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The effect of boron addition on the hydrodesulfurization activity of MoS_2/Al_2O_3 and Co–MoS_2/Al_2O_3 catalysts

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Abstract

The effect of boron addition was studied on the hydrodesulfurization (HDS) of thiophene over $MoS_2/B/Al_2O_3$ and Co–$MoS_2/B/Al_2O_3$ (CVD-Co/$MoS_2/B/Al_2O_3$), which was prepared by a CVD technique using $Co(CO)_3NO$ as a precursor of Co. The catalysts were characterized by means of NO adsorption and TEM. The HDS activity of $MoS_2/B/Al_2O_3$ catalysts kept constant up to a boron content of about 0.6 wt% and decreased with a further increase of boron content. With CVD-Co/$MoS_2/B/Al_2O_3$ catalysts, the HDS activity significantly increased as the boron content increased up to about 0.6 wt% of boron, followed by a decrease with a further increase of boron loading. Despite the activity increase, the amount of NO adsorption on $MoS_2/B/Al_2O_3$ steadily decreased with increasing boron loading, suggesting that the dispersion of MoS_2 particles is decreased by the addition of boron. A selective formation of the CoMoS phase on CVD-Co/$MoS_2/B/Al_2O_3$ was achieved by the CVD technique. The TOF of the HDS over the CVD-Co/$MoS_2/B/Al_2O_3$ catalysts, defined by the activity per Co atom forming the CoMoS phase, increased as high as 1.6 times by the addition of boron, indicating that the active phase of the catalysts shifts from less active CoMoS Type I to more active CoMoS Type II. A TEM analysis showed that the number of stacking of MoS_2 slabs was only slightly increased by the addition of boron. It is concluded that the activity increase of the CVD-Co/$MoS_2/B/Al_2O_3$ catalyst is caused by the formation of CoMoS Type II because of weakened interaction strength between the CoMoS phase and the Al_2O_3 surface by the addition of boron.

Keywords: Hydrodesulfurization; Co–Mo sulfide catalysts; Effect of boron addition; CVD technique; Turnover frequency

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1. Introduction

Regulations about decreasing the sulfur content in petroleum feedstocks have become more and more strict in order to protect the environment and living things. Hydrodesulfurization (HDS) of petroleum feedstocks has been, therefore, an indispensable reaction to produce clean fuels [1–3]. Development of highly active catalysts is a challenge for refiners and catalyst manufacturers and such a success could be more easily achieved by better knowledge of the relationship among catalyst performance, preparation, and surface property.

Sulfided Co–Mo or Ni–Mo(W)-based HDS catalysts have been extensively studied [4–7]. Since the proposal by Topsøe and co-workers [8–10], the CoMoS model, in which Co decorates the edge sites of highly dispersed MoS_2 crystallites, has been accepted as the catalytically active phase in Co–Mo sulfide catalysts. Based on their catalytic activities, there are two types of the CoMoS phase, namely CoMoS Type I and CoMoS Type II [4,9,10]. Although the origin of the two types of the CoMoS phase is still under debate [11], it is suggested that the CoMoS Type I is related to highly dispersed single slab MoS_2 particles maintaining their interactions with the support, e.g., Mo–O–Al bonds, while CoMoS

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Type II is related to less dispersed MoS_2 particles mainly stacked and not linked with the support, the latter showing a higher intrinsic activity for HDS than the former [4,9,10]. In order to increase catalyst activities, accordingly, we need to control the interactions between the support surface and active phases to obtain enhanced stackings of MoS_2 particles keeping their dispersion high.

According to the literature, the addition of boron modifies the dispersion of Mo on the surface of alumina [12,13] as well as the acidic properties of alumina [14–17]. The effect of boron addition on the activity of Co–Mo or Ni–Mo/Al_2O_3 catalysts has been widely studied [16–21]. Although some workers reported that the high acidity of alumina boria catalysts increased the hydrocracking [16] and HDN [16,17,19] activity of Ni–Mo/B/Al_2O_3, many conflicting results were obtained in the previous studies. Li et al. [16] believed that the addition of boron up to 1 mol% increased the activity of Ni–Mo/Al_2O_3 catalysts for the HDS of DBT, in contrast to the results by Lewandowski and Sarbak [17] that the addition of boron did not affect the activity of Ni–Mo/Al_2O_3 catalysts for the HDS of coal liquid. Stranick et al. [22] believed that the addition of boron to Al_2O_3 can improve the dispersion of Co and change the chemical states of Co in Co/Al_2O_3 catalysts. In addition, Morishige and Akai [12] indicated that the addition of boron decreased the dispersion of Mo in Mo/Al_2O_3 catalysts and weakens the interactions between Mo species and the Al_2O_3 surface. Thus, it is expected that the addition of boron to Co–Mo or Ni–Mo/Al_2O_3 modifies both Mo and Co(Ni) species. It will be easy to understand the effects of boron addition if we could separate the effects of boron addition on Mo and Co phases. In the present study, we tried to clarify the effect of boron addition on the Mo sulfide phase supported on Al_2O_3.

No literature can be found explaining the activity increase of Co–Mo/B/Al_2O_3 compared to the boron-free catalyst on the basis of the number of active sites and their intrinsic activity, despite the fact that this information is highly important for understanding the nature of the additive effects. In the previous study [23–27], we have shown that when a supported Mo sulfide catalyst is exposed to a vapor of $Co(CO)_3NO$ (CVD (chemical vapor deposition) technique), followed by an evacuation and resulfidation, the Co species in the resultant CVD-Co/MoS_2 catalyst are selectively transformed into the CoMoS phase and accordingly the amount of Co in the catalyst represents the amount of the CoMoS phase. In the CVD-Co/MoS_2 catalysts, the edge of MoS_2 particles is fully covered by the CoMoS phase. It is, therefore, expected that the CVD technique provides a strong clue to understand the nature of the boron addition to Co–Mo/Al_2O_3 catalysts. In the present study, we investigated the effect of boron addition on the HDS activity of CVD-Co/MoS_2/Al_2O_3 catalysts to understand the effects in terms of the number of active sites and their intrinsic activity.

2. Experimental

2.1. Catalyst preparation

A series of Mo/Al_2O_3–B_2O_3 was prepared by a double impregnation technique. γ-Al_2O_3 (JRC-ALO-7: 180 $m^2\,g^{-1}$) was first impregnated with an H_3BO_3 aqueous solution, followed by calcination at 773 K for 5 h. The boron contents were 0, 0.3, 0.6, 0.9, 1.2, 2.5, and 4.5 wt% B. Then, the Al_2O_3–B_2O_3 materials were impregnated with $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ and calcined again at 773 K for 5 h. The Mo loading was fixed at 13 wt% MoO_3.

The catalyst was sulfided in a 10% H_2S/H_2 flow. The sulfidation temperature was raised from room temperature to 373 K at a rate of 2 $K\,min^{-1}$ and kept isothermal for 1 h. Subsequently the temperature was ramped to 673 K at a rate of 5 $K\,min^{-1}$ and then kept at 673 K for 1.5 h. After the sulfidation, the sample was cooled in the H_2S/H_2 stream to room temperature to prepare a sulfide catalyst. The catalyst thus prepared is denoted MoS_2/B/Al_2O_3 hereinafter.

Co–Mo/B/Al_2O_3 catalysts were prepared by introducing $Co(CO)_3NO$ into MoS_2/B/Al_2O_3 by means of a CVD technique. The CVD technique has been described in detail previously [23,24]. In brief, a vapor pressure of $Co(CO)_3NO$ at 273 K was used to prepare $Co(CO)_3NO$/MoS_2/B/Al_2O_3, followed by the same temperature-programmed sulfidation in a 10% H_2S/H_2 stream as described above. The catalyst thus prepared is denoted CVD-Co/MoS_2/B/Al_2O_3 hereinafter. The amount of Co was analyzed by XRF. The detailed procedures have been described elsewhere [26].

2.2. Reaction procedure

The catalyst sulfided in situ was evacuated at 673 K for 1 h before the catalytic reaction. In order to evaluate the initial activity of the freshly prepared catalyst, the reaction was conducted under mild conditions using a circulation system. The HDS of thiophene was carried out at 623 K and the initial H_2 pressure of 20 kPa. The thiophene pressure was kept constant (2.6 kPa) during the reaction [23]. The reaction products were analyzed by on-line gas chromatography. The products were mainly C_4 compounds and the corresponding amount of H_2S. The HDS activity was calculated on the basis of the accumulated amount of H_2S after 1 h. The details of the reaction procedure have been described elsewhere [23].

2.3. Catalyst characterizations

2.3.1. NO adsorption

The amount of NO adsorption on MoS_2/B/Al_2O_3 was measured by a pulse technique [28]. After cooling in the H_2S/H_2 stream, the sulfided catalyst was flushed at room temperature with a high purity He stream. The detailed procedures have been described elsewhere [23,28].

2.3.2. TEM observation

Transmission electron microscopic (TEM) images of $MoS_2/B/Al_2O_3$ were taken on an electron microscope Hitachi H-800 with an accelerating voltage of 200 keV. The $MoS_2/B/Al_2O_3$ powder sample was evacuated and sealed in a glass tube without exposure to air. The catalyst sample was suspended in heptane and placed on a specimen grid in a glove bag filled with argon to avoid as much contact with air as possible. The sample was then transferred in a stream of N_2 to a sample holder attached to the microscope. The distributions of MoS_2 particle size and stacking were calculated over ca. 400 particles in four arbitrary chosen areas.

3. Results and discussion

Table 1 summarizes the BET surface area and the pore volume of $MoO_3/B/Al_2O_3$. Slight decreases of these morphological parameters were observed only around the high boron content (2.5 wt% B). This is consistent with other workers [15,21], who suggested that at a higher loading of boron, B_2O_3 particles block the micropores of alumina during calcination, yielding a low surface area.

Fig. 1 depicts the HDS activities of the $MoS_2/B/Al_2O_3$ and CVD-Co/$MoS_2/B/Al_2O_3$ catalysts as a function of boron content. The HDS activity of $MoS_2/B/Al_2O_3$ was almost constant up to 0.9 wt% B and decreased with a further increase of boron content. With CVD-Co/$MoS_2/B/Al_2O_3$, the HDS activity significantly increased with the increase of boron content up to about 0.6 wt% B and decreased with a further addition of boron. B/Al_2O_3 was found to show a very low activity comparable to that of Al_2O_3 for the HDS of thiophene under the present reaction conditions.

The activity increases of Co–Mo/B/Al_2O_3 catalysts compared to the boron-free catalysts have also been reported by others [20,21]. Ramírez et al. [21] reported that boron addition into Co–Mo/Al_2O_3 catalysts enhanced thiophene HDS activity and the maximum activity was attained at a boron content of 0.8 wt% B, in conformity with the present results, taking into consideration that the Al_2O_3 surface area (180 $m^2\,g^{-1}$) used in the present study is slightly lower than that of Ramírez et al. (190 $m^2\,g^{-1}$).

In the present study, we also measured the catalytic activity of CVD-Co/$MoS_2/B/Al_2O_3$ (SI) catalysts prepared by a simultaneous impregnation technique, in which B and Mo were impregnated in one step. As shown in Fig. 1, the HDS activities of these catalysts were essentially identical with those prepared by the double impregnation (DI) method. These results indicate that the impregnation order of B and Mo (stepwise and simultaneous) causes no effects on the dispersion and stacking of MoS_2 particles in $MoS_2/B/Al_2O_3$ catalysts.

Table 1
Surface area and pore volume of $MoO_3/B/Al_2O_3$ catalyst

Boron content (wt%)	Surface area ($m^2\,g^{-1}$)	Pore volume ($mm^3\,g^{-1}$)
0	152	951
0.3	157	957
0.6	151	950
1.2	143	953
2.5	131	910

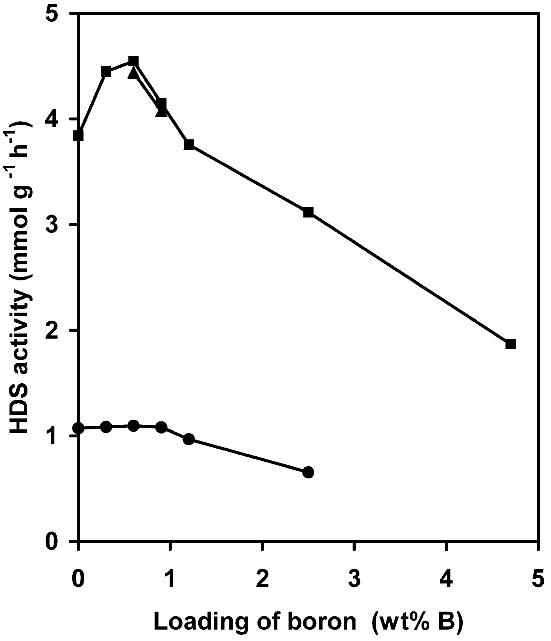

Fig. 1. HDS activity of $MoS_2/B/Al_2O_3$ (circle), CVD-Co/$MoS_2/B/Al_2O_3$ double impregnation (square), and CVD-Co/$MoS_2/B/Al_2O_3$ simultaneous impregnation (triangle) as a function of boron loading.

Nitric oxide is a probe molecule widely used to investigate the dispersion of MoS_2 slabs because NO molecules selectively adsorb on the edge sites of MoS_2 particles [28–30]. The amount of NO adsorption on $MoS_2/B/Al_2O_3$ decreased with increasing B loading, as shown in Fig. 2. This is ascribed to a decreasing dispersion of MoS_2 clusters as the amount of boron increases.

The amount of Co anchored on $MoS_2/B/Al_2O_3$ is summarized in Table 2. Obviously, it decreased as the boron content increased. Fig. 3 shows the Co/Mo atomic ratio of the CVD-Co/$MoS_2/B/Al_2O_3$ catalysts as a function of the NO/Mo ratio of the $MoS_2/B/Al_2O_3$ samples. The Co/Mo ratio is proportional to the NO/Mo ratio, this being in conformity with our previous results for CVD-Co/MoS_2/support (support: Al_2O_3, TiO_2, ZrO_2, and SiO_2) [23]. Taking into consideration selective adsorption of NO molecules on the edges of MoS_2 particles, the proportional correlation in Fig. 3 demonstrates that the Co sulfide species admitted by the CVD technique are located on the edge of MoS_2 particles in $MoS_2/B/Al_2O_3$. In our previous study, it was shown by XPS [23] and Co *K*-edge XANES [26] spectra that the Co sulfide species preferentially interact with MoS_2 particles for CVD-Co/MoS_2/support. Therefore, we conclude that the Co sulfide species prepared by the CVD technique using $Co(CO)_3NO$ as a precursor of Co is selectively transformed to the CoMoS phase irrespective of the presence of boron,

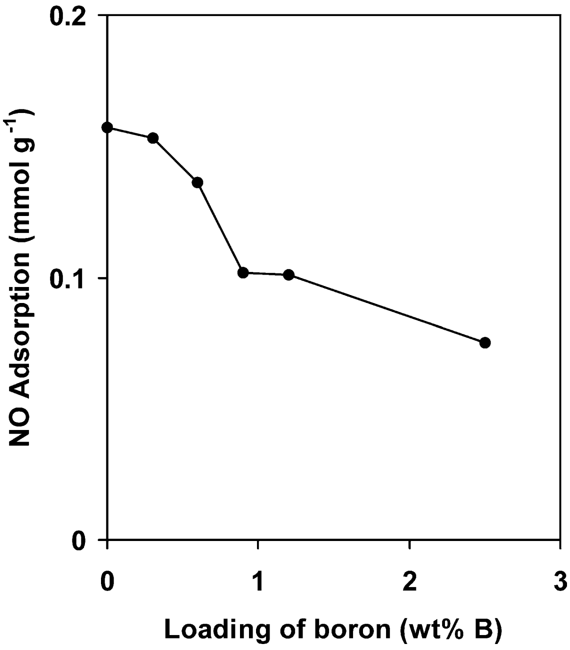

Fig. 2. NO adsorption of $MoS_2/B/Al_2O_3$ as function of boron loading.

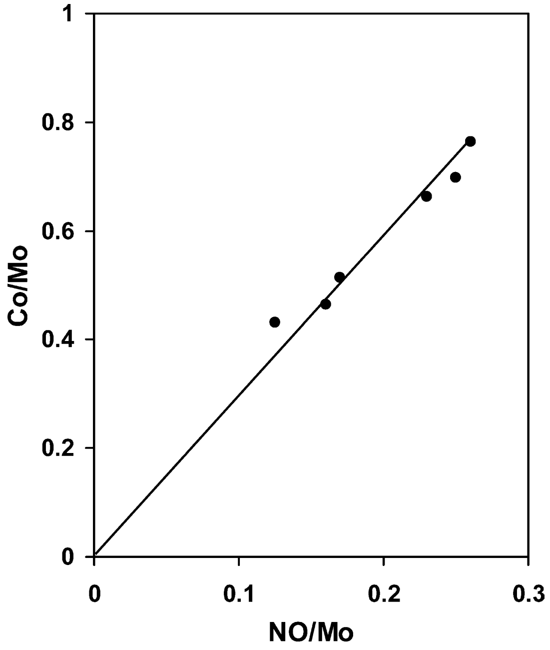

Fig. 3. Correlation between the Co/Mo atomic ratio of CVD-Co/MoS_2/B/Al_2O_3 and the NO/Mo mole ratio of $MoS_2/B/Al_2O_3$.

and that the amount of Co in CVD-Co/$MoS_2/B/Al_2O_3$ represents the amount of the CoMoS phase.

In order to explain the activity increase of CVD-Co/$MoS_2/B/Al_2O_3$ in Fig. 1, the TOF (turnover frequency, h^{-1}) of the reaction is plotted in Fig. 4 against the loading of boron. We calculated the TOF on the basis of the Co content in the catalyst. Fig. 4 clearly shows that the TOF is increased by the addition of boron up to ca. 0.8 wt% B and become constant with a further addition of boron. The increased TOF value is about 1.6 times higher than that for the boron-free catalyst. In our previous study [23], it has been shown that the TOF value of thiophene HDS over CVD-Co/MoS_2/SiO_2 is 1.7 times higher than the values over CVD-Co/MoS_2/Al_2O_3, CVD-Co/MoS_2/TiO_2, and CVD-Co/MoS_2/ZrO_2 under the present reaction conditions. Comparing these results with those of CoMoS Type I and Type II, defined by Topsøe et al. [9,10], we have concluded that the CoMoS phase of CVD-Co/MoS_2/SiO_2 is classified to CoMoS Type II, whereas the CoMoS phase of the other supported CVD-Co/MoS_2 catalysts to CoMoS Type I. Fig. 4, accordingly, suggests that the addition of boron leads to a shift of the catalyst active sites from less active CoMoS Type I to more active CoMoS Type II. Similarly, van Veen et al. [31] showed by means of ^{57}Co Mössbauer emission spectroscopy that the addition of phosphoric acid changed part of CoMoS Type I to CoMoS Type II. The decrease in the dispersion of MoS_2 particles is compensated by the increase in the TOF, leading to the maximum activity at 0.6 wt% B (Fig. 1).

The TOF on $MoS_2/B/Al_2O_3$, as calculated on the basis of NO adsorption, is also presented in Fig. 4. Fig. 4 shows that the TOF on $MoS_2/B/Al_2O_3$ is also increased by the addition of boron. It is noteworthy in Fig. 4 that the TOF values on CVD-Co/$MoS_2/B/Al_2O_3$ and $MoS_2/B/Al_2O_3$ change in a similar manner with the loading of boron. These changes in the TOF values may be ascribed to the changes in the morphology of MoS_2 particles and/or in the interactions between the support surface and the MoS_2 particles by the addition of boron.

Table 2
Amount of NO adsorption, cobalt content, and TOF on the $MoS_2/B/Al_2O_3$ and CVD-Co/$MoS_2/B/Al_2O_3$ catalysts

Boron content (wt%)	NO adsorption (mmol g^{-1})	Cobalt loading (wt%)	TOF (h^{-1})	
			$MoS_2/B/Al_2O_3$[a]	CVD-Co/$MoS_2/B/Al_2O_3$[b]
0	0.157	2.70	6.8	8.4
0.3	0.153	2.45	7.1	10.7
0.6	0.136	2.33	8.1	11.5
0.9	0.102	1.81	10.6	13.5
1.2	0.101	1.67	9.6	13.3
2.5	0.075	1.54	8.8	12.0
4.7		0.84		13.1

[a] TOF was calculated on the basis of the amount of NO adsorption.
[b] TOF was calculated on the basis of the cobalt content.

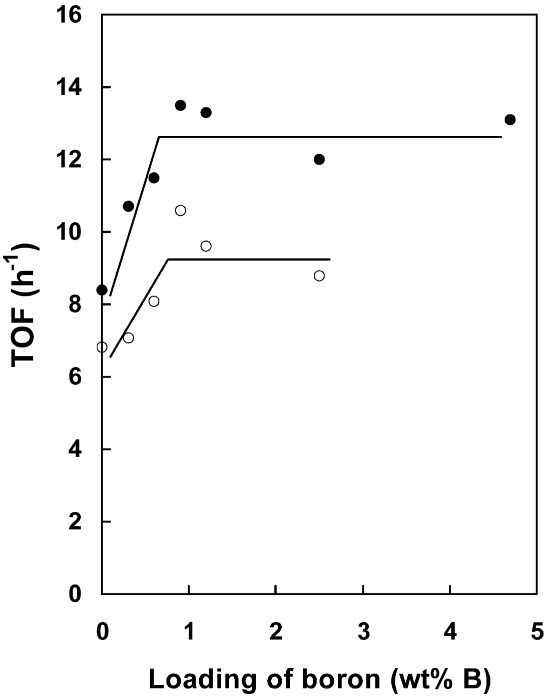

Fig. 4. Turnover frequency (TOF) of thiophene HDS on $MoS_2/B/Al_2O_3$ as calculated on the basis of NO adsorption (open circle), and on CVD-Co/$MoS_2/B/Al_2O_3$ as calculated on the basis of Co content (solid circle), as a function of boron loading.

The distributions of MoS_2 particle size and stacking number, as calculated from the TEM images of the $MoS_2/B/Al_2O_3$, are shown in Figs. 5 and 6, respectively. The averaged stacking number and slab length are summarized in Table 3. With the stacking number of MoS_2 slabs (Fig. 5), the boron addition promotes the formation of highly stacked MoS_2 particles ($\geqslant$ 2 layer) until 1.2 wt% of boron, and this trend levels off at a higher loading of boron. The increased stackings of MoS_2 slabs, and thus increased stacking of the CoMoS phase, are generally correlated to the formation of CoMoS Type II [11]. However, the increase in the stacking number is not very significant and more than 40% of MoS_2 particles are still present as single slabs even in $MoS_2/B/Al_2O_3$ having high boron contents, as shown in Fig. 5. Accordingly, we rather conclude that the formation of CoMoS Type II on CVD-Co/$MoS_2/B/Al_2O_3$ is mainly caused by weakened interactions between MoS_2 particles and Al_2O_3 surface and in part by the increased stacking of MoS_2 particles. The formation of CoMoS Type II on MoS_2 single slabs was reported for a carbon-supported Co–Mo sulfide catalyst [32].

As shown in Fig. 4, the high TOF values of the thiophene HDS are established at > 0.8 wt% B (2.5 B atoms nm^{-2}) on both $MoS_2/B/Al_2O_3$ and CVD-Co/$MoS_2/B/Al_2O_3$. Okamoto and Imanaka [33] reported on the basis of the detailed IR study of the surface hydroxyl groups on Al_2O_3 that the maximum amount of tetrahedral Mo oxide species, which is formed by the reaction of MoO_4^{2-} with the basic hydroxyl groups (3785 cm^{-1}), is 1.7 Mo atoms nm^{-2} and that

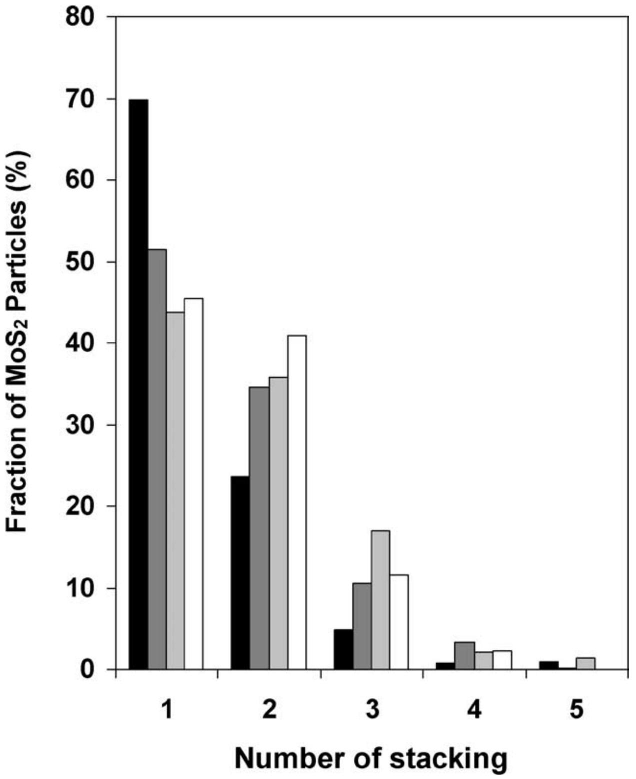

Fig. 5. The distribution of stacking number of MoS_2 particles as observed by TEM. Black bar, MoS_2/Al_2O_3; dark gray bar, MoS_2/B(0.6 wt% B)/Al_2O_3; light gray bar, MoS_2/B(1.2 wt% B)/Al_2O_3; white bar, MoS_2/B(2.5 wt% B)/Al_2O_3.

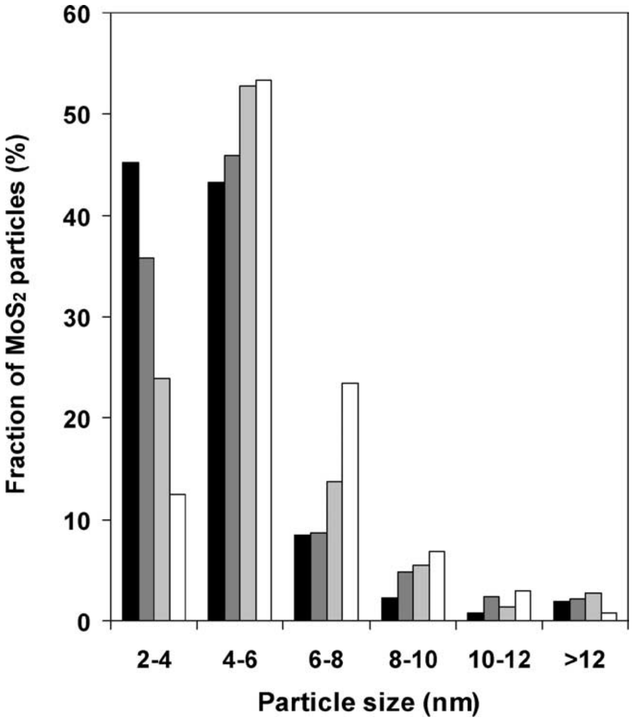

Fig. 6. The distribution of slab length of MoS_2 particles as observed by TEM. Black bar, MoS_2/Al_2O_3; dark gray bar, MoS_2/B(0.6 wt% B)/Al_2O_3; light gray bar, MoS_2/B(1.2 wt% B)/Al_2O_3; white bar, MoS_2/B(2.5 wt% B)/Al_2O_3.

Table 3
Averaged size and averaged number of stacking of $MoS_2/B/Al_2O_3$ as observed by TEM

Boron content (wt%)	Averaged size (nm)	Averaged number of stacking
0	4.42	1.40
0.6	4.71	1.66
1.2	5.01	1.82
2.5	5.62	1.71

their formation is completed at 2.5 Mo atoms nm^{-2}. They proposed that MoO_4^{2-} anions consume the basic hydroxyl groups with a stoichiometry of $OH^-/Mo = 1$ at a low Mo loading to form a robust Al–O–Mo bond. It is considered that $B(OH)_3$, a stronger acid than molybdic acid, preferentially consumes basic hydroxyl groups as MoO_4^{2-} and SO_4^{2-} anions do [33]. This was confirmed by a separate FTIR study on hydroxyl groups of B/Al_2O_3 [34]. It is, accordingly, considered that above 2.5 B atoms nm^{-2}, the Mo oxide species having robust Al–O–Mo bonds are not formed in $MoO_3/B/Al_2O_3$ and that no strong interactions generate between MoS_2 particles and Al_2O_3 surface via Al–O–MoS_2 bondings. It is likely that these weakened interactions by the addition of boron cause the formation of CoMoS Type II, accompanying a slightly increased stacking number and extensively increased size of MoS_2 particles. When Mo oxide–support interactions become much weaker as in MoO_3/SiO_2 [23] or when supported MoO_3 is sulfided at a much higher temperature [9], support–O–MoS_2 bonds are easily cleaved and highly stacked MoS_2 particles are formed. The formation of CoMoS Type II in these cases is well established [9,23]. The increased TOF on $MoS_2/B/Al_2O_3$ (Fig. 4) can also be understood in terms of the weakened support–MoS_2 interactions.

It has been reported that the acidity of B/Al_2O_3 increases the hydrodenitrogenation (HDN) activity of Ni–Mo/B/Al_2O_3 catalysts [16,17,19] and the hydrocracking (HC) ability of Ni–Mo/B/Al_2O_3 [16]. It was found, however, that B/Al_2O_3 showed only a very small thiophene HDS activity comparable to that of Al_2O_3 under the present reaction conditions, suggesting that the high acidity of B/Al_2O_3 has no significant contribution to the HDS activity of CVD-Co/MoS_2/Al_2O_3 and $MoS_2/B/Al_2O_3$ catalysts. In line with this, Lewandowski and Sarbak [17] reported that boron differently affects HDN and HDS activities; that is, high acidity of B/Al_2O_3 enhanced the HDN activity, whereas it did not practically affect the activity of Ni–Mo/B/Al_2O_3 catalysts for the HDS of coal liquid.

Concerning the size of MoS_2 particles (Fig. 6), the boron addition obviously increases the size of MoS_2 particles. The most abundant slab length is in the range of 4–8 nm for the boron-containing catalysts, in contrast to 2–6 nm for the boron-free catalyst. The size of MoS_2 slabs seems continuously increased until the highest loading of boron tested in this research, in conformity with the tendency observed for the NO adsorption (Fig. 2). A larger size of MoS_2 particles will accommodate just a smaller amount of Co forming the CoMoS phase, in conformity with the decreasing amount of Co incorporated on the MoS_2 edges of the catalyst by the addition of boron, as presented in Table 2. These results are apparently related to the decrease of the HDS activity at a higher loading of boron (> 0.6 wt%) in Fig. 1.

4. Conclusions

Summarizing the present study on the effect of boron addition on the hydrodesulfurization activity of MoS_2/Al_2O_3 and CVD-Co/MoS_2/Al_2O_3 catalysts, the conclusions are as follows:

1. Boron addition enhances the HDS activity of CVD-Co/MoS_2/Al_2O_3 catalysts until the boron content reaches 0.6 wt% of B, followed by a decrease with a further increase of B content. With the $MoS_2/B/Al_2O_3$ catalysts, the activity is kept constant until 0.9 wt% B and decreases with a further increase of B content.
2. Boron addition decreases both the dispersion of MoS_2 particles on the surface of Al_2O_3 and the amount of Co anchored to the MoS_2 edges of $MoS_2/B/Al_2O_3$.
3. The stacking number of MoS_2 particles is slightly increased by the addition of boron.
4. The TOF of HDS over CVD-Co/$MoS_2/B/Al_2O_3$ is increased by the addition of boron, apparently leading to a shift of the active phase from CoMoS Type I to CoMoS Type II.
5. The CVD technique, in which Co are selectively anchored to the MoS_2 edges of $MoS_2/B/Al_2O_3$, combined with TEM and NO adsorption is a promising technique for investigating the nature of additive effects on HDS catalysts on the basis of the number of active sites and their intrinsic activity.

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