing the conversion of thiophene. Although primary products in the HDS of thiophene are not well established, it seems that butadiene is initially produced in the reaction and that it is selectively and quickly hydrogenated to but-1-ene (*4, 8*), which is subsequently isomerized to but-2-enes on acid sites forming an equilibrium *cis/trans* ratio. This conforms to the fact that the hydrogenation of butadiene provides a product distribution similar to that in the HDS of thiophene (*8*).

The intrinsic activity of molybdenum (raw conversion per gram of MoO_3) for the HDS of thiophene is plotted in Fig. 1 as a function of the sulfidation degree of molybdenum. The correlation in Fig. 1 is identical to that reported previously (*1*) and similar to that obtained by Massoth and Kibby (*9*). The stoichiometry of S/Mo(IV) = 1.0 ± 0.2 was also confirmed by deconvoluting the Mo_{3d} spectra in the $S/Mo < 1$ region (*1*). This suggests that in the $S/Mo < 1$ region the fraction of species (**1**) with a stoichiometry of S/Mo(IV) = 1 increases with increasing the sulfidation degree of molybdenum, while in the region of $S/Mo > 1$ the proportion of MoS_2 increases with the sulfidation degree of molybdenum at the expense of species (**1**), accompanying the sintering of molybdenum (*1*). The structure of species (**1**) was proposed to be as follows (□ = anion vacancy) on the basis of the pyridine adsorption experiments (anion vacancy concentration) and the sintering behavior of molybdenum (*1*):



(1)

On the basis of the above surface structure, the volcano-type curve in Fig. 1 was previously explained (*1*); species (**1**) has higher intrinsic activity[1] for the thiophene HDS than does MoS_2 because of a higher anion vacancy concentration per molybdenum atom (monolayer structure) as evidenced by pyridine adsorption (1). On the other hand, Massoth (*10*) proposed a surface structure of sulfided MoO_3/Al_2O_3 catalysts involving Mo(III) species and Massoth and Kibby (*9*) explained their results similar to those in Fig. 1 in terms of the anion vacancy and anion (sulfur and oxygen) concentrations. However, no Mo(III) species were detected by XPS and ESR under our reaction conditions and at steady states, this being consistent with the results reported by Patterson *et al.* (*11*). Furthermore, our recent ir studies of adsorbed NO on reduced and sulfided MoO_3/Al_2O_3 catalysts (*12*) indicated that anion vacancies produced by the reduction with hydrogen were absent in the sulfided catalysts, forming anion vacancies connected with sulfur, even in the $S/Mo < 1$ region. Therefore, the surface model proposed by us (*1*) seems appropriate to explain the activity pattern in Fig. 1 and the results obtained by XPS (*1*), ESR and ir (*12*), pyridine adsorption experiments (*1*), and sintering behavior of molybdenum (*1*).

As mentioned above, the hydrogenation of butenes is a highly structure-sensitive

---

[1] The intrinsic activity defined here and in the previous papers (*1*) is based on the weight of molybdenum (conversion per gram of MoO_3). On a vacancy count, it is possible that the vacancies in MoS_2 could be as active as the vacancy in species (1) for the reactions.

reaction, whereas thiophene HDS is not. Accordingly, the relationships between the hydrogenation and the HDS would indicate the surface structure of the sulfided MoO_3/Al_2O_3 catalysts. To examine the relationships between the butene hydrogenation and the thiophene HDS activities of the catalysts, we wish to correlate the thiophene conversion (X_T, converted thiophene/initial thiophene) and the selectivity to butane (X_B, butane/C_4 products) obtained over various catalysts to the rate constants of the HDS and hydrogenation reactions. Although the literature (*13*) is not in agreement on the precise form of the rate expressions, the following simple rate equations are used here, assuming that the hydrogenation of butadiene is much faster than those of butenes (*8*) and that both the hydrogenation of butenes and the HDS of thiophene obey first-order rate equations with respect to butene (*14*) and thiophene (*14–16*) pressures:

$$r_T = k^{\circ}_{HDS} P_T P^n_H = k_{HDS} P_T, \qquad (1)$$

$$r_B = k^{\circ}_{HG} P_B P^m_H = k_{HG} P_B, \qquad (2)$$

where r_T and r_B are the reaction rates of the HDS of thiophene and the hydrogenation of butenes, k°_{HDS} and k°_{HG} are the rate constants for both reactions, P_T, P_B, and P_H denote the partial pressures of thiophene, butenes, and hydrogen, and k_{HDS} and k_{HG} are apparent rate constants defined by Eqs. (1) and (2) at a constant hydrogen pressure.

In the case of a differential reactor, X_T and X_B can be calculated to be as follows:

$$X_T = \frac{k_{HDS}\tau}{1 + k_{HDS}\tau}, \qquad (3)$$

$$X_B = \frac{k_{HG}\tau}{1 + k_{HG}\tau}, \qquad (4)$$

where τ W/F(W, catalyst weight; F, feed rate of thiophene). Combining Eqs. (3) and (4), a convenient expression can be derived:

$$\frac{k_{HG}}{k_{HDS}} = \left(\frac{X_B}{1 - X_B}\right)\left(\frac{1 - X_T}{X_T}\right). \qquad (5)$$

In order to examine the validity of Eq. (5), it was confirmed by changing the catalyst weight that the k_{HG}/k_{HDS} ratios were independent of τ within the accuracy of $\pm 5\%$ under our reaction conditions. This indicates that the k_{HG}/k_{HDS} ratio defined here is appropriate to represent the relative activities of the MoO_3/Al_2O_3 catalysts for the hydrogenation to the HDS, so long as the hydrogen pressure is kept constant.

The k_{HG}/k_{HDS} ratios are summarized in Table 1 and plotted in Fig. 2 against the sulfidation degree of molybdenum (S/Mo, atomic ratio). It is evident that the k_{HG}/k_{HDS} ratio is a function of the sulfidation degree of molybdenum regardless of the MoO_3 content, calcination temperature, and pretreatment (sulfidation) conditions, as well as the intrinsic activity for the HDS of thiophene (Fig. 1). These findings indicate that both hydrogenation and HDS activities correlate strongly with the surface structure of the sulfided MoO_3/Al_2O_3 catalysts.

The isomerization of but-1-ene to but-2-enes is a structure-sensitive reaction as well as the hydrogenation (*4*) and it is expected that the relative activity for the isomerization to the HDS of thiophene would also suggest the configuration of molybdenum atoms. However, the isomerization occurs over the exposed Al_2O_3 surface in the MoO_3/Al_2O_3 catalysts as well as over the

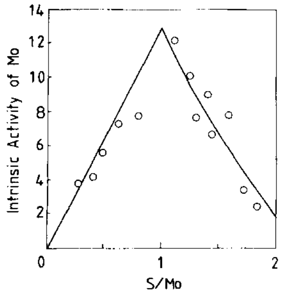


FIG. 1. Dependence of the intrinsic activity of molybdenum [(percentage conversion per gram MoO_3) $\times 10^{-2}$] on the sulfidation degree of molybdenum (S/Mo, atomic ratio) for the hydrodesulfurization of thiophene over MoO_3/Al_2O_3 catalysts at 400°C and atmospheric pressure. Solid line indicates the previous results (*1*).

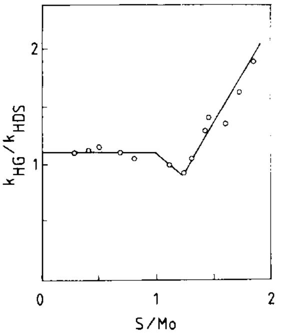
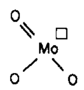


FIG. 2. Dependence of the k_{HG}/k_{HDS} ratio (relative activity for the butene hydrogenation to the hydrodesulfurization of thiophene) on the sulfidation degree of molybdenum (S/Mo, atomic ratio) in the hydrodesulfurization of thiophene over MoO_3/Al_2O_3 catalysts at 400°C and atmospheric pressure.

molybdenum and the reaction rate was too great to accurately evaluate the rate constant. Therefore, we have not discussed the isomerization further in this study.

It seems from Fig. 2 that the k_{HG}/k_{HDS} ratio is constant in the low-sulfur-content region (S/Mo $<$ 1). Subsequently, the k_{HG}/k_{HDS} ratio decreased and then increased with increasing S/Mo ratio. The constant k_{HG}/k_{HDS} ratio observed below S/Mo = 1 implies that the active sites consist of only one kind of molybdenum species, this being consistent with the previous proposal (*1*) that only molybdenum species (**1**) is present in the S/Mo $<$ 1 region and that it shows high intrinsic activity for the HDS of thiophene because of excellent dispersions. Figure 2 indicates species (**1**) to be active for the hydrogenation of butenes too. A plausible hydrogenation mechanism over species (**1**) is depicted in Fig. 3. This mechanism is analogous to that proposed by Lombardo and co-workers (*17*) for the hydrogenation of ethylene on species (**2**) (□ = anion vacancy) present in the reduced MoO_3/Al_2O_3 catalysts.



(**2**)

The reaction mechanism involves the well-documented heterolytic dissociation of H_2

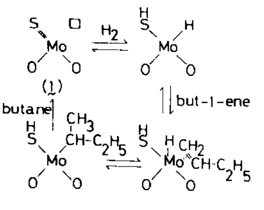


FIG. 3. Reaction mechanism for the hydrogenation of but-1-ene on species (**1**).

which occurs on ZnO (*18*, *19*), Cr_2O_3 (*20*), and Co_3O_4 (*21*, *22*). A similar reaction mechanism has been proposed for the HDS of thiophene on species (**1**) (*1*).

The k_{HG}/k_{HDS} ratio decreased with the initial formation of MoS_2 and subsequently increased with further increase in the proportion of MoS_2. According to Tanaka and Okuhara (*4*), only the molybdenum atoms at edges or corners of MoS_2 crystals are active for isomerization and hydrogenation due to their highly coordinative unsaturation. However, the molybdenum atoms in the basal plane of MoS_2 crystal are inactive for these reactions. With the relationships between the configuration of molybdenum atoms and the HDS or hydrogenation activity, Stevens and Edmonds (*5*) have shown by using MoS_2 catalysts that the butane/C_4 products ratio is much higher on the MoS_2 catalysts containing preferentially edge planes than on the basal-plane-rich MoS_2 catalysts, while the thiophene HDS activities of these catalysts are comparable. Therefore, the hydrogenation of butenes is a highly structure-sensitive reaction, whereas the HDS of thiophene would be a facile reaction. As for the morphology of MoS_2 formed on sulfided CoO–MoO_3/SiO_2–Al_2O_3 catalysts, Pollack and co-workers (*23*) have very recently demonstrated on the basis of precise X-ray diffraction studies that two-dimensional MoS_2 is formed by H_2S/H_2 sulfidation at 450°C and atmospheric pressure and that it is transformed to three-dimensional MoS_2 crystals by much more severe sulfidation with concomitant sintering of molybdenum.

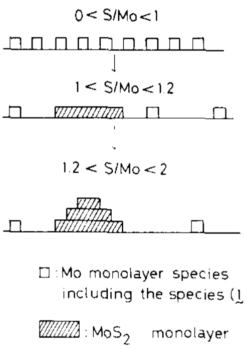


FIG. 4. Schematic surface models for the sulfided MoO_3/Al_2O_3 catalysts.

Combining these results, it may be reasonable to explain the results in Fig. 2 in terms of the crystal structure of MoS_2 formed during the presulfidation and reaction, that is, two-dimensional MoS_2 (monolayer structure) is initially formed in the region of $1 < S/Mo < 1.2$ and subsequently three-dimensional MoS_2 crystals develop with increasing the sulfidation of the catalysts ($S/Mo > 1.2$), accompanying the sintering of molybdenum. Schematic surface models are depicted in Fig. 4. These surface-structure changes with the sulfidation degree of molybdenum coincide with our previous XPS observations (*1*) that the molybdenum sintering is very significant for high S/Mo catalysts, whereas only the shrinkage of molybdenum monolayer occurs in low S/Mo catalysts. The fraction of the basal plane would be relatively high in the two-dimensional MoS_2 layer, resulting in the lower k_{HG}/k_{HDS} ratios, since the basal plane shows no activity for the hydrogenation (*4*, *5*), while it shows HDS activity (*5*). However, the edge plane would be significantly developed by further sulfidation and concomitant sintering of molybdenum (formation of MoS_2 microcrystals), whereas the exposed surface area of the basal plane would not increase as much (Fig. 4). This results in the higher k_{HG}/k_{HDS} ratios, taking into account that the edge plane shows high hydrogenation activity (*4*, *5*) and that both basal and edge planes have comparable HDS activity (*5*).[2] To rationalize the above models, it would be required to characterize the morphology of MoS_2 formed on the sulfided MoO_3/Al_2O_3 catalysts by other techniques such as the precise X-ray diffraction studies (*23*).

According to Pollack *et al.* (*23*), two-dimensional MoS_2 is formed by the sulfidation of $CoO–MoO_3/SiO_2–Al_2O_3$ catalysts with H_2S/H_2 at 450°C and atmospheric pressure. With the MoO_3/Al_2O_3 catalysts, however, two-dimensional MoS_2 monolayers and three-dimensional MoS_2 crystals are considered to be formed under mild sulfidation conditions. This discrepancy is ascribable to the stabilization effect of cobalt for the migration and sintering of molybdenum atoms in cobalt-promoted catalysts as shown previously (*24*, *25*).

In summary, it was found with the sulfided MoO_3/Al_2O_3 catalysts that the relative activities for the hydrogenation of butenes to the hydrodesulfurization of thiophene were a function of the sulfidation degree of molybdenum regardless of the molybdenum content, calcination temperature, and sulfidation conditions. It was confirmed that species (**1**) was present in partially sulfided catalysts. With the morphology of MoS_2 produced by the sulfidation, it is suggested that two-dimensional MoS_2 layers are initially formed and subsequently transformed to three-dimensional MoS_2 microcrystals by further sulfidation of the catalysts, accompanying the sintering of molybdenum. These surface-structure changes coincide with our previous XPS observations (*1*).

---

[2] An alternative explanation for the increase in the hydrogenation selectivity may be possible on the basis of a one-dimensional MoS_2 layer (instead of multilayers); the number of (**1**) sites is reduced due to sulfur incorporation but their hydrogenation selectivity remains the same and some edge sites now contribute to the increased hydrogenation activity. However, the possibility of the one-dimensional MoS_2 layer could be ruled out by the fact that molybdenum sintering is significant in the high S/Mo region (*1*).

REFERENCES

1. Okamoto, Y., Tomioka, H., Imanaka, T., and Teranishi, S., *Chem. Lett.*, 381 (1979); Okamoto, Y., Tomioka, H., Katoh, Y., Imanaka, T., and Teranishi, S., *J. Phys. Chem.* **84,** 1833 (1980).
2. Boudart, M., *Advan. Catal.* **20,** 153 (1969).
3. Siegel, S., *J. Catal.* **30,** 139 (1973).
4. Tanaka, K., and Okuhara, T., *Catal. Rev.* **15,** 249 (1977).
5. Stevens, G. C., and Edmonds, T., *in* "2nd International Conference, Chemistry and Uses of Molybdenum" (Oxford), p. 155 (1976).
6. Hargreaves, A. E., and Ross, J. R. H., *J. Catal.* **56,** 363 (1979).
7. Owens, P. J., and Amberg, C. H., *Advan. Chem. Ser.* **33,** 182 (1961).
8. Kirsh, F. W., and Shull, S. E., *Ind. Eng. Chem. Prod. Res. Develop.* **2,** 48 (1963).
9. Massoth, F. E., and Kibby, C. L., *J. Catal.* **47,** 300 (1977).
10. Massoth, F. E., *J. Catal.* **36,** 164 (1975).
11. Patterson, T. A., Carver, J. C., Leyden, D. E., and Hercules, D. M., *J. Phys. Chem.* **80,** 1700 (1976).
12. Okamoto, Y., Katoh, Y., Mori, Y., Imanaka, T., and Teranishi, S., submitted for publication.
13. Weisser, O., and Landa, S., "Sulfided Catalysts, Their Properties and Applications." Pergamon, New York, 1973.
14. Namba, S., and Aonuma, T., *Kogyo Kagaku Zasshi* **74,** 2457 (1971).
15. Namba, S., and Aonuma, T., *Kogyo Kagaku Zasshi* **74,** 1324 (1971).
16. Richardson, J. T., *Ind. Eng. Chem. Fundam.* **3,** 154 (1964).
17. Lombardo, E. A., Houalla, M., and Hall, W. K., *J. Catal.* **51,** 256 (1978).
18. Conner, W. C., Jr., and Kokes, R. J., *J. Phys. Chem.* **73,** 2436 (1969).
19. Dent, A. L., and Kokes, R. J., *J. Phys. Chem.* **73,** 3772, 3781 (1969).
20. Burwell, R. L., Jr., Littlewood, A. B., Cardew, M., Pass, G., and Stoddard, C. T. H., *J. Amer. Chem. Soc.* **82,** 6272 (1960).
21. Tanaka, K., Mihira, H., and Ozaki, A., *J. Phys. Chem.* **74,** 4510 (1970).
22. Fukushima, T., and Ozaki, A., *J. Catal.* **41,** 82 (1976).
23. Pollack, S. S., Makovsky, L. E., and Brown, F. R., *J. Catal.* **59,** 452 (1979).
24. Okamoto, Y., Nakano, H., Shimokawa, T., Imanaka, T., and Teranishi, S., *J. Catal.* **50,** 447 (1977).
25. Okamoto, Y., Tomioka, H., Imanaka, T., and Teranishi, S., *Shokubai* (*Catalyst*) **21,** 336 (1979); Okamoto, Y., Tomioka, H., Imanaka, T., and Teranishi, S., Preprint of 7th Intern. Congr. Catal. (Tokyo) A43, July (1980). Okamoto, Y., Imanaka, T., and Teranishi, S., *J. Catal.* **65,** 448 (1980).