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Elucidation of hydrodesulfurization mechanism using ^{35}S radioisotope pulse tracer methods

T. Kabe*, A. Ishihara, W. Qian, M. Godo

Department of Applied Chemistry, Tokyo University of Agriculture and Technology, 2-24-16 Nakacho, Koganei, Tokyo 184, Japan

Abstract

The sulfidation state in a series of Co-promoted Mo/Al_2O_3 catalysts was investigated using a ^{35}S pulse tracer method. ^{35}S-labeled H_2S ([^{35}S]H_2S) pulses were introduced into catalysts in a nitrogen stream until the radioactivity in the recovered pulse approached the radioactivity of the introduced pulse. From the amount of introduced [^{35}S]H_2S, the amount of sulfur accumulated on the catalyst was estimated. The result indicated that the amounts of sulfur accumulated on the catalysts increased with increasing temperature for all catalysts. Only molybdenum was sulfided in both $Co–Mo/Al_2O_3$ and Mo/Al_2O_3 catalysts below 300°C, but the sulfided states of the catalysts at 400°C were very close to the stoichiometric states where Co and Mo are present as Co_9S_8 and MoS_2. Further, hydrodesulfurization (HDS) reactions of radioactive ^{35}S labeled dibenzothiophene were carried out over the series of Co-promoted Mo/Al_2O_3 catalysts. The amount of labile sulfur and the release rate constant of H_2S were determined. The promotion effect of cobalt on activity of the molybdenum catalyst was attributed to the formation of more active sites. Moreover, the increase in the catalytic activity with Co/Mo ratio among the promoted catalysts was due to increase in the number of the sites with the same activity. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Sulfidation mechanism; Hydrodesulfurization of dibenzothiophene; Co–Mo catalysts; Radioisotope tracer method

1. Introduction

Recently, to achieve the deep hydrodesulfurization (HDS) of light gas oil, much attention has been focused on the development of novel catalysts with high catalytic activity and selectivity for products [1]. For this purpose, it is important to elucidate the structure of HDS catalysts and the mechanism of the HDS reaction [2,3]. The mechanism of the sulfidation of molybdenum-based catalysts has been studied by several investigators with the use of thermal gravimetric analysis (TGA) and temperature-programmed sulfidation (TPS) [4,5]. However, the process occurring in the appearance of the active phase from the oxidic precursor for promoted Mo/Al_2O_3 catalyst is not clear. On the other hand, a ^{35}S radioisotope tracer method has been developed to elucidate the structure of Mo-based catalysts and the mechanism of the HDS reaction under practical reaction conditions [6–11]. To investigate the behavior of sulfur on the working hydrotreating catalysts, the authors have directly performed the HDS reaction of [^{35}S]DBT on the sulfided Mo/Al_2O_3, $Co–Mo/Al_2O_3$ and $Ni–Mo/Al_2O_3$ catalysts under practical HDS conditions [12–14]. The change in radioactivity of unreacted [^{35}S]DBT and formed

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*Corresponding author. Tel.: +81-42-388-7063; fax: +81-42-387-8945.

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[^{35}S]H_2S showed that a portion of sulfur on the sulfided catalyst was labile sulfur of which the amount varied with the reaction conditions.

In this paper, the sulfidation states of a series of Co-promoted Mo/Al_2O_3 catalysts were examined. A more simple approach – [^{35}S] radioisotope pulse sulfiding method using [^{35}S]H_2S – was developed to investigate the sulfidation process of molybdenum-based catalysts. Further, in order to understand the promoting effect of Co to the Mo/Al_2O_3 catalyst, we investigated in detail the behavior of sulfur on a series of Co-promoted Mo/Al_2O_3 catalysts with different molar ratios of cobalt to molybdenum in HDS of [^{35}S]DBT.

2. Experimental

A Mo/Al_2O_3 catalyst containing 16 wt.% of MoO_3 was selected as a base catalyst for Co–Mo catalysts. The contents of cobalt in catalysts were changed from 0 to 7.7 wt.% of CoO. The catalysts used in this study were prepared by the usual impregnation method. The alumina supports were initially impregnated with an aqueous solution of ammonium heptamolybdate tetrahydrate and subsequently with an aqueous solution of cobalt nitrate hexahydrate as required. After the impregnation of every metal precursor, the catalyst was dried in an oven at 120°C for 3 h and then calcined in air at 450°C for 15 h. The catalysts were denoted as Mo(16), Co(1)–Mo(16), Co(2)–Mo(16), Co(3)–Mo(16), Co(5)–Mo(16), and Co(8)–Mo(16), respectively. The value in parentheses indicates weight percentage of cobalt oxide or molybdena in a catalyst.

In order to investigate the sulfidation process, a more simple approach – ^{35}S radioisotope pulse sulfiding method – was developed [15]. The sulfidation reactions were conducted with a pressurized fixed bed reactor (i.d. 4 mm, stainless steel) under 30 kg/cm^2. The concentration of H_2S in H_2 was about 50 vol% and the flow rate of carrier gas N_2 was 15 ml/min. After being calcined in air at 430°C for about 20 h, a catalyst was cooled in a carrier gas N_2 stream to sulfidation temperature and was pressurized with carrier gas to 30 kg/cm^2. Then a pulse of 50 vol% [^{35}S]H_2S in hydrogen was introduced with high-pressure gas sampler (2.48 ml) every 8 min. The radioactivity of [^{35}S]H_2S released from reactor, i.e., unreacted [^{35}S]H_2S, was directly monitored with a radioanalyzer. The gas released from the outlet of the radioanalyzer was passed through a basic scintillation solution-Carbsorb to absorb unreacted [^{35}S]H_2S. The total radioactivity of unreacted [^{35}S]H_2S trapped with Carbosorb was measured by a liquid scintillation counter described elsewhere [15]. The introduction of [^{35}S]H_2S pulse was continued until the counter number detected by the radioanalyzer became equal to that in the pulse introduced by the gas sampler.

[^{35}S]DBT tracer experiments were carried out with a fixed-bed reactor of conventional design. The details of apparatus are described elsewhere [12]. After being calcined at 430°C in air overnight, the catalyst was presulfided with a mixture of 5% H_2S in H_2 flowing at 1.8 l/h, atmospheric pressure, and 400°C for 3 h. After the presulfidation, the reactor was cooled in H_2S/H_2 stream to the reaction temperature and was pressurized with hydrogen. Then, a decalin solution of DBT was fed into the reactor by a high pressure liquid pump (Kyowa Seimitsu KHD-16).

Typical reaction conditions were: H_2 flow rate 25 l/h, WHSV 28 h^{-1}, reaction pressure 50 kg/cm^2, concentrations of DBT in decalin 1.0 wt.% and reaction temperature 240–320°C. The typical operation procedure was described in the previous paper [12].

3. Results and discussion

3.1. Sulfidation of supported oxide

Fig. 1 shows the change in radioactivity of eluted [^{35}S]H_2S during the sulfidation of Co(3)–Mo(16) at 100°C, which was directly monitored by the radioanalyzer. The radioactivity of unreacted [^{35}S]H_2S increased with the number of introduced pulses and approached the constant value, that is the radioactivity of one introduced pulse. Therefore, it could be considered that the sulfidation at this temperature has almost been completed. The total radioactivity of unreacted [^{35}S]H_2S trapped with Carbosorb was measured with a liquid scintillation counter after the complete of sulfidation, and was consistent with that measured by the radioanalyzer. The number of the pulses incorporated to the catalyst (N_T) could be calculated from the balance of radioactivity between

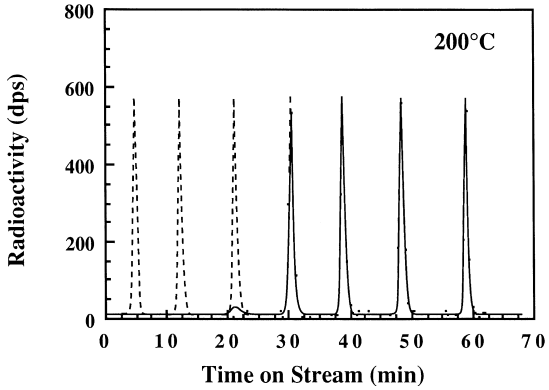

Fig. 1. Sulfidation of Co(3)–Mo(16) catalyst with [^{35}S]H_2S pulse at 200°C. The solid and dotted lines represent the radioactivities of [^{35}S]H_2S unreacted and that incorporated into the catalyst, respectively.

introduced and released:

$$N_T = N_p - R_{trap}/R_p \qquad (1)$$

where N_p is the number of introduced pulses; R_p is the amount of radioactivity in a standard pulse; R_{trap} is the amount of total radioactivity collected by the trap at the outlet of the reactor. The uptake amount of sulfur to the catalyst in the sulfidation was obtained from:

$$S_T = N_T \times S_p \qquad (2)$$

where S_p is the amount of sulfur in a standard pulse. A sulfidation degree was used to evaluate the sulfidation extent of the catalyst. The sulfidation degree (*R*) is defined as a ratio of the uptake amount of sulfur in the sulfidation to total sulfur which was calculated when all metal sulfides were present in MoS_2 and Co_9S_8.

The results for Co–Mo/Al_2O_3 catalysts are shown in Table 1. The amounts of sulfur accumulated on every catalyst increased with increasing temperature. The amounts of sulfur accumulated on Co(3)–Mo(16) catalyst at 100, 200, 300 and 400°C were 46.3, 54.2. 70.2 and 82.4 mg-sulfur/g-catalyst, respectively. This indicates that even at lower temperatures such as 100°C, significant O–S exchange in all catalysts occurred. The change in the sulfidation degree (100% when Co and Mo in Co–Mo/Al_2O_3 are present in the forms Co_9S_8 and MoS_2) of the catalysts at various temperatures is shown in Fig. 2. The sulfidation degrees at 300°C and 400°C remained constant despite changes in the molar ratio of cobalt to molybdenum. Moreover, the sulfidation degrees of all catalysts at 400°C were almost 100%, corresponding to the sulfided state when Co and Mo are present as Co_9S_8 and MoS_2. This indicates that all catalysts could be completely sulfided to the stoichiometric state at 400°C.

Table 1
Sulfidation state of Co–Mo/Al_2O_3 and Mo/Al_2O_3 catalysts

Catalyst	Temperature (°C)			
	100	200	300	400
Mo(16)	48.6	55.3	65.0	82.1
Co(2)–Mo(16)	47.6	52.7	68.8	79.8
Co(3)–Mo(16)	46.3	54.2	70.2	82.4
Co(5)–Mo(16)	44.7	56.4	73.5	94.3
Co(8)–Mo(16)	49.2	59.4	91.6	111.2

The amounts of sulfur accumulated during sulfidation with hydrogen sulfide, mg-sulfur/g-catalyst.

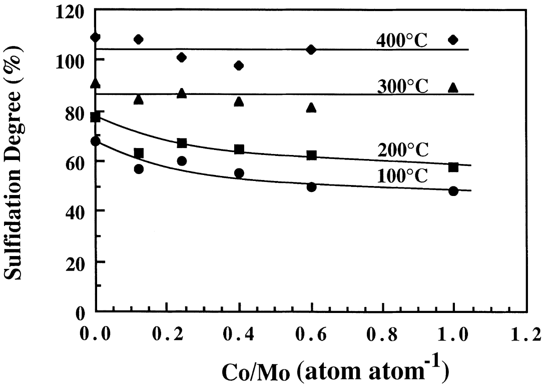

Fig. 2. Effect of Co/Mo ratio on sulfidation degree at various temperatures.

On the basis of the results of X-ray photoelectron spectroscopy (XPS) in a series of studies of the sulfidation of model compounds such as crystalline MoO_3, and $(NH_4)_2MoOS_2$ or model catalysts such as CoMoS phase, Mo/SiO_2/Si(100), CoMo/SiO_2Si(100) etc., Niemantsverdriet and co-workers also found that O–S exchange can begin below 100°C presumably forming Mo^{4+} oxysulfides on the surface and MoO_2 species in the inside [16–19]. Sulfur was present partly as S^{2-}, and partly as S_2^{2-} species. Above 200°C, the molybdenum oxides and oxysulfides are converted to MoS_2, and the S_2^{2-} species disappear probably because of hydrogenation to H_2S. In accordance with this study, de Boer et al. showed by use of EXAFS that MoO_xS_y species are formed by O–S exchange on a Mo/SiO_2 catalyst, even at room temperature [20]. They believed that the sulfidation reaction started at low temperatures with an exchange of terminal O^{2-} ligands of the oxide for S^{2-} by reaction with H_2S from the sulfiding atmosphere. Increasing the temperature to 150°C seemed to result in a MoS_3-like structure, which was transformed to MoS_2 at temperature above 200°C. These were consistent with the results shown in Fig. 2, where the exchange of O–S on all catalysts occurred even at 100°C. Low temperature sulfiding was also observed by Lojacono et al., who observed that the relative intensity of a Mo^{5+} ESR signal initially increased to a maximum at about 100°C during sulfiding, then steeply decreased and essentially disappeared at around 500°C, presumably because of a reduction to Mo^{4+} [21].

The sulfidation mechanism of promoted Mo/Al_2O_3 catalysts is more complicated. The influence of the addition of Co on the sulfidation of Mo/Al_2O_3 catalyst was investigated by Leliveld et al. [22] and Moulijn's group [5,23]. In these studies, it was suggested that the addition of Co enhanced the sulfiding rate of Mo. At the same time, Leliveld et al. also indicated that no observable change was obtained from the EXAFS data [22]. Comparing the sulfided state of Mo/Al_2O_3 with Co-promoted catalysts, as shown in Table 1, the uptake amount of sulfur at 100 and 200°C did almost change regardless of the increase in ratio of Co/Mo, whereas they increased with increasing the ratio of Co/Mo at 300 and 400°C. This result implies that molybdenum oxide may be preferably sulfided at lower temperatures and the sulfidation of cobalt oxide in the $Co–Mo/Al_2O_3$ catalysts may be very difficult. That is, higher temperatures are necessary for sulfiding cobalt oxide.

3.2. *HDS of [^{35}S]DBT*

The HDS reaction of [^{35}S]DBT was carried out on a sulfided $Co–Mo/Al_2O_3$ catalyst (Co(5)–Mo(16)) at 240°C and 50 kg/cm^2. Fig. 3 shows a typical result using the ^{35}S radioisotope pulse tracer method. Initially, a decalin solution of 1 wt.% [^{35}S]DBT was pumped into the reactor until the conversion of DBT became constant. After that, decalin solution of 1 wt.% [^{35}S]DBT was substituted for that of [^{32}S]DBT at about 90 min and was reacted until the formation amount of [^{35}S]H_2S became constant. When [^{35}S]DBT was introduced at about 90 min, the radioactivity of unreacted [^{35}S]DBT in the liquid product increased and approached a steady state immediately. In the case of produced [^{35}S]H_2S, however, about 210 min was needed to approach a steady state in radioactivities of produced [^{35}S]H_2S. In order to more accurately determine the extent of exchanged sulfur, the [^{35}S]DBT solution was replaced by decalin solvent at about 315 min. It was observed that a portion of ^{35}S, which is represented by the shaded area A in Fig. 3, remained on the catalyst when decalin solvent was substituted for the reactant solution of [^{35}S]DBT. When decalin and H_2 were used to purge the catalyst for about 2.5 h, less release of [^{35}S]H_2S was detected. This indicates that the sulfur accommodated on the catalyst could not be eluted without supply of sulfur derived from hydrodesulfurization of DBT. However, when the reactant solution was replaced with [^{32}S]DBT at about 480 min, this portion of ^{35}S can be released again as [^{35}S]H_2S, as shown in Fig. 3 (area B). This portion of ^{35}S was approximately equal to shaded area A, which represented the total amount of labile sulfur on the catalyst under this reaction condition. According to a method reported in Ref. [12], the amount of labile sulfur can be calculated from total radioactivity of released [^{35}S]H_2S after [^{32}S]DBT was introduced again, i.e., area B. To more accurately discuss the release process of [^{35}S]H_2S, the release rate of [^{35}S]H_2S in the range of area B can be fit with a

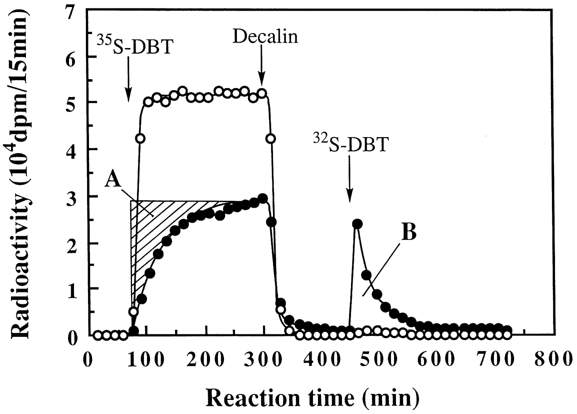

Fig. 3. Change in the radioactivity of unreacted [^{35}S]DBT (○) and formed [^{35}S]H_2S (●) with reaction time.

Table 2
Amount of labile sulfur, the release rate constant of H_2S and activity of hydrogenation and hydrodesulfurization at 280°C on sulfided Co-promoted Mo/Al_2O_3 catalysts

Catalyst	Conversion (%)	S_0 (atom nm^{-2})	k_{ER} (10^{-4} s^{-1})	k_{HDS} (10^{-4} atom s^{-1} nm^{-2})	k_{HYD} (10^{-4} atom s^{-1} nm^{-2})
Mo(16)	9.4	0.27	2.43	1.1	0.17
Co(1)–Mo(16)	64.3	0.87	8.12	11.6	0.66
Co(2)–Mo(16)	83.5	1.13	7.92	20.5	1.08
Co(3)–Mo(16)	91.8	1.30	8.00	29.1	0.94
Co(5)–Mo(16)	94.7	1.38	8.25	34.9	1.14

first-order reaction. Thus, the release rate constant of $[^{35}S]H_2S$ (k_{ER}), i.e., the rate constant of sulfur exchange, was determined from the slope of the first order plot.

The effect of Co/Mo ratio on the behavior of sulfur in the catalysts was also investigated. The values of S_0, corresponding to area B in Fig. 3, are given in Table 2. Similarly, the rate constants of sulfur exchange for all promoted catalysts were much more than that for the unpromoted molybdena catalyst whereas little difference in k_{ER} values was observed among the promoted catalysts at the same temperature. In order to understand the promotion effect of cobalt on the activity of molybdena catalyst, the relative increases in the amount of labile sulfur (S_0) and in the rate constant of H_2S release (k_{ER}) at 280°C with content of cobalt are shown in Fig. 4. The relative increase means the ratio of the value of S_0 or k_{ER} on the Co–Mo catalysts to the value of S_0 or k_{ER} of the base catalyst Mo(16), which are shown in Table 2. The increase in amount of labile sulfur increased linearly with increasing ratio of cobalt to molybdenum up to about 0.5, but decreased slightly above 0.5 of Co/Mo molar ratio. In contrast to this, the rate constant of H_2S release (k_{ER}) remarkably increased with the addition of cobalt at first whereas it no longer varied with the increase in ratio of cobalt to molybdenum.

This tracer method allows us to simultaneously evaluate the HDS and HYD activity of the catalyst as well as to determine the amount of labile sulfur and the rate constant of sulfur exchange. The rate constants of hydrodesulfurization of DBT (k_{HDS}) and hydrogenation of DBT to CHB (k_{HYD}) were determined; they are also listed in Table 2. The values of the ratio k_{HDS}/k_{HDS0} are plotted against the ratio of cobalt to molybdenum at 280°C in Fig. 5, where the k_{HDS} denotes the rate constant of HDS on Co–Mo catalyst, and k_{HDS0} denotes the rate constant of HDS on the Mo(16) catalyst. Thus, k_{HDS}/k_{HDS0} means the enhanced degree of the rate constant of HDS reaction on the Co–Mo

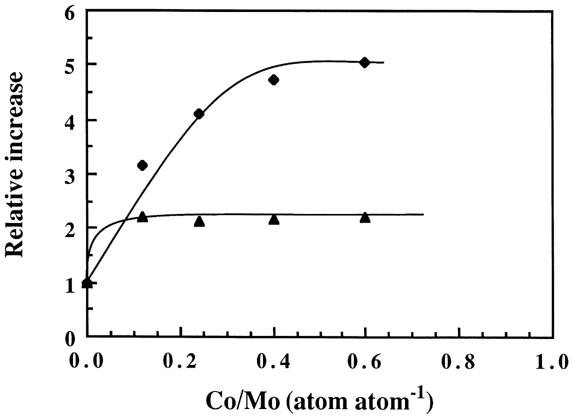

Fig. 4. Effect of Co/Mo on the increase in S_0 (◆) and k_{RE} (▲) relative to those of Mo(16) catalyst at 280°C.

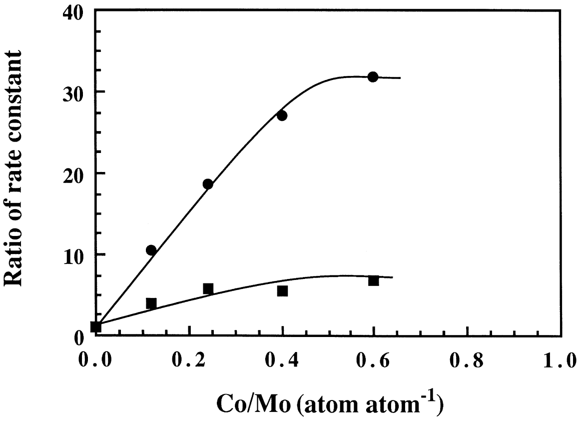

Fig. 5. Effect of Co/Mo on k_{HDS} and k_{HYD} relative to those of Mo(16) catalyst at 280°C. ● k_{HDS}/k_{HDS0}; ■ k_{HYD}/k_{HYD0}.

series catalysts as compared with the Mo(16) catalyst. In the same way, the values of the ratio k_{HYD}/k_{HYD0} are also plotted against Co/Mo molar ratio in Fig. 5, where k_{HYD} denotes the rate constant of HYD on Co–Mo catalyst, and k_{HYD0} denotes the rate constant of HYD on the Mo(16) catalyst. A significant promotion effect of cobalt on the molybdena catalyst for both HDS and HYD activity was observed. k_{HDS} and k_{HYD} increased linearly with increasing the content of cobalt at lower content of cobalt. At 0.6 of Co/Mo, the values of k_{HDS}/k_{HDS0} and k_{HYD}/k_{HYD0} were 32 and 7, respectively.

The apparent activation energies of catalysts obtained from Arrhenius plots of the reaction rate constants were 23 ± 2 and 25 ± 1 kcal/mol for HDS reaction and HYD reaction, respectively. There is no significant difference in the apparent activation energies within this series of catalysts. This indicates that there is essentially no difference in the mechanism of reaction for all catalysts, regardless of the addition of cobalt. As shown in Fig. 5, both k_{HDS} and k_{HYD} were remarkably enhanced with the addition of cobalt. For instance, k_{HDS}/k_{HDS0} and k_{HYD}/k_{HYD0} at Co/Mo=0.12 were 11 and 4, respectively. On the other hand, the enhancement in k_{HDS} and k_{HYD} among the promoted catalysts did not increase significantly with increasing the content of cobalt. Both k_{HDS} and k_{HYD} at Co/Mo=0.6 were only about 2–3 times as high as those at Co/Mo=0.12. Therefore, the promotion effect of cobalt on the molybdenum catalyst was due to the formation of a more active phase while the increase in the catalytic activity with the ratio of cobalt to molybdenum was due to the increase in the number of the sites with the same activity.

4. Conclusions

This study showed that all catalysts could be sulfided even at 100°C and the sulfiding state of the catalysts approached the stoichiometric state. Comparison of Co-promoted Mo/Al_2O_3 catalysts with Mo/Al_2O_3 catalyst suggested that at low temperature only molybdenum was sulfided to molybdenum sulfide while the sulfidation of cobalt oxide needs a temperature higher than 300°C.

This study enable us to understand the promoting effect of Co to Mo/Al_2O_3 catalyst. The HDS and HYD activity of Mo/Al_2O_3 catalysts were remarkably enhanced on the addition of cobalt. For the Mo(16) catalyst, the amount of labile sulfur and the rate constant of sulfur exchange increased significantly on addition of cobalt, indicating that cobalt makes the sulfur more mobile and that the active phases in the promoted catalysts are different from that in the unpromoted catalyst. It was suggested, therefore, that the promoting effect of cobalt is attributed to the change in the nature of active sites, i.e., the formation of more active sites. Moreover, the enhancement in k_{HDS} and k_{HYD} did not increased significantly with increasing Co content. On the other hand, the maximum enhancement in both k_{HDS} and k_{HYD} increased only by a factor of ca. 2 when the ratio of Co/Mo increased from 0.12 to 0.6. Therefore, it can be considered that the increase in the catalytic activity with the Co/Mo ratio is due to the increase in the number of the same active sites.

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