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Effect of Boron Addition on the Intrinsic Activity of Al_2O_3-Supported Cobalt–Tungsten and Cobalt–Molybdenum Sulfide Catalysts for the Hydrodesulfurization of Thiophene

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The effect of boron addition was studied on the intrinsic activity of Al_2O_3-supported cobalt–molybdenum and cobalt–tungsten sulfide catalysts prepared by a CVD technique using $[Co(CO)_3NO]$ as a precursor of Co. The catalysts were characterized by means of NO adsorption and Raman spectroscopy. The intrinsic activity of the catalysts are discussed in terms of the turnover frequency (TOF) of the hydrodesulfurization of thiophene, calculated on the basis of the amount of the Co–Mo(W)–S phase. The intrinsic activity on the Co–Mo–S phase and the Co–W–S phase was increased by the addition of boron in a different way depending on the presulfidation temperature. The addition of a proper amount of boron weakened the interactions between molybdenum (tungsten) oxides and the Al_2O_3 surface, leading to an increase in the TOF on the Co–Mo–S phase and the Co–W–S phase by a factor of 1.6 and 1.3, respectively, when $Mo(W)S_2/Al_2O_3$ was presulfided at 673 K. As for the catalyst presulfided at 773 K, the addition of boron increased the TOF on both CVD-Co/MoS_2/B/Al_2O_3 and CVD-Co/WS_2/B/Al_2O_3 by a factor of 1.9. A reverse correlation was observed between the strength of the molybdenum (tungsten) oxides–Al_2O_3 interactions and the intrinsic activity on the Co–Mo(W)–S phase.

In connection with recent strict regulations of the sulfur content in petroleum feedstocks, development of highly active hydrodesulfurization (HDS) catalysts has become one of the most urgent issues in the petroleum industry.[1–3] Sulfided molybdenum- or tungsten-based catalysts have been widely used for industrial HDS reactions.[4–7] Topsøe and co-workers[5,8,9] have proposed that the catalytically active phase in the promoted catalysts is the so called Co(Ni)–Mo–S phase, in which Co(Ni) atoms are located on the edge of MoS_2 particles. Based on the intrinsic catalytic activity, they have shown that there are two types of Co–Mo–S phase, namely Co–Mo–S Type I and Co–Mo–S Type II.[5,8,9] Although the origin of the two types of Co–Mo–S phase is still under debate,[10] it is suggested that Co–Mo–S Type I is related to the highly dispersed single slab MoS_2 particles maintaining their interactions with the support, e.g., Mo–O–Al bonds, while Co–Mo–S Type II is related to MoS_2 particles mainly stacked and not linked with the support, the latter showing about 2 times higher intrinsic activity for HDS than the former.[5,8,9]

It is well known that the addition of Co or Ni to MoS_2, and of Ni to WS_2 catalysts significantly enhances the activity for the HDS of organic sulfur compounds, e.g., thiophene.[4–7] However, such a strong catalytic synergy has not been observed in a Co-promoted WS_2 catalyst, which is generally regarded as an unsuccessful combination.[11] Reports on supported Co–W catalysts, therefore, are very scarce. According to recent studies,[12,13] the reason for the lack of synergy between Co and WS_2 is caused, at least in part, by a greater difference in the sulfidation temperature between Co and W than that between Co and Mo, resulting in a lower coverage of Co on the edge of WS_2 particles than that on the edge of MoS_2 particles. The addition of a chelating agent to the impregnation solution of Co increased the sulfidation temperature of Co due to a complex formation, accompanying a significant increase in the HDS activity of Co–W catalysts.[12,13] Nevertheless, the reason of the weak catalytic synergy between cobalt and tungsten sulfides is not clear enough at present.

A new insight into the nature of the Co–Mo–S and Co–W–S structures has been suggested in our separate study on SiO_2- and Al_2O_3-supported cobalt–tungsten and cobalt–molybdenum sulfide catalysts.[14] Based on the TOF value, we have found that the intrinsic activities of Al_2O_3-supported Co–Mo–S Type I and Co–W–S Type I are very close to each other. We also found that the intrinsic activity of SiO_2-supported Co–W–S pseudo Type II is comparable with that of Co–Mo–S pseudo Type II.[14] Louwers and Prins[15] also suggested that the intrinsic catalytic activities of the Ni–Mo–S phase and Ni–W–S phase are identical for the HDS of thiophene. Therefore, we concluded that there should be strong synergetic effects in the combination of Co and WS_2, as well as that of Co and MoS_2; thus, it could generate a very high catalytic activity, if it were prepared by a proper technique.

In our previous study,[16,17] we have shown that the addition of boron to a $CoMo/Al_2O_3$ catalyst results in weakened interactions between molybdenum oxides and the alumina surface. Thus, the TOF of the boron-added $CoMo/Al_2O_3$ increased by 60%, accompanying a significant increase in the HDS activity of the cobalt–molybdenum sulfide catalyst.[16] In line with this, some workers have also reported that the addition of boron increased the activity of Ni(Co)-promoted molybdenum sulfide catalysts for reactions of hydrodenitrogenation (HDN),[18–20] hydrocracking (HC),[18] and hydrodesulfurization (HDS)[18,21,22]

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of some compounds.

In this sense, it is reasonable to assume that the addition of boron also affects the intrinsic activity of the Al_2O_3-supported Co–W–S structure as observed for the Mo counterpart. In the present study, therefore, we tried to compare the effect of boron addition on the intrinsic activity between the Co–Mo–S phase and the Co–W–S phase supported on alumina. Boron-modified Mo(W)/Al_2O_3 catalysts were prepared by an impregnation technique, whereas Co was introduced to the catalyst by means of a chemical vapor deposition (CVD) technique. It has been reported previously[23–26] that Co atoms admitted by the CVD technique are selectively anchored to the edge of MoS_2 particles to form the Co–Mo–S structure without a concomitant formation of cobalt sulfide clusters having a low catalytic activity. The catalyst preparation by the CVD technique is truly important in gaining real information on the nature of the Co–Mo–S phase as well as the Co–W–S phase to compare their intrinsic activities. The results revealed that the intrinsic activity of the Co–Mo–S phase and the Co–W–S phase are increased by the addition of boron in a different way depending on the presulfidation temperature.

Experimental

Catalyst Preparation. A series of boron-modified alumina was prepared by an impregnation technique. γ-Al_2O_3 (JRC-ALO-7: $180\,m^2\,g^{-1}$) was impregnated with an aqueous H_3BO_3 solution, followed by calcination at 773 K for 5 h.[16,17] The boron contents were 0, 0.3, 0.6, 0.9, 1.2, and 2.5 wt % B. Then, the Al_2O_3–B_2O_3 materials thus prepared, denoted as B/Al_2O_3 hereinafter, were impregnated with either $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ to prepare MoO_3/B/Al_2O_3 or $(NH_4)_6H_2W_{12}O_{40}$ to prepare WO_3/B/Al_2O_3, followed by calcination at 773 K for 5 h. The Mo and W loadings were fixed at 13 wt % MoO_3 and 22 wt % WO_3, respectively.

The MoO_3/B/Al_2O_3 or WO_3/B/Al_2O_3 catalyst was presulfided in a 10% H_2S/H_2 flow either at 673 K for 1.5 h or at 773 K for 1.5 h (MoO_3/B/Al_2O_3), or 2 h (WO_3/B/Al_2O_3). The sulfidation procedures have been described elsewhere.[23] Cobalt was introduced to the catalyst by a CVD technique.[23–26] Briefly, the presulfided catalyst was first evacuated at 673 K for 1 h, and subsequently exposed for 5 min at room temperature to a vapor of $[Co(CO)_3NO]$ (Strem Chemicals) kept at 273 K (CVD technique). After 10 min of evacuation at room temperature, the sample was sulfided again at 673 K for 1.5 h to prepare CoMo/B/Al_2O_3 or CoW/B/Al_2O_3, regardless of the presulfidation temperature. The amount of Co incorporated by the CVD technique was determined by means of XRF (Rigaku RIX2000) within an accuracy of ±5%.[26] The catalysts thus prepared are denoted as CVD-Co/MoS_2/B/Al_2O_3 and CVD-Co/WS_2/B/Al_2O_3, followed by the sulfidation temperature in parentheses if necessary, for the Mo-based and W-based catalysts respectively, hereinafter.

Reaction Procedure. The initial activity of the freshly prepared catalyst for the HDS of thiophene was evaluated at 623 K using a circulation reaction system made of glass under mild reaction conditions (initial H_2 pressure, 20 kPa). The partial pressure of thiophene (2.6 kPa) was kept constant during the reaction. The HDS activity was calculated on the basis of the accumulated amount of H_2S. The details of the reaction procedures have been reported previously.[23]

Catalyst Characterizations. NO Adsorption: The amount of NO adsorption on MoS_2/B/Al_2O_3 was measured by a pulse technique.[23,27] After cooling in the H_2S/H_2 stream, the sulfided catalyst was flushed at room temperature with a high purity He stream. The details of the procedures have been described elsewhere.[23,27]

LRS Measurement: The laser Raman spectra of WO_3/B/Al_2O_3 were measured at room temperature in air on an NRS-2100 spectrometer (JASCO) equipped with a CCD detector. The 514.5 nm line of an Ar^+ laser was used for excitation at an intensity of 10 mW at the source.

Results

The catalytic activities of CVD-Co/MoS_2/B/Al_2O_3 and CVD-Co/WS_2/B/Al_2O_3 are shown in Fig. 1 for the HDS of thiophene as a function of boron loading. The previous results of CVD-Co/MoS_2/B/Al_2O_3(673)[16] are also shown in Fig. 1 for comparison. Apparently, the addition of a proper amount of boron enhanced the HDS activity of CVD-Co/MoS_2/Al_2O_3 and CVD-Co/WS_2/Al_2O_3, irrespective of the presulfidation temperature. The optimum loading of boron for the highest HDS activity was ca. 0.6 wt % B, irrespective of the presulfidation temperature or the kind of metal (Mo or W). The decrease in the HDS activity at a high boron loading was more prominent for CVD-Co/WS_2/B/Al_2O_3 than that for CVD-Co/MoS_2/B/Al_2O_3. In conformity with the present results, Ramírez et al.[22] reported that boron addition to CoMo/Al_2O_3 catalysts enhanced thiophene HDS activity and the maximum activity was attained at a boron content of 0.8 wt % B. Irrespective of the presulfidation temperature and the addition of boron, the HDS activity of CVD-Co/WS_2/Al_2O_3 was considerably lower than that of CVD-Co/MoS_2/Al_2O_3. However, it is worthy of note in Fig. 1 that the catalytic activity of CVD-

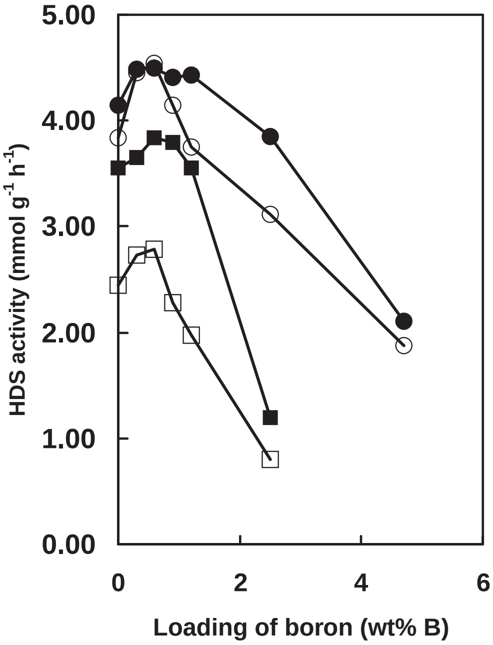

Fig. 1. HDS activity of CVD-Co/MoS_2/B/Al_2O_3 (circle) and CVD-Co/WS_2/B/Al_2O_3 (square) as a function of boron loading. Open symbols: presulfided at 673 K and closed symbols: presulfided at 773 K. The activity of CVD-Co/MoS_2/B/Al_2O_3(673) is taken from Ref. 16 for comparison.

Table 1. Amount of NO Adsorption and Co Content for CVD-Co/Mo(W)S_2/B/Al_2O_3 as a Function of B Content

Boron content /wt % B	Co loading/wt % Co				Amount of NO adsorption /mmol g^{-1}	
	CVD-Co/MoS_2/B/Al_2O_3		CVD-Co/WS_2/B/Al_2O_3			
	673 K[a),c)]	773 K[b)]	673 K[a)]	773 K[b)]	MoS_2/B/Al_2O_3[a),c)]	WS_2/B/Al_2O_3[a)]
0	2.70	2.93	1.66	2.13	0.157	0.069
0.3	2.45	2.53	1.68	1.87	0.153	0.072
0.6	2.33	2.27	1.58	1.61	0.136	0.060
0.9	1.81	1.87	1.35	1.53	0.102	0.052
1.2	1.67	1.61	1.12	1.25	0.101	0.043
2.5	1.54	1.42	0.48	0.45	0.075	
4.7	0.84	0.73				

a) The catalyst was presulfided at 673 K. b) The catalyst was presulfided at 773 K. c) The data are taken from Ref. 16 for comparison.

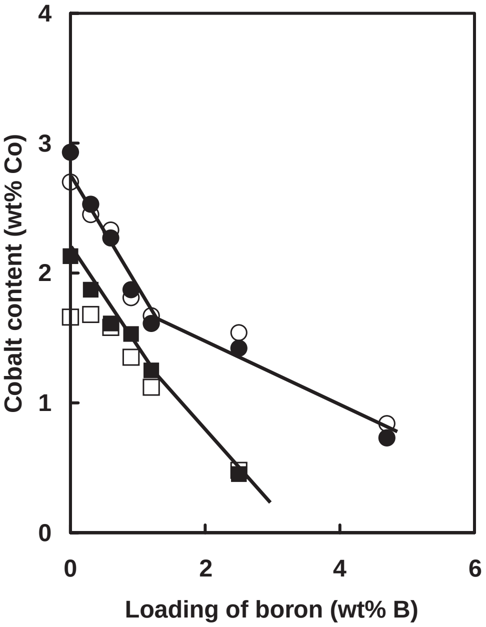

Fig. 2. Amount of Co atoms anchored on CVD-Co/MoS_2/B/Al_2O_3 (circle) and CVD-Co/WS_2/B/Al_2O_3 (square) as a function of boron loading. Open symbols: presulfided at 673 K and closed symbols: presulfided at 773 K.

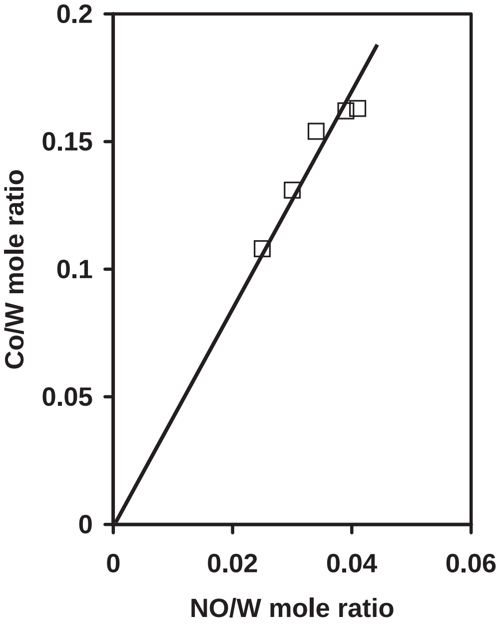

Fig. 3. Correlation between the Co/W mole ratio for CVD-Co/WS_2/B/Al_2O_3 and the NO/W mole ratio for WS_2/B/Al_2O_3.

Co/WS_2/Al_2O_3(773) is significantly higher compared with that of CVD-Co/WS_2/Al_2O_3(673) and close to that of CVD-Co/MoS_2/Al_2O_3(673).

The amount of NO adsorption on WS_2/B/Al_2O_3(673) was measured to evaluate the edge dispersion of WS_2 particles. The adsorption results are summarized in Table 1. The amount of NO adsorption on Mo(W)S_2/B/Al_2O_3 gradually decreased as the boron loading increased, suggesting that the addition of boron decreases the dispersion of MoS_2 or WS_2 clusters on the alumina surface. Figure 2 shows the amount of Co incorporated in CVD-Co/MoS_2/B/Al_2O_3 and CVD-Co/WS_2/B/Al_2O_3 as a function of boron content. The amount of cobalt anchored to MoS_2 and WS_2 particles linearly decreased as the boron content increased up to 1.2 wt %, and more gradually decreased above 1.2 wt %, as shown in Fig. 2. The amount of Co in CVD-Co/MoS_2/B/Al_2O_3 was much higher than that in CVD-Co/WS_2/B/Al_2O_3 in the whole range of B loading, regardless of the presulfidation temperature. The amount of Co accommodated was independent of the presulfidation temperature except for CVD-Co/WS_2/B/Al_2O_3 at a low boron loading, in which the Co loading was greatly increased as the presulfidation temperature was increased from 673 to 773 K in contrast to CVD-Co/MoS_2/B/Al_2O_3.

Figure 3 shows a proportional correlation between the amount of Co accommodated (as expressed by Co/W mole ratio) and the amount of NO adsorption (NO/W mole ratio) for CVD-Co/WS_2/B/Al_2O_3(673) as observed for CVD-Co/MoS_2/support (support: Al_2O_3, TiO_2, ZrO_2, and SiO_2)[23] and CVD-Co/MoS_2/B/Al_2O_3(673).[16] The results in Fig. 3 indicate that all cobalt atoms admitted by the CVD technique are selectively located on the edge of WS_2 particles[16,23] and that the amount of Co in CVD-Co/Mo(W)S_2/B/Al_2O_3 represents the amount of the Co–Mo(W)–S phase.[23,27]

The intrinsic activity of the catalyst was evaluated in terms of a turnover frequency (TOF) calculated on the basis of the amount of Co anchored by the CVD technique, assuming that the Co–Mo(W)–S phase is selectively prepared by the present technique. The TOF is shown in Fig. 4 as a function of boron loading and the TOF value is summarized in Table 2. The TOF over boron-free CVD-Co/MoS_2/Al_2O_3 and CVD-Co/WS_2/Al_2O_3 are essentially identical, as shown in Fig. 4, in agree-

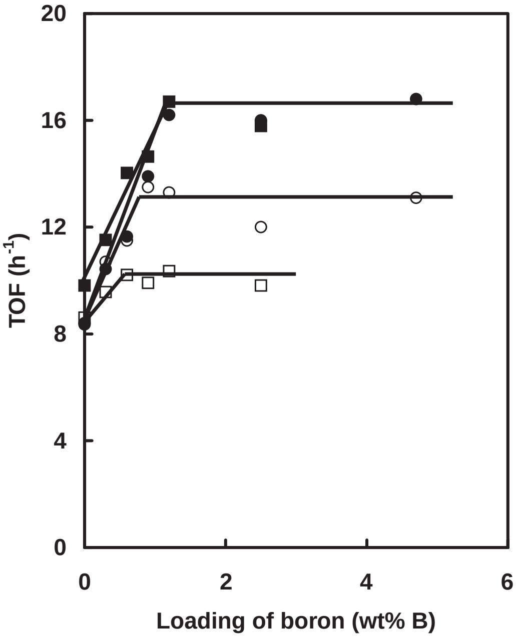

Fig. 4. TOF of the thiophene HDS over CVD-Co/MoS_2/B/Al_2O_3 (circle) and CVD-Co/WS_2/B/Al_2O_3 (square) as a function of boron loading. Open symbols: presulfided at 673 K and closed symbols: presulfided at 773 K.

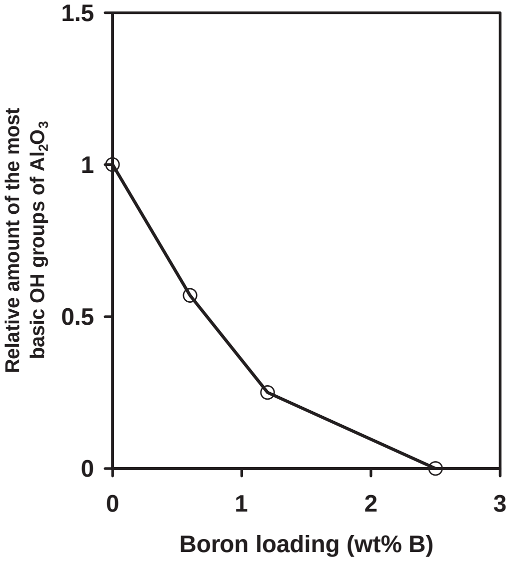

Fig. 5. Amount of the most basic OH groups (3772 cm^{-1}) of B/Al_2O_3 relative to that of Al_2O_3 as a function of boron loading.

Table 2. TOF of Thiophene HDS on the Co–Mo(W)–S Phase for CVD-Co/Mo(W)S_2/B/Al_2O_3 as a Function of Boron Loading

Boron content /wt % B	TOF/h^{-1}				Relative TOF			
	CVD-Co/MoS_2/B/Al_2O_3		CVD-Co/WS_2/B/Al_2O_3		CVD-Co/MoS_2/B/$Al_2O_3$$^{a)}$		CVD-Co/WS_2/B/$Al_2O_3$$^{b)}$	
	673 K$^{c)}$	773 K	673 K	773 K	673 K	773 K	673 K	773 K
0	8.4	8.4	8.6	9.8	1	1	1	1.1
0.3	10.7	10.4	9.6	11.5	1.3	1.2	1.1	1.3
0.6	11.5	11.7	10.2	14.0	1.4	1.4	1.2	1.6
0.9	13.5	13.9	9.9	14.6	1.6	1.7	1.2	1.7
1.2	13.3	16.2	10.4	16.7	1.6	1.9	1.2	1.9
2.5	12.0	16	9.8	15.8	1.4	1.9	1.1	1.8
4.7	13.1	16.8			1.6	2.0		

a) Relative TOF is defined as the ratio of the TOF value on CVD-Co/MoS_2/B/Al_2O_3 catalyst to the one on boron-free CVD-Co/MoS_2/Al_2O_3 catalyst presulfided at 673 K. b) Relative TOF is defined as the ratio of the TOF value on CVD-Co/WS_2/B/Al_2O_3 catalyst to the one on boron-free CVD-Co/WS_2/Al_2O_3 catalyst presulfided at 673 K. c) The data are taken from Ref. 16 for comparison.

ment with the previous results.[14] The addition of about 0.9 wt % B significantly increased the TOF on CVD-Co/MoS_2/B/Al_2O_3(673) and CVD-Co/WS_2/B/Al_2O_3(673) by factors of 1.6 and 1.2, respectively. The TOF kept constant with a further increase of boron loading. As for CVD-Co/Mo(W)S_2/B/Al_2O_3(773), the addition of boron up to ca. 1.2 wt % B linearly increased the TOF as high as 1.9 times compared to that of the boron-free catalysts presulfided at 673 K, followed by a constant TOF with the further addition of boron.

The Al_2O_3 surface modified by the addition of boron has been analyzed by means of FTIR in our previous study.[17] The addition of boron resulted in the depletion of the intensity of the peaks at 3772 and 3727 cm^{-1} that are assigned to basic OH groups of alumina, indicating that boric acid preferentially reacts with the basic OH groups of alumina.[17] Figure 5 shows the relative amount of the most basic OH groups of Al_2O_3 at 3772 cm^{-1} as a representative of the basic OH groups against the boron loading. Apparently, it decreased as the boron content increased and completely disappeared at 2.5 wt % B. The band at 3727 cm^{-1} showed a similar change in intensity with that of the band at 3772 cm^{-1}. However, the band was superimposed with the bands at a lower wavenumber, and thus, the band intensity could not be evaluated as accurately as the band intensity at 3772 cm^{-1}. In order to find a correlation between the surface property of B/Al_2O_3 and the intrinsic activity of the Co–Mo(W)–S phase, we tried to correlate the relative amount of the most basic OH groups (3772 cm^{-1}) of B/Al_2O_3 with the relative TOF in Table 2 for CVD-Co/MoS_2/B/Al_2O_3 and CVD-Co/WS_2/B/Al_2O_3. As shown in Fig. 6, the relative TOF linearly increased as the relative amount of OH groups of B/Al_2O_3 decreased to about 0.2, and leveled off with a further decrease of the amount of the OH groups of B/Al_2O_3.

The Raman spectra for a MoO_3/B/Al_2O_3 catalyst have been reported in a previous study,[17] showing a decrease of

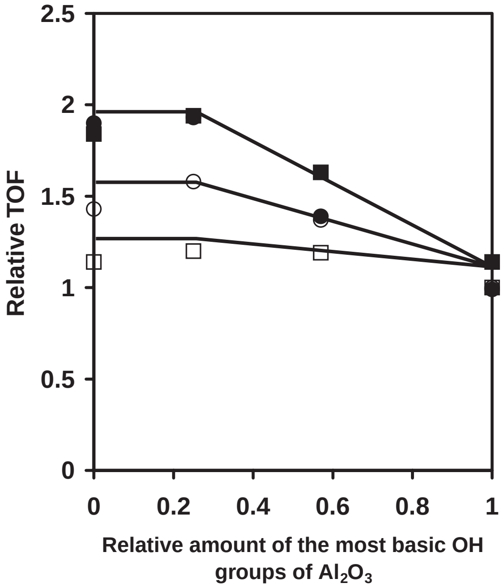

Fig. 6. Correlation between the intrinsic activities of CVD-Co/MoS_2/B/Al_2O_3 (circle) and CVD-Co/WS_2/B/Al_2O_3 (square) and the amount of the most basic OH groups (3772 cm^{-1}) of B/Al_2O_3 relative to that of Al_2O_3. Open symbols: presulfided at 673 K and closed symbols: presulfided at 773 K.

the dispersion of molybdenum oxides by the addition of boron. Figure 7 depicts the Raman spectra of WO_3/B/Al_2O_3. The Raman shifts of the main peaks are summarized in Table 3. Due to a very high background of the spectra for the boron-free WO_3/Al_2O_3, it was hard to detect a peak at around 990 cm^{-1} that is assigned to a W=O fundamental stretching vibration mode due to polytungstate clusters.[28] It is likely, however, that the formation of WO_3 on the boron-free catalyst is excluded by the absence of the sharp peaks due to WO_3. As for the 0.3 wt % B catalysts, a new set of clearly visible bands assigned to crystalline WO_3 appeared at ca. 810 and 720 cm^{-1} along with a 990 cm^{-1} band. The increase of the boron content enhanced the peak intensities due to crystalline WO_3 relative to that due to polytungstate species. It is concluded that the dispersion of WO_3 particles is decreased by the addition of boron, in conformity with the NO adsorption results in Table 1.

Discussion

Selective Formation of the Co–Mo(W)–S Phase by the CVD Technique. XPS[23] and Co K-edge XANES[26] spectra in our previous study on CVD-Co/MoS_2/support (support: Al_2O_3, TiO_2, ZrO_2, and SiO_2) catalysts have shown that the cobalt sulfide species, admitted by the CVD technique using [$Co(CO)_3NO$], preferentially interact with MoS_2 particles. The edge dispersions of MoS_2 and WS_2 particles were evaluated by using the adsorption capacity of NO molecules at room temperature, since NO molecules adsorb selectively on the edge of the particles.[29,30] Figure 3 shows a proportional correlation between the Co/W and the NO/W mole ratios for the W-based catalysts, demonstrating that the Co–W–S phase is selectively formed by the CVD technique for CVD-Co/WS_2/B/Al_2O_3 irrespective of the B content, as well as the Co–Mo–S phase.[16,23–25] A proportional correlation was also observed for CVD-Co/WS_2/Al_2O_3(773).[31] Comparing the slope in Fig. 3 and that for CVD-Co/MoS_2/B/Al_2O_3,[16] the former is 1.7 times as high as the latter, in agreement with the results for SiO_2-supported CVD-Co/Mo(W)S_2 catalysts.[31] This suggests that the probability of the formation of NO adsorption sites on the edge of MoS_2 particles is 70% higher than that of WS_2 particles as suggested previously,[31] since the edge of the MoS_2 particles is essentially fully covered by the Co atoms in the Co–Mo–S phase under the present CVD conditions.[23–25]

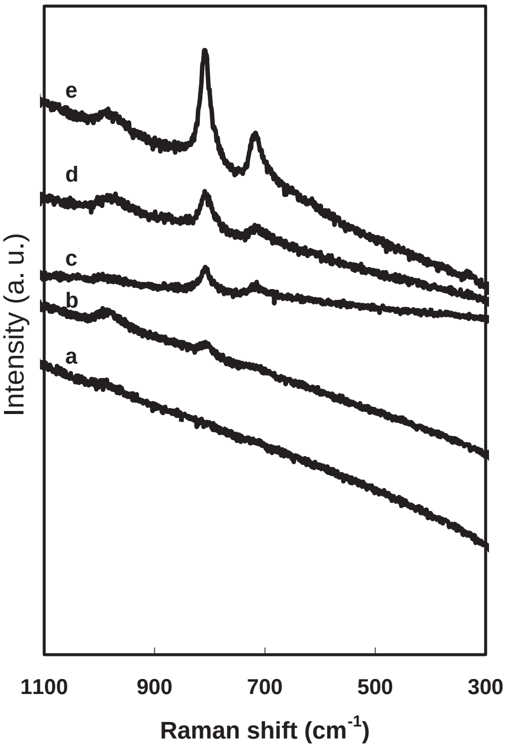

Fig. 7. Raman spectra of WO_3/B/Al_2O_3: a) 0, b) 0.3, c) 0.6, d) 0.9, and e) 1.2 wt % B.

Table 3. Raman Shifts of the Main Peaks for WO_3/B/Al_2O_3

Catalyst	Wavenumbers/cm^{-1}		
WO_3/Al_2O_3	989		
WO_3/B/Al_2O_3 (0.3 wt % B)	990	808	717
WO_3/B/Al_2O_3 (0.6 wt % B)	990	809	719
WO_3/B/Al_2O_3 (0.9 wt % B)	991	809	719
WO_3/B/Al_2O_3 (1.2 wt % B)	990	809	719
Crystalline WO_3[a)]		802	712

a) Ref. 28.

Effects of Boron Addition and Presulfidation Temperature on the Intrinsic Activity of the Co–Mo(W)–S Phase. As shown in Fig. 4, the TOF values of the thiophene HDS on the Co–Mo–S phase and the Co–W–S phase in the boron-free CVD-Co/MoS_2/Al_2O_3 and CVD-Co/WS_2/Al_2O_3 catalysts presulfided at 673 K are identical under the present reaction conditions. In line with this, Louwers and Prins[15] suggested, on the basis of the activity increase by the addition of Ni, that the intrinsic activities of the Ni–Mo–S phase and the Ni–W–S phase supported on activated carbon are identical. Topsøe et al.[5,8,9] defined two types of the Co–Mo–S phase, depending on the intrinsic activity, Co–Mo–S Type I and Type II. Co–Mo–S Type II, which is formed by high temperature sulfidation (875–1275 K), is about twice as active for the HDS of thiophene than Co–Mo–S Type I formed by low temperature sulfidation (675 K). Accordingly, it is considered that the Co–Mo(W)–S phase formed in the boron-free CVD-Co/MoS_2/Al_2O_3 and CVD-Co/WS_2/Al_2O_3 presulfided at 673 K is classified to Type I by definition.[5]

The addition of boron up to 0.9 wt % B increases the TOF on CVD-Co/MoS_2/B/Al_2O_3(673) by a factor of 1.6, and the TOF is not varied by further addition of boron. On the basis of the results, we previously concluded the formation of Co–Mo–S Type II on CVD-Co/MoS_2/B/Al_2O_3(673).[16] However, as shown in Fig. 4, the TOF over CVD-Co/MoS_2/B/Al_2O_3 (>1.2 wt %) is further increased by presulfidation at 773 K. The TOF over CVD-Co/MoS_2/B/Al_2O_3(773) is 1.9 times as high as that over boron-free CVD-Co/MoS_2/Al_2O_3(673). The extent of the increase in TOF is consistent with that observed for CVD-Co/MoS_2/SiO_2(673), but smaller than that expected for the shift from Co–Mo–S Type I to Type II (2.3 times increase).[14] Accordingly, it is suggested that the Co–Mo–S phase in both high B-content CVD-Co/MoS_2/B/Al_2O_3 catalysts presulfided at 673 and 773 K is classified to "pseudo" Co–Mo–S Type II, having an intermediate TOF between Type I and Type II.[14] It is unlikely to assume that Co–Mo–S pseudo Type II in CVD-Co/MoS_2/B/Al_2O_3 is a simple mixture of Co–Mo–S Type I and Type II, since the TOF on Co–Mo–S pseudo Type II is not varied by B loading above 0.9 and 1.2 wt % for the catalysts presulfided at 673 and 773 K, respectively (Fig. 4). In addition, in our previous study on SiO_2-supported cobalt–molybdenum sulfide catalysts,[14] in which MoS_2 particles interact only weakly with the SiO_2 surface[32] and are completely sulfided at 673 K,[33–35] we found that the presulfidation of CVD-Co/MoS_2/SiO_2 at 673 K forms only Co–Mo–S pseudo Type II. The real Co–Mo–S Type II was formed only when the catalyst was presulfided at 873 K or higher.[36]

With the W-based catalysts, the addition of boron exhibits similar effects on the intrinsic activity to the Mo counterparts as shown in Fig. 4, except that the increase in the TOF on CVD-Co/WS_2/B/Al_2O_3(673) is only 1.2 times, in contrast to 1.6 times for that on CVD-Co/MoS_2/B/Al_2O_3, presumably being caused by incomplete sulfidation of W at 673 K.[14] Similarly, we suggest the formation of Co–W–S pseudo Type II in both CVD-Co/WS_2/B/Al_2O_3 presulfided at 673 and 773 K. The TOF on CVD-Co/WS_2/B/Al_2O_3(773) with a B content >1.2 wt % B is very close to that of the MoS_2 counterparts, as shown in Fig. 4. The lower catalytic activity of CVD-Co/WS_2/B/Al_2O_3 than the MoS_2 counterpart, regardless of the presulfidation temperature as shown in Fig. 1, is merely caused by a smaller amount of the Co–W–S active phase due to poorer dispersion of WS_2 particles than in MoS_2 particles, as evidenced by the amount of NO adsorption (Table 1) and by the amount of anchored Co atoms by the CVD technique (Fig. 2). It is widely accepted[5] that WO_3/Al_2O_3 catalyst is much more difficult to sulfide than MoO_3/Al_2O_3 catalyst. Therefore, the great increase in the HDS activity of CVD-Co/WS_2/B/Al_2O_3, which is observed at a low B content as the presulfidation temperature is increased from 673 to 773 K, can be attributed to the increase in the sulfidation degree of W,[14] accompanying the increase in the amount of anchored Co atoms, as shown in Fig. 2.

Correlation between the Strength of the Mo(W)O_3–Al_2O_3 Interactions and the Intrinsic Activity. We have concluded by FTIR, Raman spectroscopy, and XPS study that the addition of boron weakens the interactions between molybdenum oxides and the Al_2O_3 surface, resulting in a 1.6 times increase in the TOF on CVD-Co/MoS_2/B/Al_2O_3(673).[16,17] Similarly, as evidenced by Raman spectroscopy (Fig. 6), we conclude that the addition of boron to the W-based catalyst weakens the interactions between tungsten oxides and the Al_2O_3 surface, leading to an increase in the TOF on CVD-Co/WS_2/B/Al_2O_3(673) by a factor of 1.2 (Fig. 4), and a slight increase in the HDS activity (Fig. 1). It is safe to assume that the interactions of Mo(W)O_3–Al_2O_3 can be represented by the amount of the most basic OH groups of Al_2O_3, since MoO_3–Al_2O_3 strong interactions are formed by the reaction of $MoO_4{}^{2-}$ with the basic hydroxy group of Al_2O_3.[37] As shown in Fig. 6, a reverse correlation is observed between the amount of the most basic OH groups of the support and the relative TOF, regardless of the presulfidation temperature and the kind of metal. This suggests that the TOF of the Co–Mo(W)–S phase can be essentially elucidated by the extent of strong interactions between Mo(W)S_2 and the support, presumably via Mo–O–Al linkages remaining after the presulfidation. When most of the basic OH groups are consumed by reaction with boric acid at a high B content, the interactions between Mo(W)S_2 and the Al_2O_3 surface become much weaker, resulting in the formation of Co–Mo(W)–S pseudo Type II.

When the catalyst was presulfided at 773 K, a further increase (1.9 times increase) in the TOF was observed for CVD-Co/Mo(W)S_2/B/Al_2O_3. This may be attributed to the formation of Mo(W)S_2 particles of better crystallinity. It is very rational to assume that the sulfidation temperature at a fixed H_2S/H_2 pressure strongly determines the crystallinity of Mo(W)S_2 particles. In line with this, Kooyman et al.[38] clearly showed by HRTEM that the crystallinity of supported MoS_2 particles is improved by sulfidation at 873 K compared to the one formed at 673 K. Nevertheless, in order to confirm this suggestion, further systematic studies are required to get direct evidence about the formation of Mo(W)S_2 particles with improved crystallinity on CVD-Co/Mo(W)S_2/B/Al_2O_3(773).

Based on the results, we can summarize the effects of boron addition on the intrinsic activity of Al_2O_3-supported Co–Mo and Co–W sulfide catalysts; that is, the addition of boron weakens the interactions between molybdenum (tungsten) oxides and Al_2O_3 surface,[17] thus increasing the TOF on CVD-Co/MoS_2/B/Al_2O_3(673) and CVD-Co/WS_2/B/Al_2O_3(673) by a factor of 1.6 and 1.2, respectively. The sulfidation at 773 K weakens Mo(W)S_2–support interactions, brought about by the boron addition and increased sulfidation degree in the case of the W catalysts, thus increasing the TOF by a factor of 1.9, irrespective of the kind of metal. The higher TOF may be correlated to the increased crystallinity of Mo(W)S_2 particles at the higher temperature of presulfidation.[14] However, the excessive loading of boron results in detrimental effects, i.e., the Mo(W)S_2 particles become easily sintered by the addition of boron as a consequence of the weakened interactions between Mo(W)S_2 and Al_2O_3, thus causing the great decrease in the HDS activity at a high boron loading. The addition of a small amount of boron (<2.5 wt % B) hardly affects the surface area of MoO_3/Al_2O_3; however, a slight decrease in the surface area was observed at a high boron content.[16] It is considered from the above results that WS_2 particles are much more prone to sintering than MoS_2 particles, especially when presulfided at 773 K, as shown in Fig. 1. This is substantiated by the greater decrease of the amount of Co in CVD-Co/WS_2/B/Al_2O_3 by the addition of >2.5 wt % B than that in the Mo counterpart (Fig. 2).

Conclusion

In the present study, we evaluated the effect of boron addition and the presulfidation temperature on the intrinsic activity of the Co–W–S phase for the HDS of thiophene and compared with the effect of boron on the intrinsic activity of the Co–Mo–S phase. The CVD technique was used to prepare Al_2O_3-supported cobalt–molybdenum and cobalt–tungsten sulfide catalysts, in which all the Co atoms form the active phase. The catalysts were characterized by NO adsorption and LRS. The salient findings in the present study are as follows:

1. The Co–W–S phase was selectively formed by the CVD technique using $Co(CO)_3NO$ as a precursor of Co as observed for the Co–Mo–S phase.
2. The TOF on the Co–W–S phase in CVD-Co/WS_2/Al_2O_3(673) are essentially identical with that on the Co–Mo–S phase in CVD-Co/MoS_2/Al_2O_3(673).
3. The TOFs on the Co–Mo–S phase and the Co–W–S phase were increased by the addition of boron in a different way depending on the presulfidation temperature.
4. The addition of boron weakened the interactions between Mo(W)S_2 and the Al_2O_3 surface, resulting in the increase in the TOF for CVD-Co/MoS_2/B/Al_2O_3(673) and CVD-Co/WS_2/B/Al_2O_3(673) by factors of 1.6 and 1.2, respectively.
5. The presulfidation at 773 K further increased the TOF by a factor of 1.9 for both CVD-Co/MoS_2/B/Al_2O_3 or CVD-Co/WS_2/B/Al_2O_3, presumably being caused by the increased crystallinity of Mo(W)S_2 particles at a higher temperature.
6. There is a reverse correlation between the strength of the interactions of Mo(W) oxides–Al_2O_3 and the intrinsic activity.

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