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# **Characterization and Hydrodesulfurization Activity of CoMo Catalysts Supported on Boron-Doped Sol-Gel Alumina**

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## Abstract

A series of hydrodesulfurization (HDS) catalysts was prepared by impregnation of Co and Mo on sol-gel B-Al<sub>2</sub>O<sub>3</sub> supports with B/Al ratios of 0, 0.02, 0.04, 0.08, 0.20, 0.32, 0.49, and 0.61. The thiophene HDS and dibenzothiophene (DBT) HDS activities were both maximal for the catalyst with B/Al = 0.04, with respective values 70% and 42% higher than those for an industrial reference catalyst. These maxima in HDS activity correlated with the previously reported presence of isolated BO<sub>4</sub> surface species. These BO<sub>4</sub> species were responsible for a local maximum in the acidity of the B-Al<sub>2</sub>O<sub>3</sub> supports when B/Al = 0.04. In contrast, the formation of mixed oxides (A<sub>9</sub>B<sub>2</sub> and A<sub>2</sub>B) or B<sub>2</sub>O<sub>3</sub> that also resulted in enhanced acidity of the B-Al<sub>2</sub>O<sub>3</sub> supports had a detrimental effect on the HDS activity.

The 4,6-dimethyldibenzothiophene (4,6-DMDBT) HDS activity over the CoMo/B-Al<sub>2</sub>O<sub>3</sub> catalysts decreased when the B/Al ratio was increased. This was attributed to the strong direct desulfurization character of the CoMo catalysts supported on the B-Al<sub>2</sub>O<sub>3</sub> supports, because high hydrogenation ability toward the C=C double bonds is essential prior to sulfur removal from 4,6-DMDBT. The excellent performance in the thiophene and DBT HDS of the CoMo/B-Al<sub>2</sub>O<sub>3</sub> catalysts is particularly useful for ultra-deep HDS of light fractions.

**Keywords:** Hydrodesulfurization, boron, alumina, sol-gel, thiophene, DBT, 4,6-DMDBT, acidity

## 1. Introduction

Sulfur-containing compounds in transportation fuels have not only direct detrimental effects on the atmosphere but are also responsible for deactivation of NO<sub>x</sub> removal catalysts in vehicles [1]. Reduction in the sulfur content in transportation fuels is essential to satisfy the NO<sub>x</sub> emission regulations that are being introduced in developed countries. The maximum quantity of sulfur tolerated in gasoline in the US has been decreased to 15 ppm [2], and that in all the transportation fuels in EU must be reduced to less than 10 ppm by 2009 [3] and by 2007 in Japan [1]. These regulations have forced refineries to develop increasingly efficient hydrodesulfurization (HDS) processes that are called 'ultra-deep HDS processes'. Among possible technological choices to satisfy these stringent regulations, improvement in the HDS catalytic formulations is one of the most practical from an economical point of view, because for example, there is no need to build new facilities for deeper HDS.

The most typical HDS catalysts consist of a MoS<sub>2</sub> active phase promoted by Co or Ni atoms, called 'CoMoS' or 'NiMoS' phase, both of which have been extensively researched [4-9], and by porous  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> supports. Noble metals have often been proposed as newly developed active phases. Improvement in the properties of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> based supports and enhancement of the catalytic functions of CoMoS or NiMoS phase might be achieved by the use of newly developed supports such as TiO<sub>2</sub> or mixed oxides, carbon, or zeolites, and/or by doping with third elements such as fluorine, phosphorus, or boron [10-28]. Recently, we reported that fine-tuning of the physical and chemical properties of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> supports by sol-gel synthesis improves the catalytic HDS performance of CoMo catalysts [29-31]. First, we found that during preparation the textural and physical properties of the sol-gel Al<sub>2</sub>O<sub>3</sub>

powders can be finely tuned by changing the ratio of hydrolysis (R), defined as  $[\text{H}_2\text{O}]/[\text{aluminum-tri-sec-butoxide (ASB)}]$  [29]. Then, we showed that the HDS performance of CoMo catalysts supported on sol-gel prepared  $\text{Al}_2\text{O}_3$  powders depend on R. The catalytic activities were maximal for  $R = 8 \sim 10$  and superior to that of an industrial reference catalyst (IRC) for HDS of thiophene and dibenzothiophene (DBT), whereas inferior to the IRC for HDS of 4,6-dimethyldibenzothiophene (4,6-DMDBT) [31], which is well known as one of the most HDS-refractory compounds present in diesel oil fractions [32,33]. That particular study also showed that HDS of 4,6-DMDBT requires the hydrogenation (HYD) of 4H-4,6-DMDBT to 6H-4,6-DMDBT, which is promoted over catalysts with  $R = 8 \sim 10$  that exhibit the largest proportion of strong acid sites relative to the total quantity of acid sites [31].

In a further study, Dumeignil *et al.* [34-36] investigated modification of sol-gel  $\text{Al}_2\text{O}_3$  with a fixed  $R = 10$  by introducing boron (B) at various B/Al ratios during the sol-gel synthesis. Their results showed that the B/Al ratio affected the structure and properties of the sol-gel prepared B- $\text{Al}_2\text{O}_3$  powders, and suggested that the catalytic performance of the catalysts prepared on these B- $\text{Al}_2\text{O}_3$  powders might depend on the B/Al ratio. In particular, an increase in the acidity of the  $\text{Al}_2\text{O}_3$  by the introduction of B is expected to improve the HDS properties of the catalysts.

In this current study, we prepared CoMo HDS catalysts using B- $\text{Al}_2\text{O}_3$  powders with various B/Al ratios and then investigated the effects of B/Al ratio on the properties and HDS performance of the CoMo catalysts. By choosing thiophene, DBT, and 4,6-DMDBT as probe molecules for HDS catalytic activity tests, we examined the relationships among structure, properties, and activity of the B- $\text{Al}_2\text{O}_3$  supported CoMo catalysts.

## 2. Experimental

### 2.1. Catalysts preparation

B-Al<sub>2</sub>O<sub>3</sub> supports were synthesized using a sol-gel method with R = 10 selected according to our previous study [31] and nominal B/Al ratios of 0, 0.02, 0.04, 0.08, 0.3, 0.5, 0.8, and 1. Table 1 lists the B/Al values corrected taking into account the evaporation of B during calcination, which is described in our previous study [36]. The preparation methods are described elsewhere [34-36]. The CoMo/B-Al<sub>2</sub>O<sub>3</sub> oxidic catalysts (10 wt.% Mo as metallic Mo with a fixed Co/(Co + Mo) ratio ( $\alpha$ ) of 0.4, equivalent to 4.1 wt.% Co as metallic Co) were prepared by simultaneous incipient wetness impregnation of aqueous solutions of cobalt nitrate and molybdenum heptamolybdate. After impregnation, the catalysts were kept in a closed vessel during two hours for aging, and then dried overnight in an oven at 373 K. Calcination was performed under a flow of air at 773 K (reached at a rate of 40 K h<sup>-1</sup>) during 3 h.

### 2.2. Catalyst characterization

#### 2.2.1. XRD patterns

XRD patterns of the dried and calcined B-Al<sub>2</sub>O<sub>3</sub> and the calcined CoMo/B-Al<sub>2</sub>O<sub>3</sub> powders were recorded at room temperature using an MXP 18 diffractometer (Mac Science Co. Ltd.) equipped with a copper anode (0.154 nm, 50 kV x 35 mA) with a secondary monochromator. The measurements were done using the  $\theta$ -2 $\theta$  method from  $2\theta = 5^\circ$  to  $2\theta = 75^\circ$  with a scanning step of  $0.2^\circ$  and a scanning rate of  $4^\circ \text{ min}^{-1}$ .

#### 2.2.2. Porosimetry

The N<sub>2</sub> adsorption and desorption isotherms of the B-Al<sub>2</sub>O<sub>3</sub> supports and the

CoMo/B-Al<sub>2</sub>O<sub>3</sub> oxidic catalysts were measured using a Micromeritics ASAP 2010 system. The BET specific surface area (SSA) and BJH pore volume (PV) were calculated using the software provided with this system. The water PV was measured according to a method described elsewhere [29].

### **2.2.3. NH<sub>3</sub> temperature-programmed desorption (TPD)**

The acidity of the calcined B-Al<sub>2</sub>O<sub>3</sub> powders was measured by using the NH<sub>3</sub> TPD method with a BEL-Japan TPD-1S system equipped with a quadra-pole mass spectrometer. The total acidity was obtained by integrating the TPD profile from 373 K to 823 K. The proportion of strong acid sites was calculated based on the area of high temperature peak at about 523 K obtained by deconvolution of the TPD profile relative to the total acidity. The deconvolution was conducted using two Gaussian profiles with the maxima at 443 K and 623 K.

### **2.2.4. Laser Raman spectroscopy**

The Raman spectra of the oxidic catalysts were recorded between 200 and 1400 cm<sup>-1</sup> by using a LabRam Infinity spectrometer. The excitation power of the 532 nm line of the YAG laser was fixed at 5 mW.

## **2.3. Catalytic activity tests**

The catalytic activity for HDS of thiophene was measured at atmospheric pressure in a fixed-bed flow-type reactor with 0.2 g of catalyst. Before reaction, the oxidic catalysts were sulfided at 673 K for 3 h under a flow (20 cm<sup>3</sup> min<sup>-1</sup>) of H<sub>2</sub>S / H<sub>2</sub> (10 / 90) and then cooled to a reaction temperature of 573 K. Thiophene was introduced after purification by two successive vacuum distillations into the reactor at

a constant pressure of 6.65 kPa using a hydrogen flow ( $20 \text{ cm}^3 \text{ min}^{-1}$ ) [31]. The catalytic activities were measured after reaching the steady state, typically after 3 h of reaction.

The catalytic activity tests for HDS of DBT and 4,6-DMDBT were done at 603 K for 1 h using a batch reaction system [31] with catalysts presulfided in the same way as that described in the preceding paragraph.

The catalytic activities of the prepared catalysts were compared with that of a commercially available CoMo/Al<sub>2</sub>O<sub>3</sub> (hereinafter called industrial reference catalyst, or IRC) loaded with 15 wt.% Mo as metallic Mo that had been recently developed for deep HDS. Its detailed characteristics were confidential.

### 3. Results

#### 3.1. Morphology and properties of B-Al<sub>2</sub>O<sub>3</sub> supports

##### 3.1.1. Structure of B-Al<sub>2</sub>O<sub>3</sub> supports

The recorded XRD diffraction patterns in the dried (Fig. 1a) and calcined (Fig. 1b) states well corresponded to the schematic structural models shown in Fig. 2, that were derived from the results obtained by previous studies [34-36]. Four domains (I, II, III, and IV) depending on the B/Al ratio (0 to 0.06, 0.06 to 0.15, 0.15 to 0.47, and over 0.47, respectively) were identified on the dried solids as shown in Fig. 2b. The B/Al ratio for the boundary between domains II and III (0.15) and that between domains III and IV (0.47) agreed with those previously defined by Gielisse *et al.* [37], who proposed a phase diagram for B-Al<sub>2</sub>O<sub>3</sub> mixed oxides, with the boundaries at B/Al = 0.22 ('G1' in Fig. 2) and B/Al = 0.51 ('G2' in Fig. 2). These four domains remained after calcination of the solids (Fig. 2c) [36]. A relatively large structural modification after calcination was observed in domain III, where some sufficiently long BO<sub>3</sub> chains partly volatilized during calcination.



The key result here is that the creation of isolated surface  $\text{BO}_4$  species in domain I ( $\text{B}/\text{Al} < 0.06$ ) produced a particular morphology that deviated from the diagram proposed by Gielisse *et al.* [37]. Note that this local perturbation of the surface of the  $\text{Al}_2\text{O}_3$  is catalytically important, as will be discussed in § 4 (Discussion).

### 3.1.2. Texture of B- $\text{Al}_2\text{O}_3$ supports

Table 1 shows the textural and acidic properties of the sol-gel prepared B- $\text{Al}_2\text{O}_3$  supports. Due to evaporation of  $\text{BO}_3$  chains during calcination, the B/Al ratios of the calcined powders for  $\text{B}/\text{Al} > 0.15$  were smaller than those used for the preparation [36]. Therefore, as described in the Experimental section, the B/Al ratios in Table 1 are the corrected values using the relationship obtained in our previous study [36].

The SSA increased with increasing B/Al up to  $\text{B}/\text{Al} = 0.08$ , and then remained relatively constant at about  $550 \pm 50 \text{ m}^2 \cdot \text{g}^{-1}$  as shown in Fig. 3. In contrast, PV decreased with increasing B/Al up to  $\text{B}/\text{Al} = 0.20$ , and then increased with further increase in B/Al. As a result, the average pore diameter (APD) was minimum when  $\text{B}/\text{Al} = 0.20 \sim 0.32$ , but was larger than 4.5 nm that is necessary for HDS of distillate fractions of petroleum. The water PV decreased with increasing B/Al ratio except at  $\text{B}/\text{Al} = 0.61$ . However, the B- $\text{Al}_2\text{O}_3$  support with the smallest water PV ( $\text{B}/\text{Al} = 0.49$ ) still had a PV large enough for loading active components of Co and Mo necessary for HDS catalysts.

In most of the past studies, B- $\text{Al}_2\text{O}_3$  supports were prepared by impregnation or coprecipitation. For samples prepared by impregnation (generally  $\text{H}_3\text{BO}_3$  on  $\text{Al}_2\text{O}_3$  or on boehmite), the SSA was often reported to decrease due to pore plugging by B-containing oxidic species [38-40]. For samples prepared by coprecipitation (generally  $\text{H}_3\text{BO}_3$  and  $\text{Al}(\text{NO}_3)_3$  in the presence of ammonia), SSA increased [41-43]. Some studies [43,44] reported that APD decreased by a factor of *ca.* 2 upon introduction of

B by coprecipitation. Similarly, in the present study, introduction of B induced an increase in SSA and a decrease in APD by a factor up to *ca.* 2 (Table 1: 9.3 nm for B/Al = 0 and 4.6 nm for B/Al = 0.20).

The increase in the SSA upon addition of B can be attributed to two factors. The first factor is that replacing Al atoms by B atoms induces a weight decrease. For example, if 50% of the Al atoms of an Al<sub>2</sub>O<sub>3</sub> network were replaced with B atoms (*i.e.*, for B/Al = 1) without any structural change, the SSA would accordingly increase by *ca.* 12%. The second factor is that the introduction of B induces network modifications and/or changes in the size of the first-order particles. The first factor can be neglected; for example, for B/Al = 0.61, a large increase in SSA of *ca.* 67% was observed (Table 1). Thus, the increase in SSA upon introduction of B is mainly due to the second factor. In particular, volatilization of BO<sub>3</sub> chains for B/Al > 0.15 was likely responsible for the dislocation of the structure [36], which would lead to a significant increase in SSA.

### 3.1.3. Acidity of B-Al<sub>2</sub>O<sub>3</sub> supports

Figure 4 shows the TPD profiles of the B-Al<sub>2</sub>O<sub>3</sub> supports, and Fig. 5 shows the effect of B/Al ratio on total acidity. The total acidity first increased with increasing B/Al up to B/Al = 0.04 (2.51 mmol g<sup>-1</sup>), then decreased until B/Al = 0.08 (1.85 mmol g<sup>-1</sup>), and finally increased again when 0.08 < B/Al < 0.61. Note that the powder with B/Al = 0.61 produced a particularly large level of acidity (4.09 mmol g<sup>-1</sup>). As shown in Fig. 5, the proportion of strong acid sites relative to total acidity decreased from 85.9% for B/Al = 0 to 58.2% for B/Al = 0.08 and then remained relatively constant at 62 ± 6% for the B-Al<sub>2</sub>O<sub>3</sub> powders that had B/Al > 0.08.

Some past studies dealt with the acidity of B-Al<sub>2</sub>O<sub>3</sub> supports prepared by various methods. Similarity in the preparation method used in this study allowed comparison

between the results obtained here and those obtained for powders prepared by coprecipitation. Peil *et al.* [41,45] reported that the strength of the strongest acid sites increased drastically until B/Al  $\sim$  0.15 and then remained relatively constant. Wang *et al.* reported the B/Al dependence of the total acidity [46], where the total acidity moderately increased with increasing B/Al ratio up to B/Al  $\sim$  0.7 and then drastically increased with further increase in B/Al ratio to B/Al = 1 (Fig. 5). The global trend of the B/Al dependence profile reported by Wang *et al.* [46] is similar to that observed in our current study, although there is inconsistency in the B/Al ratio. In addition to the global increasing trend, the profile obtained in the present study showed a local maximum at B/Al  $\sim$  0.04, which corresponded to the boundary between domain I and domain II (Fig. 2). Note that the B/Al ratio at this local maximum coincided with the ratio that yielded the maximum quantity of the BO<sub>4</sub> species in domain I [35,36]. This result indicates that the surface BO<sub>4</sub> species created in domain I was most likely the cause of the specific acid property yielding the local maximum at B/Al  $\sim$  0.04.

### 3.2. Properties of CoMo/B-Al<sub>2</sub>O<sub>3</sub> oxidic catalysts

After impregnation of the metallic species and subsequent re-calcination, the SSA of all the oxidic catalysts exhibited relatively constant values at  $ca. 360 \pm 25 \text{ m}^2 \text{ g}^{-1}$  (Table 2; Fig. 3). The PV of the oxidic catalysts as a function of B/Al ratio exhibited a similar tendency as that observed for the B-Al<sub>2</sub>O<sub>3</sub> powders, *i.e.*, with increasing B/Al ratio, PV decreased when  $0 < \text{B/Al} < 0.20$  and then increased when  $\text{B/Al} > 0.20$ . The decrease in the SSA observed upon loading metallic species (Table 2) ranged between 22% and 53%, except for the B-free support, where SSA increased after the loading due to formation of bumpy structures [31]. A decrease in SSA due to the weight gain by loading 15 wt.% of MoO<sub>3</sub> and 5.2 wt.% of CoO was calculated at *ca.*

17 % [31]. Thus, the decreases in SSA from 22% to 53% indicated that solid sintering or pore plugging occurred during the impregnation or the following calcination procedure. Indeed, the decrease in PV ranged from 24% to 59% (Table 2), which is a decrease larger than the calculated PV decrease of about 21% induced by loading of MoO<sub>3</sub> and CoO [31].

As a result of the decreases in both SSA and PV, the APD of most of the oxidic catalysts ranged between 5.1 nm and 6.5 nm. For the catalysts with higher B/Al ratios (> 0.20), the APD increased after Co-Mo loading supposedly due to a decrease in the contribution of pores with smaller pore diameters. In particular, the APD for B/Al = 0.61 increased after the Co-Mo loading by ca. 30%, probably because the high SSA B-Al<sub>2</sub>O<sub>3</sub> structure with numerous small pores surrounded by thin walls containing BO<sub>3</sub> chains was unstable and collapsed during the Co-Mo impregnation. Part of the BO<sub>3</sub> chains was likely dissolved during the impregnation procedure [38,47,48]. In contrast, variation in the APD by Co-Mo loading was small (lower than 10%) for the catalysts with B/Al = 0.02 ~ 0.08. This suggests that the decrease in PV by pore plugging and sintering was compensated by the decrease in the contribution of unstable small pores.

The XRD patterns of the oxidic catalysts (Fig. 1c) were almost identical to those of the supports (Fig. 1b). The smaller signal-to-noise ratios were probably due to large X-ray adsorption coefficients of the heavy metals (Co and Mo). Note that peaks due to undesirable oxides, such as CoMoO<sub>4</sub>, were not observed. Figure 6 shows the Raman spectra of the oxidic catalysts. The global shape of all the spectra was identical irrespective of the B/Al ratio, namely, a main broad peak appeared between 700 and 1000 cm<sup>-1</sup>. This broad peak is characteristic of the monomolybdate phase (main line at 930 cm<sup>-1</sup>) or of the polymolybdate phase (main line at 952 cm<sup>-1</sup>) [49,50].

These phases indicate that CoMo oxidic precursors were well dispersed on the B-Al<sub>2</sub>O<sub>3</sub> supports in the form of mono- or polymolybdate species, without formation of undesirable bulk MoO<sub>3</sub> or CoMoO<sub>4</sub> species. These results agree well with the XRD results (see Fig. 1c).

In brief, the texture and structure of the oxidic catalysts were favorable for the HDS reactions of petroleum distillates, namely, the presence of well-dispersed polymeric or monomeric Mo-oxo species and sufficiently high SSA, about 360 m<sup>2</sup> g<sup>-1</sup>, and APD over 5 nm, irrespective of the B/Al ratio. These results suggest that the effect of the pore structures on the catalytic performance would not be significant.

### 3.3. Catalytic activities of sulfided CoMo/B-Al<sub>2</sub>O<sub>3</sub> catalysts

Tables 3, 4, and 5 summarize the results of the catalytic activity tests for the HDS of thiophene, DBT and 4,6-DMDBT, respectively. Figure 7 shows the promotion factor for each model compound defined as (activity)<sub>B/Al=X</sub>/(activity)<sub>B/Al=0</sub> as a function of B/Al ratio. Introduction of B yielded similar promotion effects on the catalytic activities in the HDS of thiophene and DBT, namely, maxima at B/Al = 0.04 and a decrease with further increase in B/Al ratio. The promotion effects for thiophene were more prominent than those for DBT. The HDS activity over B-Al<sub>2</sub>O<sub>3</sub> supported catalysts for thiophene were higher than that over the B-free catalyst, except for B/Al = 0.61 (Table 3), whereas the HDS activity over the B-Al<sub>2</sub>O<sub>3</sub> supported catalysts for DBT were higher than that over the B-free catalyst only for B/Al = 0.02 and 0.04 (Table 4). In addition, the thiophene HDS activity of the B-Al<sub>2</sub>O<sub>3</sub> supported catalyst was up to 70% higher than that of the IRC (B/Al = 0.04; Table 3), whereas the DBT HDS activity was only up to 42% higher (B/Al = 0.04; Table 4).

In HDS of thiophene, the butane selectivity decreased with increasing B/Al ratio

(Table 3). The butane selectivity over the prepared catalysts, including the B-free catalyst, was almost the same as or lower than that over the IRC. Although the reaction mechanisms in the HDS of thiophene are still controversial [51-53], the decrease in the butane selectivity is likely attributed to a decrease in the HYD activity toward C=C bonds upon introduction of B.

In HDS of DBT, the BP selectivity as compared with the cyclohexylbenzene (CHB) selectivity increased with increasing B/Al ratio up to B/Al = 0.20 and then decreased with further increase in B/Al ratio (Table 4). Irrespective of the B/Al ratio, the BP selectivity over the prepared catalysts was much higher than that over the IRC (*i.e.*, *ca.* 76% for the IRC vs.  $92 \pm 3\%$  for the prepared catalysts). As we previously reported [31], the prepared catalysts supported on sol-gel Al<sub>2</sub>O<sub>3</sub> are direct desulphurization (DDS)-oriented, whereas the IRC used in this study is HYD-oriented. The relatively DDS-oriented character of the sol-gel prepared catalysts relative to the IRC was not altered by the introduction of B.

As we previously discussed [31], high selectivity to 4H-DBT can be attributed to low HYD activity of the remaining C=C bonds in 4H-DBT. Namely, Table 4 shows that the introduction of a small amount of B (*i.e.*, B/Al = 0.02) led to an increase in the HYD activity of C=C bonds, but further introduction decreased the HYD activity. All the above results for the catalytic selectivity in the HDS of thiophene and DBT show that in general the addition of B enhanced the DDS-oriented character and reduced the HYD-oriented character of the sol-gel prepared Al<sub>2</sub>O<sub>3</sub> supported Co-Mo catalysts.

In contrast to HDS of thiophene or DBT, no promotion effect was achieved on HDS of 4,6-DMDBT by the introduction of B, irrespective of B/Al (Fig. 7). The promotion factor decreased with increasing B/Al ratio up to B/Al = 0.08 and then remained relatively constant at about 0.2 with further increase in B/Al ratio. With

increasing B/Al ratio, the 3,3'-DMCHB selectivity decreased from 86.3% for B/Al = 0 to less than 60% for B/Al > 0.08 (Table 5). In contrast, the selectivity to cracked products (methylcyclohexane (MCH) and toluene) drastically increased from less than 10% for B/Al < 0.04 to ca. 30% or higher for B/Al > 0.04. In addition, the ratio of toluene/MCH progressively increased from 1.08 for B/Al = 0 to ca. 1.40 for B/Al = 0.32 or higher (Table 5). This increase was probably because MCH was more easily decomposed than toluene over the active catalytic sites for cracking. The high yields for cracked products and high toluene/MCH ratios are likely attributed to the cracking or isomerization character of the acidic B-Al<sub>2</sub>O<sub>3</sub> supported catalysts with higher B/Al ratios.

#### 4. Discussion

The HDS catalytic performance of supported Co-Mo catalysts is mainly governed by the (1) acidity and (2) pore structure of the catalyst supports, and by the (3) dispersion and (4) structure of the active CoMoS active phase [54]. In the present B-Al<sub>2</sub>O<sub>3</sub> supported catalysts, the B/Al ratio influenced these properties and thus the catalytic performance depended on the B/Al ratio. As described in § 3.2, the differences in pore structure among the prepared catalysts were not significant. In the following discussion, we therefore omit the effects of the pore structure of the catalyst supports and focus on the other three factors by using the schematic structural model shown in Fig. 2.

The DBT and thiophene HDS activities exhibited similar profiles, namely, a maximum at B/Al = 0.04 (Fig. 7). This B/Al ratio of 0.04 corresponds to the threshold value above which BO<sub>3</sub> chains start to develop from isolated BO<sub>4</sub> species created in domain I (Fig. 2). This correspondence indicates that the active HDS catalytic sites

with promotion properties for thiophene and DBT HDS on CoMo/B-Al<sub>2</sub>O<sub>3</sub> are correlated with the 'isolated' BO<sub>4</sub> species present on the surface of the support [35,36]. Figure 5 shows that these species are also responsible for a local increase in the acidity at B/Al = 0.04. In contrast, the creation of the mixed oxides, such as A<sub>9</sub>B<sub>2</sub>, A<sub>2</sub>B, and B<sub>2</sub>O<sub>3</sub> observed for B/Al > 0.06 (Fig. 2a), did not produce any promotion effect on the HDS of thiophene and DBT, as evidenced by the progressive decrease in the catalytic activity (Fig. 7). This contrasts with the increasing acidic function with increasing B/Al ratio that was evidenced in the decreasing selectivity to 3,3'-DMCHB and increasing toluene/MCH ratios in the 4,6-DMDBT HDS (Table 5). Also, four B-Al<sub>2</sub>O<sub>3</sub> powders in each domain in Fig. 2 were previously analyzed for Beckmann rearrangement of cyclohexanone, and obtained the highest caprolactam selectivity for the B-Al<sub>2</sub>O<sub>3</sub> powders in domain IV with the largest acidity [55]. All the acid sites created by the B introduction accelerated typical acidic reactions, but only part of the acid sites that was originated from the surface isolated BO<sub>4</sub> species in domain I promoted the HDS performance of the CoMo catalysts.

The above described relationship between the HDS activity and the B/Al ratio was consistent with many past studies, although was not consistent with a few studies that concluded that B introduction to HDS catalysts had almost no effect (NiMo/B-Al<sub>2</sub>O<sub>3</sub>, HDS of coal liquid [24]) or even a detrimental effect (CoMo/B-Al<sub>2</sub>O<sub>3</sub>, thiophene HDS [10]) on HDS activity. Decanio *et al.* [56] reported that the addition of small quantities of B (up to 1.2 wt.% of B) to a commercial NiMo/Al<sub>2</sub>O<sub>3</sub> catalyst induced an increase in the HDN activity of light atmospheric gasoil treated in pilot units, although the introduction of larger amounts of B (1.8 wt.%) led to the formation of a bulk B<sub>2</sub>O<sub>3</sub> phase and a decrease in the HDN activity. Wu *et al.* [14,15,25] reported that the catalytic HDS activity of CoMo catalysts supported on coprecipitated B-Al<sub>2</sub>O<sub>3</sub> was



maximum when B/Al = 0.29 in the HDS of Kuwait gas oil [14], heavy Kuwait residue oil [15], and Kuwait crude oil [25]. They correlated the maximum HDS activity to the quantity of acidic sites, which was also maximum at B/Al = 0.29. Li *et al.* [19] reported that the HDS activity of DBT was maximal near B/Al ~ 0.01 (SSA of Al<sub>2</sub>O<sub>3</sub> = 209 m<sup>2</sup> g<sup>-1</sup>) among CoMo catalysts supported on B-Al<sub>2</sub>O<sub>3</sub> prepared by impregnation of H<sub>3</sub>BO<sub>3</sub> on Al<sub>2</sub>O<sub>3</sub>. Ramírez *et al.* [12] and Usman *et al.* [26] reported that the HDS activity of thiophene was maximal near B/Al ~ 0.04 (SSA of Al<sub>2</sub>O<sub>3</sub> = 190 m<sup>2</sup> g<sup>-1</sup> and 180 m<sup>2</sup> g<sup>-1</sup>, respectively).

Most studies, including our present study, concluded that B introduction had a promotion effect on the catalytic HDS activity but that this promotion effect was limited to the catalysts with relatively low B/Al ratio (< 0.3). This low optimal ratio confirms the above discussion that acid sites originating from the mixed oxide phases do not improve the HDS performance. The differences in the B/Al ratio that yield maximum HDS activity among the above-mentioned studies were likely due to the different structure and properties of the supports, such as SSA or acidity, as well as the preparation methods of the B-Al<sub>2</sub>O<sub>3</sub> supports. This also might explain the inconsistency in the B/Al ratio for the acidity between the present results and the results by Wang *et al.* [46] in Fig. 5.

Although the present study did not involve structural analysis of the active sulfide phase, the effects of B on the structure of the active phase have been reported. For example, Morishige *et al.* [57] showed that the molybdenum dispersion on Mo/B-Al<sub>2</sub>O<sub>3</sub> catalysts decreased with increasing B/Al ratio. Recently, Usman *et al.* [26,58] investigated in detail the effects of B on the dispersion of MoS<sub>2</sub> slabs on B-Al<sub>2</sub>O<sub>3</sub> supported catalysts. They observed an increase in the size of the MoS<sub>2</sub> slabs with a slight increase in the stacking upon B introduction, and deduced that B introduction

caused the change in the active catalytic phase from CoMoS Type I with lower activity to CoMoS Type II with higher activity [54].

Stranick *et al.* [59] reported that B was responsible for better dispersion of Co species for Co/B-Al<sub>2</sub>O<sub>3</sub> catalysts. Houalla and Delmon [60] reported that B promoted the interaction between cobalt oxide and Al<sub>2</sub>O<sub>3</sub> and caused an increase in the number of octahedral Co<sup>2+</sup> species. Ramírez *et al.* [12] reported that the introduction of B to CoMo/Al<sub>2</sub>O<sub>3</sub> catalysts decreased the proportion of tetrahedrally coordinated Co<sup>2+</sup> species, whereas the number of Mo<sup>6+</sup> species in strong interaction with the support decreased.

The above studies [26,57,58] pointed out that B introduction decreased the dispersion of the active (Co-promoted or unpromoted) MoS<sub>2</sub> species due to the decreasing interaction between MoS<sub>2</sub> and the Al<sub>2</sub>O<sub>3</sub> support. However, the decreasing dispersion of the CoMoS phase was not so significant. In fact, the absence of features due to undesirable bulk oxides in the XRD patterns (Fig. 1) and the Raman spectra (Fig. 6) indicates that B introduction did not yield serious agglomeration of the CoMo precursors that would result in a significant decrease in the number of catalytically active MoS<sub>2</sub> edge sites. The beneficial effect due to the formation of CoMoS type II was larger than the detrimental effect due to the slight decrease in the number of active catalytic sites of the CoMoS phase for the B-Al<sub>2</sub>O<sub>3</sub> supported catalysts with B/Al = 0.02 and 0.04. It is likely that the surface BO<sub>4</sub> species created in domain I decreased the interaction between the active phase and the support and resulted in the formation of CoMoS type II structure.

The superiority of the CoMo/B-Al<sub>2</sub>O<sub>3</sub> catalysts over the B-free CoMo/Al<sub>2</sub>O<sub>3</sub> catalyst with B/Al = 0 was limited to the HDS of thiophene and DBT (Fig. 7), because B-Al<sub>2</sub>O<sub>3</sub> supported catalysts were highly DDS-oriented even when compared with sol-gel

prepared  $\text{Al}_2\text{O}_3$  supported catalysts. Due to this strong DDS-oriented character, the superiority of the CoMo/B- $\text{Al}_2\text{O}_3$  for the HDS of thiophene that did not require HYD character was more significant than that for DBT. Furthermore, B introduction had a detrimental effect on the HDS activity of 4,6-DMDBT (Fig. 7) that required HYD of one benzene ring before sulfur removal [31,61,62]. We previously reported that HYD of the remaining double bond of 4H-4,6-DMDBT is the crucial step to obtain high performance for the HDS of 4,6-DMDBT [31]. Table 5 shows that the selectivity to 4H-4,6-DMDBT over B- $\text{Al}_2\text{O}_3$  supported catalysts was higher than that over the B-free catalyst, especially at B/Al > 0.08. This high selectivity to 4H-4,6-DMDBT was due to the lack of HYD ability toward the non-aromatic C=C double bonds.

We previously reported that the HYD activity of 4H-4,6-DMDBT is related to the strong acid sites present on the sol-gel  $\text{Al}_2\text{O}_3$  supports [31]. The present study also gives a good relationship between the HDS activity for 4,6-DMDBT and the proportion of strong acid sites as shown in Fig. 8. This relationship suggests that a high proportion of strong acid sites that result in adjacent strong acid sites is necessary to hydrogenate the C=C double bonds of 4H-4,6-DMDBT.

The roles of acidity in the 4,6-DMDBT HDS are complicated. The acidic function of the catalyst increased with increasing B/Al ratio, but the 4,6-DMDBT HDS activity simultaneously reached a very low level with a value of about  $0.2 \times 10^{-6} \text{ mol.gcat}^{-1}.\text{s}^{-1}$  for B/Al > 0.04 (Table 5; Fig. 7). This low activity might be partly ascribed to rapid catalytic deactivation by coking due to acidity as proposed by Torres-Mancerra *et al.* [27]. In contrast, the acidity due to the surface isolated  $\text{BO}_4$  species increased the thiophene and DBT HDS activities without increasing the cracking function (Table 3 and 4). Also, the presence of these  $\text{BO}_4$  species effectively functioned in the hydrogenation of the C=C double bonds of 4H-4,6-DMDBT with selectivities in 4H-

4,6-DMDBT lower than 2% for B/Al  $\leq$  0.04 (Table 5). These beneficial effects of the acid sites in the HDS reactions were not directly related to acidic functions such as cracking or isomerization but likely enhanced other catalytic functions such as sulfur extraction through the formation of CoMoS type II or hydrogenation.

## 5. Conclusion

Eight different CoMo catalysts were prepared using sol-gel prepared B-Al<sub>2</sub>O<sub>3</sub> supports with various B/Al ratios. The supports were characterized in detail elsewhere [34-36]. Characterization and HDS activity tests of the catalysts prepared from these supports yielded the following conclusions.

- (1) The specific surface area and average pore diameter of the CoMo/B-Al<sub>2</sub>O<sub>3</sub> catalysts did not differ significantly, namely, from 341 - 391 m<sup>2</sup> g<sup>-1</sup> and 5.1 - 6.5 nm, respectively, except those with B/Al = 0.61. These properties are favorable for use as catalysts for HDS of petroleum fractions.
- (2) In general, the total acidity increased with increasing B/Al ratio. This was likely due to the formation of 9Al<sub>2</sub>O<sub>3</sub>· 2B<sub>2</sub>O<sub>3</sub>, 2Al<sub>2</sub>O<sub>3</sub>· B<sub>2</sub>O<sub>3</sub> and B<sub>2</sub>O<sub>3</sub>. In addition, a local maximum in the acidity was observed at B/Al = 0.04, where isolated BO<sub>4</sub> species were the most abundant at the surface of the supports.
- (3) HDS activity of the CoMo/B-Al<sub>2</sub>O<sub>3</sub> catalysts for thiophene and DBT was maxima at B/Al = 0.04. The HDS rate of the catalyst with B/Al = 0.04 was superior by 70% to that of an industrial reference catalyst for thiophene and by 42% for DBT.
- (4) High HDS activity discussed in (3) above was due to weakening the interaction between the active phase and the support. This weakening was caused by the acid sites that originated from the isolated BO<sub>4</sub> species located at the surface of the supports. The acidity due to mixed oxides such as 9Al<sub>2</sub>O<sub>3</sub>· 2B<sub>2</sub>O<sub>3</sub> and 2Al<sub>2</sub>O<sub>3</sub>·

$B_2O_3$  functioned as a solid acid catalyst but did not enhance the HDS activity.

(5) In contrast to (4) above, the HDS activity in each of the  $B-Al_2O_3$  supported catalysts for 4,6-DMDBT decreased with increasing B/Al ratio and was significantly inferior to that of the industrial reference catalyst. This low performance was due to the strong direct desulfurization character of the  $B-Al_2O_3$  supported catalysts. Namely, the  $B-Al_2O_3$ -supported catalysts did not possess the high hydrogenation activity for C=C double bonds that is essential for the HDS of 4,6-DMDBT. These results suggest that B-doped sol-gel  $Al_2O_3$ -supported catalysts are suitable for HDS of light fractions such as gasoline.

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## Figure captions

Figure 1. XRD diffraction patterns of (a) dried B-Al<sub>2</sub>O<sub>3</sub> powders, (b) calcined B-Al<sub>2</sub>O<sub>3</sub> supports, and (c) calcined CoMo/B-Al<sub>2</sub>O<sub>3</sub> oxidic precursors at different B/Al ratios.

Figure 2. Phases and schematic structure of sol-gel-prepared B-Al<sub>2</sub>O<sub>3</sub> powders as a function of B/Al. (a) Phases present in each domain. (b) Schematic structure before calcination. (c) Schematic structure after calcination. A<sub>9</sub>B<sub>2</sub> = 9Al<sub>2</sub>O<sub>3</sub>.2B<sub>2</sub>O<sub>3</sub> phase; A<sub>2</sub>B = 2Al<sub>2</sub>O<sub>3</sub>.B<sub>2</sub>O<sub>3</sub> phase.

<sup>1</sup> Bulk BO<sub>3</sub> species that were created concomitantly to the BO<sub>4</sub> species in domain I are not represented. In addition to the octahedral aluminum species network constituting the boehmite, tetrahedral aluminum species linked with the boron-oxo species were created, and when B/Al > 0.26, pentrahedral aluminum species were created.

<sup>2</sup> Bulk BO<sub>3</sub> species created in domain I are not represented.

Figure 3. BET specific surface area (SSA) of B-Al<sub>2</sub>O<sub>3</sub> and CoMo/B-Al<sub>2</sub>O<sub>3</sub> as a function of B/Al ratio.

Figure 4. NH<sub>3</sub> temperature-programmed desorption (TPD) profiles for calcined B-Al<sub>2</sub>O<sub>3</sub> powders for various B/Al ratios. The insertion gives an example of deconvolution for B/Al = 0.02. AS: Acid sites.

Figure 5. Total amount of acid sites ( $\Delta$ ) and proportion of strong acid sites ( $\bullet$ ) on calcined B-Al<sub>2</sub>O<sub>3</sub> powders as a function of B/Al ratio. Total amount of acid sites reported by Wang *et al.* ( $\blacksquare$ ) [46] is also shown.

Figure 6. Raman spectra of Co-Mo oxidic precursors of prepared catalysts for various B/Al ratios.

Figure 7. Relative HDS activity of CoMo/B-Al<sub>2</sub>O<sub>3</sub> catalysts in the reaction of thiophene, DBT, and 4, 6-DMDBT. Relative HDS activity is normalized by that of the catalyst with B/Al = 0 (*i.e.*, B-free catalyst).

Figure 8. 4,6-DMDBT HDS activity and proportion of strong acid sites as a function of B/Al ratio.

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