# Spectroscopic Characterization of Ni–Mo/<sub>γ</sub>-Al<sub>2</sub>O<sub>3</sub>–B<sub>2</sub>O<sub>3</sub> Catalysts for Hydrodesulfurization of Dibenzothiophene

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The effects of boron on the dispersion of active metal species and hydrodesulfurization (HDS) activity of dibenzothiophene (DBT) over Ni-Mo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> containing boron were studied by means of BET surface area measurement, powder X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), Mo *K*-edge extended X-ray absorption fine structure (EXAFS), and B *K*-edge X-ray absorption near-edge structure. The HDS activity of DBT over Ni-Mo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-B<sub>2</sub>O<sub>3</sub> reaches a maximum at the B<sub>2</sub>O<sub>3</sub> loading of about 1 mol%, in agreement with the basal dispersion and thus with the hydrogenation ability of the catalysts. It has been proven that the combination of XRD, XPS, and EXAFS techniques gives a complete description of the dispersion of active metal species in heterogeneous environmental catalysts. © 1997 Academic Press

#### INTRODUCTION

Mo and W sulfide catalysts, promoted by Co or Ni and supported on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, have been applied in industry for the hydrotreating processes of petroleum and coal liquefactions and extensively investigated. The chemistry and structure of these catalysts, particularly the Co-Mo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst, have been reviewed (1–11). Several structural models for the active phases have been proposed; these include the monolayer model (12), intercalation model (13), contact synergy model (14, 15), and Co-Mo-S complex (16, 17). <sup>57</sup>Co Mössbauer spectroscopy (7), more recently Co, Ni, and Mo *K*-edge EXAFS results (e.g., 18–21), and radioisotope <sup>35</sup>S tracer studies (22) consistently indicated that the so-called "Co-Mo-S complex phases," in which Co is located at the edges of MoS<sub>2</sub> are most likely to be the active sites for the Co-Mo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst.

Aluminium borates are acid catalytic materials and were shown to have high catalytic activity for 2-propanol dehydration. The presence and coordination of boron have a dramatic effect on the acidity of these materials, the high acidity being closely related to the relative concentration of BO<sub>4</sub> (23). For alumina-supported boria, Sato *et al.* indicated that these materials exhibited high catalytic efficiency for the vapor phase Beckmann rearrangement of cyclohexanone oxime (24). Curtin *et al.* furthermore pointed out that the increase in the boria content resulted in an increasing caprolactam selectivity. The control of the boria level on the alumina surfaces would result in the optimum number and strength of the acid sites and thus in an improved caprolactam selectivity (25).

The effect of adding boron to these conventional  $Co(Ni)-Mo(W)/\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts on their catalytic activity has been studied in the past. For example, the hydrogenolysis activity of Ni–Mo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts was shown to increase with the increasing boron content in the support (26). Stranick *et al.* believed that the addition of boron to  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> can improve the dispersion of Co and change the chemical states of Co in  $Co/\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts (27). However, Morishige and Akai indicated that boron addition decreases the dispersion of Mo in  $Mo/\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts and weakens the interaction between Mo species and the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> surface (28). Chen et al. showed that the hydrodesulfurization (HDS) activities of atmospheric gas oil (AGO) and residue oil over Co-Mo/alumina-aluminium borate (prepared by coprecipitation) catalysts improve significantly compared to conventional Co-Mo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts, and the optimum HDS activity of AGO was found at the Al/B ratio of about 3.5 (29, 30). Nevertheless, Ramírez et al. recently prepared Co-Mo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-B(x) by wet impregnation and studied the effect of boron addition on the activity and selectivity of the HDS reaction of thiophene over these catalysts. They found that the conversion rate reached the maximum point at the loading of 0.8 wt% B (31).

Co(Ni)–Mo(W)/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts containing B have been made by several different approaches (wet impregnation, coprecipitation, hydrolysis of alkoxides, and kneading). Previous studies on the effect of boron on the dispersion and catalytic activities of the catalysts are contradictory. The description of the dispersion of active metal phases in heterogeneous MoS<sub>2</sub> catalysts was incomplete, because MoS<sub>2</sub> has a layered and anisotropic structure. In this work, Ni–Mo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>–B<sub>2</sub>O<sub>3</sub> catalysts were prepared by wet impregnation, and the HDS reaction of dibenzothiophene (DBT) over these catalysts was carried out. DBT was chosen as model compound to test the catalytic activity of the catalysts, because DBT is a main component containing sulfur in actual petroleum residues and coal liquefactions, and the HDS of DBT includes hydrogenation and hydrocracking reactions. The structure of the catalysts is characterized by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), Mo *K*-edge extended X-ray absorption fine structure (EXAFS), and B *K*-edge X-ray absorption near-edge structure (XANES). The main purpose of this work is to give a complete description of the dispersion (both basal plane and edge dispersion) of active metal species in the heterogeneous Ni–Mo sulfide catalysts and to discuss the effects of adding boron to Ni–Mo/  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts on the dispersion of active metals and on the HDS activity of DBT by using spectroscopic techniques.

#### **EXPERIMENTAL**

## Catalyst Preparation

H<sub>3</sub>BO<sub>3</sub> was dissolved in aqueous ammonia solution (pH 9.7  $\pm$  0.2), and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (VGS-1, BET surface area  $209 \text{ m}^2/\text{g}$ , and pore volume 0.81 ml/g) was impregnated with the H<sub>3</sub>BO<sub>3</sub> solution to prepare the supports with different B<sub>2</sub>O<sub>3</sub> loadings, depending on the initial concentration of  $B_2O_3$  in the solution. The  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-B<sub>2</sub>O<sub>3</sub> slurries were dried for 4 h in a rotary kiln and then calcined at 550°C for 3 h in air. The  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-B<sub>2</sub>O<sub>3</sub> materials were used as the supports and coimpregnated with a  $Ni(NO_3)_2 \cdot 6H_2O$ and (NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub> · 4H<sub>2</sub>O containing aqueous ammonia solution (pH 9.0 $\pm$ 0.2). The loadings of NiO and MoO<sub>3</sub> were kept constant at 3 and 12 wt%, respectively, so that the molar NiO/MoO3 ratio was about 0.48 for all the catalysts. The Ni-Mo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-B<sub>2</sub>O<sub>3</sub> catalysts, designated as NMABx ( $x = B_2O_3$  mol% in supports), were dried at 200°C for 2 h in a rotary kiln and then calcined at 550°C for 3 h in air. Thereafter, the catalysts were dried at 400°C for 2 h under N<sub>2</sub> atmosphere and sulfided at the same temperature for another 2 h in a stream of H<sub>2</sub>-H<sub>2</sub>S mixture (the volume percentage of  $H_2S$  in the mixture is 5.04%) before the catalytic activity tests.

#### Catalytic Activity

DBT was dissolved in decalin to give a solution with a sulfur content of 1 wt%. The catalytic reactions of DBT (10 ml) over the NMAB*x* catalysts (0.1 g) were performed at 360°C and on H<sub>2</sub> pressure of 6.92 MPa for 1 h using a batch microreactor. The conversion rate was calculated on the basis of the integrated areas for the reaction products, diphenyl (DP) and cyclohexylbenzene (CHB), and on the remaining DBT in the gas chromatography analysis:

The total conversion rate = 
$$(Area_{DP} + Area_{CHB})/$$
  
 $(Area_{DP} + Area_{CHB} + Area_{DBT}).$ 

## Catalyst Characterization

BET surface areas of representative Ni–Mo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>– B<sub>2</sub>O<sub>3</sub> catalyst samples were measured using a Micromeritics chemisorption controller (Shimadzu). XRD patterns of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>–B<sub>2</sub>O<sub>3</sub> supports and NMAB*x* series catalysts were taken using a Phillip MXP18 powder diffractometer (Material Analysis and Characterization) at 40 kV and 50 mA and with a scan rate of 3°/min and a sampling width of 0.02°. The Cu K $\alpha$  ( $\lambda$  = 1.5405 Å) was used as the radiation source.

XPS spectra of the calcined and sulfided NMABx catalysts were collected at the chamber pressure of  $\sim 10^{-9}$  Torr  $(1 \text{ Torr} = 1.33 \times 10^{-4} \text{ MPa})$  using a Phi-5500 ESCA spectrometer (Perkin–Elmer). The monochromatized Al  $K\alpha$  ( $h\nu =$ 1486.7 eV) was used as the source of excitation. The sample preparations of freshly sulfided catalysts for XPS measurements were performed in a  $N_2$  glove box; SO<sub>4</sub> species in the S 2p line of each sulfided sample were not observed and, thus, the feasibility of this approach could be proven. The binding energy (BE) of Al 2p, B 1s, Mo 3d, Ni 2p, and S 2p lines were calibrated using C 1s BE of 284.6 eV; these XPS lines were decomposed by fitting. Several constraints were included in the decomposition of the Mo 3d envelope to give physical significance to the peaks obtained: (i) the spinorbit splitting of the Mo 3d peak is 3.15 eV; (ii) the Mo  $3d_{5/2}$ Mo  $3d_{3/2}$  area ratio was kept constant at the theoretical value of 1.5; (iii) the full width at half maximum of the Mo  $3d_{5/2}$  and Mo  $3d_{3/2}$  peaks of the Mo<sup>5+</sup> and Mo<sup>6+</sup> oxidation states was equal to the corresponding width of the peaks of the Mo<sup>4+</sup> species (32). The atomic concentration ratio on the surface of the catalysts was calculated using  $n_A/n_B = I_A S_B/I_B S_A$ , where  $n_i$  is the atomic number of species i (i = A or B),  $I_i$  is the integrated intensity of species *i*, and *S<sub>i</sub>* is the sensitivity factor given by XPS spectral measurement. The sensitivity factor depends mainly on the photoionization cross-section  $\sigma_{j}$ , but also on the effects of exciting X-ray energy, takeoff angle of measurement, detector efficiency, and kinetic energy; the formula used to calculate the atomic concentration is similar to the Kerkhof-Moulijn model (33).

Mo *K*-edge EXAFS data were recorded at room temperature using a channel-cut Si(311) double crystal monochromator at the Photon Factory (BL10B) of the National Laboratory for High Energy Physics. Each sample was ground to a fine powder and pressed into a disk the thickness (*x*) of which was such that the absorption  $\mu x$  was 1, thus allowing an EXAFS spectrum of optimal quality for collection by transmission measurement. The disk was then sealed into a plastic bag, so that the sample was kept in an inert atmosphere during the EXAFS measurement. Fourier transformation of the  $k^3$ -weighted EXAFS data for  $\Delta k = 9.0$ ( $3.9 \le k \le 13.55$ ) was performed to obtain a radial distribution function around Mo. Reducing procedures of EXAFS data have been described elsewhere (34).

B K-edge XANES spectra of catalysts NMAB1 and NMAB2 were recorded by total electron yield (TEY) using a Grasshopper beamline at the Aladdin storage ring, University of Wisconsin. This beamline uses a grazing incident system with a grating of 1800 Grooves/mm and an energy resolution of about 0.1 eV at 100 eV (35). The B K-edge spectrum of each of these samples is the sum of three measurements, the linear background being removed. The B Kedge XANES spectra of samples NMAB5 and NMAB8 were collected by TEY using the BL13C beamline in the Photon Factory (36). For all the B K-edge measurements, the catalyst samples were carefully pressed, not ground, into powder under static pressure, in order to minimize the structural state change of tetrahedrally coordinated boron, caused by grinding, on the surface of samples (see our unpublished data). The B K-edge XANES spectra were calibrated using the B *K*-edge peak of B<sub>2</sub>O<sub>3</sub> at 194.0 eV (37).

#### RESULTS

#### Catalytic HDS Activity of DBT

Figure 1A shows the HDS conversion rate of DBT over NMAB*x* series catalysts (*x* from 0 to 17) against the  $B_2O_3/Al_2O_3$  ratio in the supports. The total HDS conversion

FIG. 1. The conversion rate (A) and selectivity (B) of DBT over Ni–Mo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>–B<sub>2</sub>O<sub>3</sub> catalysts as a function of the molar B<sub>2</sub>O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> ratio. (A) Filled squares and solid line, the total conversion rate; filled triangles and dotted line, conversion rate to diphenyl; filled circles and dashed line, conversion rate to cyclohexylbenzene. (B) Open triangles and solid line, selectivity to diphenyl; open circles and dashed line, selectivity to cyclohexylbenzene.



(filled squares and solid line) or DBT increases with the increasing loadings of  $B_2O_3$  and reaches the maximum point at about 1 mol% of  $B_2O_3$  in the support and then decreases with a further increase in the content of  $B_2O_3$  (up to 17 mol%). The conversion of DBT to diphenyl (filled triangles and dotted line) generally increases with increasing loadings of  $B_2O_3$ . The general profile of the conversion rate to cyclohexylbenzene (filled circles and dashed line) with a loading of  $B_2O_3$  is parallel to the total conversion of DBT, indicating that the total HDS activity of DBT over the NMAB*x* catalysts depends mostly on the conversion rate to cyclohexylbenzene.

The selectivity of diphenyl and cyclohexylbenzene was calculated using the respective conversion rates over the total HDS activity and are plotted as a function of  $B_2O_3/Al_2O_3$ in Fig. 1B. The selectivity of diphenyl (empty triangles and solid line) increases and that of cyclohexylbenzene (empty circles and dashed line) decreases to about 10 mol% with increasing loadings of  $B_2O_3$ ; thereafter, the selectivity for both diphenyl and cyclohexylbenzene remains nearly constant.

## XRD Patterns and Dispersion of Ni and Mo Species in Bulk Catalysts

Figure 2 shows representative XRD patterns of the NMAB*x* catalysts. For the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-B<sub>2</sub>O<sub>3</sub> supports, the XRD patterns are similar to those of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> until the loading of B<sub>2</sub>O<sub>3</sub> reaches about 14 mol% at which point a





crystalline B<sub>2</sub>O<sub>3</sub> phase first occurs; its diffraction peaks at  $2\theta = 13.58^{\circ}$  and 27.98° become sharper and more prominent with increasing loadings of B<sub>2</sub>O<sub>3</sub>. The XRD patterns of NMAB0 and NMAB1 are very similar to that of the original  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, but when the loading of B<sub>2</sub>O<sub>3</sub> reaches about 5 mol%, a broad peak at about  $2\theta = 27^{\circ}$  first appears and becomes stronger with further loadings of B<sub>2</sub>O<sub>3</sub>. This broad peak may be attributed to the MoO<sub>3</sub> phase. In addition, BET surface area measurements of representative NMAB1, NMAB8, and NMAB17 are 183, 165, and 153 m<sup>2</sup>/g, respectively, decreasing with the increasing loadings of B<sub>2</sub>O<sub>3</sub>.

## XPS and Concentrations of Ni and Mo Species on the Catalyst Surface

XPS spectra of the calcined and sulfided catalysts were collected. The Ni 2*p* XPS spectra of a representative NMAB5 catalyst are shown in Fig. 3. The spectra are decomposed by fitting, in which the dotted line represents the experimental data, the dashed lines are the Gaussian components and the solid line the envelope of decomposed features. The two main peaks in the XPS spectrum of the calcined sample are assigned to the spin-splitting Ni 2*p*<sub>3/2</sub> and Ni 2*p*<sub>1/2</sub> and the two broad peaks to the envelopes of their corresponding satellite lines. The Ni 2*p* XPS spectrum suggests that the nickel species in the calcined catalyst can be assigned to Ni<sup>2+</sup> in interaction with alumina and/or with



FIG. 3. Ni 2p XPS spectra of calcined and sulfided Ni–Mo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>–B<sub>2</sub>O<sub>3</sub> catalyst (NMAB5) and their decompositions. Filled dotted lines, experimental data; dashed lines, Gaussian components; solid lines, the corresponding envelopes. In the spectrum of the sulfided catalyst, S stands for sulfide and O for oxide species.



**FIG. 4.** Mo 3*d* XPS spectra of calcined and sulfided Ni–Mo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>–B<sub>2</sub>O<sub>3</sub> catalyst (NMAB5) and their decomposition. Filled dotted lines, experimental data; dashed lines, Gaussian components; solid lines, the corresponding envelopes.

molybdenia, as we expected. The Ni 2p XPS spectrum of the sulfided catalyst is more complex, decomposing into two set of Gaussian components, one for the Ni oxide species, as seen in the calcined catalyst, the other for the Ni sulfide species. The Ni sulfide species are assumed to be Ni<sub>3</sub>S<sub>2</sub> at the sulfiding conditions and the so-called Ni-Mo-S phase is assumed to be the active phase for the catalysis.

Mo 3*d* XPS spectra of the same catalyst are shown in Fig. 4. For the calcined catalyst, it is well known that two peaks are assigned to the spin-splitting Mo 3*d*<sub>5/2</sub> and Mo 3*d*<sub>3/2</sub> lines of the Mo oxide species. The Mo 3*d*XPS spectrum of the sulfided catalyst decomposed into three sets of doublets, corresponding to Mo<sup>6+</sup>, Mo<sup>5+</sup>, and Mo<sup>4+</sup> species in the order of decreasing binding energy, and a broad peak at about 226.3 eV assigned to S 2*s* line. The Mo<sup>6+</sup> species are obviously Mo oxide species that were not completely sulfided. The Mo<sup>5+</sup> species may be a Mo oxy-sulfide species, and the Mo<sup>4+</sup> species are MoS<sub>2</sub> and the Ni–Mo–S phase.

As shown above, the Al 2*p*, Mo 3*d*, Ni 2*p*, and S 2*p* (for sulfided samples only) of calcined and sulfided catalysts were decomposed by fitting. The integrated areas for Al 2*p*, Mo 3*d*<sub>5/2</sub>, and Ni 2*p*<sub>3/2</sub> were used to calculate the atomic concentration ratios of Mo and Ni over Al. The Mo 3*d*<sub>5/2</sub>/Al 2*p* and Ni 2*p*<sub>3/2</sub>/Al 2*p* ratios at the surface of the calcined and sulfided catalysts are also plotted against the molar B<sub>2</sub>O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> ratio (Figs. 5 and 6). However, for the sulfided catalysts, the integrated area of sulfide species only was used for the calculation. For both calcined and sulfided catalysts, both Mo 3*d*<sub>5/2</sub>/Al 2*p* and Ni 2*p*<sub>3/2</sub>/Al 2*p* ratios reached the maximum points at a B<sub>2</sub>O<sub>3</sub> loading of about 1 mol%, in



**FIG. 5.** Ni/Al atomic concentration ratio on the surface of calcined (filled circles and solid line) and sulfided (open squares and dashed line) catalysts as a function of the molar  $B_2O_3/Al_2O_3$  ratio in the bulk catalysts. The Ni/Al atomic ratio on the surface was calculated according to the integrated area of the Ni  $2p_{3/2}$  and Al 2p XPS lines.

good agreement with the total HDS activity of DBT and the conversion of DBT to cyclohexylbenzene over these catalysts (see Fig. 1). The S  $2p_{3/2}$  BE is about 162.2 eV, close to that of MoS<sub>2</sub>. The S/(0.67Ni + 2Mo) ratio varies from 0.98 (NMAB0), 1.04 (NMAB1), to 0.82 (NMAB5), indicating that the sulfidation degree of the catalysts decreases with the increasing loading of B<sub>2</sub>O<sub>3</sub>.

## Mo K-Edge EXAFS

Figure 7 shows the radial distribution functions derived from the Fourier transforms of the  $k^3$ -weighted EX-AFS oscillations at the Mo *K*-edge of sulfided Ni–Mo/  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-B<sub>2</sub>O<sub>3</sub> catalysts. The two dominant peaks, visible at about 2.0 and 2.8 Å, are shown for all the samples, respectively, corresponding to Mo–S shell at the bond distance of



**FIG. 6.** Mo/Al atomic concentration ratio on the surface of calcined (filled circles and solid line) and sulfided (open squares and dashed line) catalysts as a function of the molar  $B_2O_3/Al_2O_3$  ratio in the bulk catalysts. The Mo/Al atomic ratio on the surface was calculated according to the integrated area of the Mo  $3d_{5/2}$  and Al 2p XPS lines.



**FIG.** 7. Fourier transforms  $(3.9 \le k \le 13.55)$  of the Mo *K*-edge EX-AFS for sulfided Ni-Mo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-B<sub>2</sub>O<sub>3</sub> catalysts.

about 2.42 Å (after phase shift correction) and Mo-Mo scattering at the bond distance of about 3.16 Å (after phase shift correction). These results are very similar to those of X-ray diffraction of MoS<sub>2</sub> and those of Mo K-edge EXAFS analyses of MoS<sub>2</sub> crystal and Mo/Al<sub>2</sub>O<sub>3</sub> (21, 39) and Ni-Mo/C catalysts (19). The Mo-Ni scattering may contribute to the peak at about 2.0 Å. However, based on our previous EX-AFS analyses (39), this contribution does not seem to be very significant. The peak at about 2.8 Å tends to sharpen with the addition of small amounts of boron (from NMAB0 to NMAB2) and broadens again with further loadings of boron (from NMAB2 to NMAB17), indicating a slight change in the disorder-order states. The Fourier transform magnitude (FTM) of the two main peaks are correlated with the coordination numbers and Debye-Waller factors of the corresponding to Mo-S and Mo-Mo scattering and may provide important information on the edge dispersion of active Mo species in the catalysts (39).

The FTM (in arbitrary units) of the two notable peaks corresponding to Mo–S (filled squares and solid line) and Mo–Mo (filled circles and dashed line) shells in the EXAFS analyses of the catalysts are plotted as a function of B<sub>2</sub>O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> in Fig. 8A. The FTM of both Mo–S and Mo–Mo shells dramatically increases on adding a small amount of boron (0.5 mol%) to  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, and then gradually decreases with increasing loadings of boron. The FTM ratio for Mo–Mo and Mo–S shells (FTM(Mo–Mo)/ FTM(Mo–S)) is shown as a function of B<sub>2</sub>O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> in Fig. 8B. The solid line best fits the experimental data (filled rhombuses). The FTM(Mo–Mo)/FTM(Mo–S) ratio also increases markedly when a small amount of boron was added to  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, and gradually decreases with further loadings of boron, generally parallel to the XPS and HDS activity results.

## B 1s XPS and B K-Edge XANES

Figure 9 compares theoretical (solid line) and experimental (filled circles and dash line) XPS peak intensity ratios ( $I_{B 1}$ ,  $I_{A 12p}$ ) as functions of  $B_2O_3/Al_2O_3$ . The theoretical values were calculated according to the Kerkhof–Moulijn model, assuming that boron species form a monolayer on alumina and that the difference in the kinetic energies of B 1*s* and Al 2*p* electrons is not very large (33):

$$\frac{I_{\rm B\,1s}}{I_{\rm Al\,2p}} = \left(\frac{p}{s}\right)_{\rm b} \frac{\sigma_{\rm B\,1s}}{\sigma_{\rm Al\,2p}} \frac{\beta}{2} \frac{1+e^{-\beta}}{1-e^{-\beta}},$$

where  $I_{B1s}$  and  $I_{A12p}$  are relative XPS intensities of the B 1s and Al 2p electrons,  $(p/s)_b$  is the bulk atomic ratio,  $\sigma_{B1s}$ (0.486) and  $\sigma_{A12p}$  (0.356) are the photoionization cross sections at 1487 eV (40), and  $\beta = 2/(\rho \cdot S \cdot \lambda)$  in which  $\rho$  is the density of the alumina  $(3.7 \times 10^6 \text{ g/m}^3)$ , S is the surface area of the support, and  $\lambda$  is the escape depth of electrons (2.68 nm) for the Al 2p electrons at a kinetic energy of 1390 eV (41). If the surface area of the alumina (209 m<sup>2</sup>/g) is used in the calculation, the theoretical equation is  $I_{B1s}/I_{A12p} = 1.42 \cdot (B_2O_3/Al_2O_3)$  (see thin solid line in







**FIG. 9.** Comparison of the theoretical (both thin and thick solid line) and experimental (filled circles and dash line) XPS peak intensities  $(I_{B 15}/I_{A12p})$  as a function of the  $B_2O_3/Al_2O_3$  ratio. The thin and thick solid lines represent the theoretical equations when the surface area (*S*) of the support was used as 209 m<sup>2</sup>/g (pure alumina) and 153 m<sup>2</sup>/g (sample NMAB17), respectively.

Fig. 9); if the lower surface area of the borium-containing samples is corrected, for example, the surface area of sample NMAB17 (153 m<sup>2</sup>/g) is used in the calculation, the theoretical equation is  $I_{B 1s}/I_{Al 2p} = 1.50 \cdot (B_2O_3/Al_2O_3)$  (see thick solid line if Fig. 9). The experimental values from XPS measurements were calculated as shown above. The results indicate that boron species are well dispersed and form monolayers on alumina at low loadings of  $B_2O_3$ . At a  $B_2O_3$  content of 17 mol%, however, the dispersion of the boron species decreases and deviates from the monolayer model, in good agreement with the previous XPS measurements (28) and our XRD results mentioned above.

In order to study the structural states of boron in the catalysts, we measured B *K*-edge XANES spectra of the NMAB*x* catalysts before sulfiding (Fig. 10) and compared them with those of model compounds B<sub>2</sub>O<sub>3</sub> containing trigonally coordinated B (<sup>[3]</sup>B) only and BPO<sub>4</sub> containing tetrahedrally coordinated B (<sup>[4]</sup>B) only. The sharp peak at about 194.0 eV is attributed to <sup>[3]</sup>B in the boron species, and is further assigned to the transition of B 1*s* electrons to the unoccupied B  $2p_z(\pi^*)$  states for <sup>[3]</sup>B with oxygen (37). However, the B *K*-edge spectra show no evidence of the presence of <sup>[4]</sup>B with oxygen in the NMAB*x* catalysts investigated. The B species is most likely to be B<sub>2</sub>O<sub>3</sub>.

## DISCUSSION

#### Speciation and Structural States of Additive Boron

The structure and chemical speciation of boron in aluminium borates which were prepared by the co-precipitation technique, were studied by means of magic-angle

<sup>[4]</sup>B (23).



FIG. 10. B K-edge XANES spectra of calcined Ni-Mo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-B<sub>2</sub>O<sub>3</sub> catalysts, as compared with those of B<sub>2</sub>O<sub>3</sub> containing trigonally coordinated B (<sup>[3]</sup>B) only and BPO<sub>4</sub> containing tetrahedrally coordinated B (<sup>[4]</sup>B) only.

spinning nuclear magnetic resonance (23). For aluminium borates calcined at 500°C, both <sup>[3]</sup>B and <sup>[4]</sup>B species are present, and the proportion of the tetrahedral boron species increases with the increasing B/Al ratio. The relative strength of the acid sites is correlated with the higher proportion of the tetrahedral boron species. However, the structure and chemical speciation of boron in  $\gamma$ - $Al_2O_3$ - $B_2O_3$  materials, prepared by wet impregnation, have not been reported, even though Ramírez et al. speculated that  $B^{3+}$  is predominantly tetrahedrally coordinated in the  $Co-Mo/\gamma - Al_2O_3 - B(x)$  catalysts they investigated (31). The B K-edge XANES spectra of our NMABx catalysts indicated that boron is trigonally coordinated with oxygen. Thus, boron may not enter the tetrahedral positions in the lattice of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. The boron species probably form monolayers on the surface of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> particles when the content of  $B_2O_3$  is low (Fig. 9). With further increases in the  $B_2O_3$  loadings, the boron species may form multiple layers and the interaction between  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and the boron species becomes weaker. However, the boron species are well dispersed until the B<sub>2</sub>O<sub>3</sub> loading reaches about 14 mol% at which point an crystalline  $B_2O_3$  phase appears, as shown in the XRD patterns (Fig. 2). The boron species is most likely to be  $B_2O_3$ , even though the borate species containing <sup>[3]</sup>B only are not excluded. In addition, the NH<sub>3</sub> temperatureprogrammed desorption of our NMABx catalysts showed that the addition of boron to alumina only slightly improves

#### Dispersion of Active Metal Species

The chemical states and dispersion of active metal species in the supported Co(Ni)-Mo(W)/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts have been widely studied using chemisorption of probe molecules (42), XRD (43), XPS (43, 44), EXAFS (39), infrared (45), Mössbauer (16, 17), transmission electron microscopy (46), and diffuse reflectance spectroscopy (31). We did not attempt to investigate the structural states of Ni and Mo in the calcined Ni-Mo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-B<sub>2</sub>O<sub>3</sub>. However, it is generally believed that both Ni<sup>2+</sup> and Mo<sup>6+</sup> may be tetrahedrally and octahedrally coordinated with oxygen and that Ni and Mo species may enter the lattice of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and/or are present on the surface of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> particles (11).

As shown above, the majority of Mo atoms are present as MoS<sub>2</sub> in sulfided Ni–Mo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>–B<sub>2</sub>O<sub>3</sub> catalysts, even though small amounts of oxide and oxy-sulfide species may be present. It was assumed that the "Ni-Mo-S" phases, in which Ni is located at the edges of the MoS<sub>2</sub> crystallites, are responsible for the HDS catalytic activity. Thus, it is important to investigate the dispersion of the active metal phases. The term "dispersion" often simply means the fraction of surface atoms relative to the total number of atoms. However, for anisotropic and layered MoS<sub>2</sub>, this term is not sufficient to describe the dispersion of metals. The basal and edge dispersions must be determined, because for MoS<sub>2</sub> particles with a fixed number of layers, the basal plane dispersion is similar, irrespective of the lateral dimension of the particles; in this case, however, the number of edge plane atoms and the edge dispersion are different. The information on the basal dispersion was obtained by XPS measurements from which the fraction of surface atoms relative to the total number of atoms was calculated. On the other hand, EXAFS has been proven to be a powerful technique for studying the edge dispersion or lateral dimension of active metal phases in the Ni-Mo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts (18, 39).

For calcined Ni–Mo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>–B<sub>2</sub>O<sub>3</sub> catalysts, the basal dispersion of Ni and Mo species increases markedly when even a small amount of boron was added to  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, as evidenced by the higher concentrations of Ni and Mo on the surface of catalysts (Figs. 5 and 6). However, the further increase in the loading of B<sub>2</sub>O<sub>3</sub> reduces the basal dispersion of the Ni and Mo species and, thus, the atomic concentrations of Ni and Mo on the surface of catalysts decrease. These results are in good agreement with the XRD patterns of these catalysts (Fig. 2), which showed that a crystallite MoO<sub>3</sub> phase first appears at the B<sub>2</sub>O<sub>3</sub> loading of about 5 mol%, and its diffraction intensity increases with further loadings of  $B_2O_3$ . The sulfidation did not cause significant change in the basal dispersion of Mo and Ni, since the atomic concentrations of Ni and Mo in both the calcined and the sulfided catalysts are similar in profiles (Figs. 5 and 6). Of course, the different loadings of B may affect the chemical states of Ni and Mo in the catalysts. For example, B species may prevent Ni and Mo from entering the lattice of alumina (27), which may result in the change in the atomic concentrations calculated by XPS.

The lateral size or edge dispersion of the MoS<sub>2</sub> particles is an important parameter for hydrotreating Ni(Co)-Mo sulfide catalysts. As shown in Fig. 8A, the FTM of both Mo-S and Mo-Mo shells increase markedly with the addition of boron and then slightly decrease with further loadings of  $B_2O_3$ . These results show that the average coordination numbers of S (N(S)) and Mo (N(Mo)) around Mo also increase markedly with the addition of boron and then slightly decrease with the increasing content of  $B_2O_3$  if it is assumed that the order-disorder states of the absorbing Mo atoms are similar for these samples (47). In fact, we noted that the disorder of these catalysts may be slightly different, for example, the Mo-Mo disorder (see Fig. 7) may partially contribute to the FTM(Mo-Mo), because the FTM is also inversely proportional to the power of the square of the disorder. However, we could not make a thorough quantitative EXAFS analysis to distinguish the contributions of coordination number and the structural disorder to the FTM using our current EXAFS software. Thus, only for a qualitative comparison, the lateral size appears to increase, and the edge dispersion decreases with the addition of a small amount of boron to  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, and the further loadings of boron may slightly increase the edge dispersion.

## *Effects of Boron on the Dispersion of Active Metal Species and HDS Activity of DBT*

Previous studies on the effects of additives to the conventional Co(Ni)-Mo(W)/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> focused on catalytic activity, selectivity, and catalyst lifetime. Less work has been done on the effects of additives on the structure, nature, and dispersion of active metal species in the catalysts. Phosphorus is one of the most commonly used additives in the molybdenum-based hydrotreating catalysts supported on alumina. A great deal of research was done to understand the effects of phosphorus on the chemical states and dispersion of active species and HDN and HDS catalytic activities. However, the real functions of phosphorus as an additive in the Ni-Mo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> are still unclear (48). The few studies on boron as an additive suggest that it has effects similar to those of phosphorus (29-31). However, the effects of boron on the chemical states and dispersion of active species and the catalytic activity of the catalysts are even more controversial.

As discussed above, the addition of boron to the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> support causes the redistribution of Mo and Ni oxide pre-

cursors. When the content of B<sub>2</sub>O<sub>3</sub> is low, the boron species forms monolayers on the surface of Al<sub>2</sub>O<sub>3</sub> particles, which is speculated to prevent Ni and, perhaps, Mo atoms from entering into the lattice of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, thus increasing the proportion of octahedral Ni species and favoring the formation of Ni-Mo-S phases in the sulfided catalysts. At the B<sub>2</sub>O<sub>3</sub> loading of about 1 mol%, Mo and Ni oxide phases form well-dispersed monolayers on the surface of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> particles, and the lateral dimension of the Ni and Mo species is relatively large. However, increasing loadings of B<sub>2</sub>O<sub>3</sub> reduce the surface area and pore size of the support (31), promote the formation of the multiple-layered boron species and weaken the interaction of both Mo and Ni oxide precursors with the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-B<sub>2</sub>O<sub>3</sub> supports. Thus, the Mo and Ni oxide phases tend to form multiple layers with limited lateral dimensions. The Mo oxide phase may agglomerate and form crystallites. The sulfidation extension of the Ni-Mo/  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-B<sub>2</sub>O<sub>3</sub> catalysts also decreases with additional loadings of B<sub>2</sub>O<sub>3</sub>.

The HDS activity of DBT over the NMABx catalysts depends both on the conversion rates to diphenyl (by hydrocracking) and to cyclohexylbenzene (by hydrogenation). The incorporation of boron into  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> has a beneficial effect on the HDS of DBT over the conventional Ni-Mo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts. At a B<sub>2</sub>O<sub>3</sub> loading of about 1 mol%, the acidity and thus the hydrocracking ability of the catalysts have a more marked increase, and meanwhile the basal dispersion of the active metal phases reaches an optimum. Thus, the total HDS activity of DBT over the Ni-Mo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-B<sub>2</sub>O<sub>3</sub> catalysts reaches a maximum. However, the HDS of DBT is more dependent on the high basal dispersion of metal species and the conversion rate to cyclohexylbenzene. The maximum conversion rate to cyclohexylbenzene may be related to the synchronized tendencies of the atomic concentrations or basal dispersion of the active Mo and Ni phases on the surface of the catalysts. With additional loadings of  $B_2O_3$ , the interaction of both Mo and Ni oxide precursors with the supports becomes weaker. The Mo oxide precursor may also agglomerate to form a crystalline phase. Thus, the hydrogenation ability of the catalysts and, thus, the total HDS activity of DBT over these catalysts decrease. Our results on the effects of boron on the basal dispersion of active Ni and Mo species and, thus, on the HDS activity of DBT are in good agreement with those of phosphorus in Ni-Mo/  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts (48), even though the exact functions of addition of boron to these catalysts require elucidation.

## CONCLUSIONS

XRD, XPS, and EXAFS were used to characterize the dispersion of active Ni and Mo species in the Ni–Mo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-B<sub>2</sub>O<sub>3</sub> catalysts. These three techniques provide complementary information on the dispersion of the active species: XRD is used to reveal the distribution and speciation of the Ni and Mo phases in the bulk catalysts; XPS

determines the surface atomic concentrations and basal dispersion of the active species; and Mo *K*-edge EXAFS is a powerful technique for studying the number of edge atoms and the edge dispersion. The combination of these three techniques provide a complete picture for characterizing the dispersion of the active metal species and important information needed to understand the catalytic activity and selectivity of hydrotreating Ni(Co)–Mo(W) sulfide catalysts.

Adding boron to  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> generally increases the acidity of the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-B<sub>2</sub>O<sub>3</sub> supports and slightly improves the hydrocracking ability of Ni-Mo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-B<sub>2</sub>O<sub>3</sub>. Thus, the conversion rate of DBT to diphenyl increases slightly with additional loadings of B<sub>2</sub>O<sub>3</sub>. The conversion rate of DBT to cyclohexylbenzene first increases with increasing amounts of  $B_2O_3$ , up to about 1 mol% of  $B_2O_3$ , and then decreases with increasing amounts of  $B_2O_3$ . This is in good agreement with the dispersion of active Mo and Ni phases and the hydrogenation ability of Ni-Mo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-B<sub>2</sub>O<sub>3</sub> catalysts. As a result, the total conversion rate of DB over Ni-Mo/  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-B<sub>2</sub>O<sub>3</sub> reaches a maximum at a B<sub>2</sub>O<sub>3</sub> content of about 1 mol% and then decreases with further increases in  $B_2O_3$ , which is more dependent on the dispersion of the active metal phases and the hydrogenation ability of the Ni-Mo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-B<sub>2</sub>O<sub>3</sub> catalysts.

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