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# Characterization of boria-alumina mixed oxides prepared by a sol-gel method.

## Part 2: Characterization of the calcined xerogels

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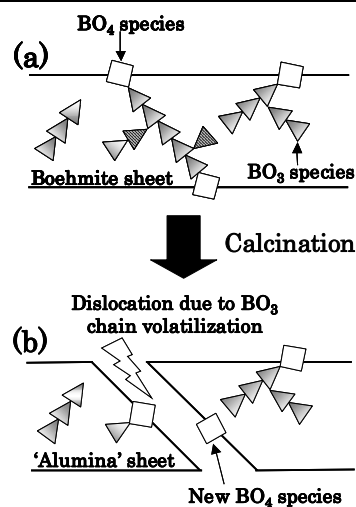
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New  $\text{BO}_4$  species incrustated in the surface of alumina matrix are present after calcination of dried B-alumina xerogels with  $\text{B} / \text{Al} > 0.15$  prepared by the sol-gel method, consecutively to volatilization of sufficiently long  $\text{BO}_3$  chains crossing over the original host boehmite matrix.



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**Keywords:** sol-gel, alumina, boron, solid state MAS-NMR, structure

## Abstract

Sol-gel boria-alumina mixed oxides with a wide range of B / Al atomic compositions have been characterized as dried xerogels in the preceding paper in which a structural model with four domains of composition was proposed. The present paper presents the results obtained on the same series of solids after calcination at 500°C. It was found that the structure of the dried xerogels has a strong influence on the structure of the final oxides. In particular, in the dried xerogel state from B / Al  $\sim$  0.15, BO<sub>3</sub> chains crossed over the solid matrix and this ratio was also a crucial limit for the calcined solids structure. Indeed, during calcination some BO<sub>3</sub> chains were volatilized, giving a measured B / Al ratio lower than the theoretical one; the oxides were dislocated and their SSA brutally increasing from  $\sim$  500 m<sup>2</sup>.g<sup>-1</sup> up to  $\sim$  650 m<sup>2</sup>.g<sup>-1</sup>. Cleavage resulted in the exposition of new external surfaces that exhibited BO<sub>3</sub>OH species incrustated in the host alumina matrix, conferring then an epitactic character to the solids. Further, the <sup>11</sup>B MAS-NMR spectra of the solids exhibited a feature constituted of BO<sub>3</sub> and BO<sub>4</sub> (hydrated surface BO<sub>3</sub> species) components that were resolved by a software simulation. While for B / Al < 0.15 the quadrupolar interaction on the BO<sub>4</sub> species was of about 0.4 MHz, it increased up to about 0.9 MHz for B / Al > 0.15. This increase originated in a strain on the new BO<sub>3</sub> species trapped along the cleaved surfaces. Further, XRD and XPS results showed that while for B / Al < 0.15, the system can be considered as an alumina matrix locally modified by insertion of BO<sub>3</sub> species, for B / Al > 0.15 a mixed phase was progressively formed. In good agreement, the <sup>27</sup>Al MAS-NMR spectra of the solids with high B / Al ratio were similar to that expected for model boria-alumina mixed phases. In addition, the BO<sub>4</sub> / BO<sub>3</sub> ratios calculated by simulation of the <sup>11</sup>B MAS-NMR spectra simulation were consistent with the XPS results. We calculated the proportion of B species (in wt.%) present on the surface of the solids (i.e. BO<sub>4</sub> species), which

can be potentially involved in catalytic reactions. It was remarkable that the tendency observed for the  $\text{BO}_4$  wt.% as a function of the B / Al ratio was consistent with a boria-alumina phase diagram previously proposed by Gielisse *et al.*.

## Introduction

As we previously reported<sup>1</sup>, different boria-alumina mixed-oxides have been widely used for catalytic applications by themselves<sup>2-25</sup> or as supports for various active phases<sup>26-31</sup>, or more specifically as supports for hydrotreating catalysts<sup>32-53</sup>. Nevertheless, the structure of the boria-alumina system with high specific surface areas is not yet satisfactorily described and the present work aims at proposing a detailed analysis of  $\text{B}_2\text{O}_3$ - $\text{Al}_2\text{O}_3$  carriers prepared by an original sol-gel method. In a preliminary study, the structure of solids with low boron loadings<sup>54</sup> ( $\text{B} / \text{Al} < 0.14$ ) was elucidated and it was decided to further extend the investigation to a wider range of B / Al compositions. In the preceding paper, the structure of the dried solids prepared by a sol-gel synthesis method (xerogels) with a wide range of B / Al atomic composition (from 0 up to 1.643) was described. This first study was carried out by interpreting the  $^{11}\text{B}$  and  $^{27}\text{Al}$  spectra obtained by solid-state magic angle spinning nuclear magnetic resonance (MAS-NMR) spectroscopy. The results suggested that the structure of the solids depends on the B / Al atomic ratio and four domains have been identified:

- In domain I ( $\text{B} / \text{Al} < 0.06$ ), matrix and surface tetrahedral aluminum species were created in addition to the usually observed octahedral aluminum species of the host boehmite structure. For  $\text{B} / \text{Al} = 0.06$ , 1 % of the aluminum species were in a tetrahedral coordination surrounded by 4 boron oxo-species;

- In domain II ( $0.06 < \text{B} / \text{Al} < 0.15$ ), new tetrahedral aluminum species were not created;  $\text{BO}_3$  chains started to develop from the tetrahedral aluminum species already present in domain I;

- In domain III ( $0.15 < B / Al < 0.48$ ), the  $BO_3$  ribbons progressively crossed over the boehmite matrix and emerged on its surface leading to the creation of new surface tetrahedral aluminum species at their ends. These new surface aluminum tetrahedral species became nucleation points of new  $BO_3$  chains. Further, supposedly due to particularly strong strains, some tetrahedral alumina species were converted into pentahedral aluminum species.

- In domain IV ( $B / Al > 0.45$ ), the new  $BO_3$  chains further developed into the host matrix.

The above-described model, built by interpreting NMR results, fits very well with the results of various characterization techniques presented in the present paper for the solids of the same origin, but after calcination in air. Indeed, in addition to the use of solid state MAS-NMR spectroscopy, specific surface area measurements, XRD, XPS and atomic composition determination permitted to thoroughly characterize the calcined mixed oxides, the calcination stage being necessary to convert the boron modified boehmite phase into a catalytically utilizable boron modified  $\gamma$ -alumina ( $B_2O_3$ - $Al_2O_3$ ) support. The results of the various techniques matched up very well each other and it was demonstrated that the final structure of the calcined mixed oxides strongly depended on the initial structure of the dried xerogels from which they are issued.

## **Experimental section**

### **Mixed oxides synthesis**

The boria-alumina supports were synthesized according to an original sol-gel method described elsewhere<sup>1,54</sup>. After hydrolysis, stirring and drying, the obtained dried xerogels<sup>1</sup> were further calcined for three hours in flowing air at 500°C, this temperature being reached at a rate of 40°C.h<sup>-1</sup>.

### **Sample compositions**

Bulk atomic composition of the calcined samples was determined at the *Service Central d'Analyses du CNRS* (Vernaison, France) by X fluorescence. The objectives of these analyses were to compare the actual compositions of the calcined oxides with the theoretical ones.

### **X-Ray Diffraction**

A Siemens D 5000 diffractometer equipped with a copper anode and a secondary monochromator, which tension of was adjusted at 50 kV (35 mA) was used. The sample was deposited at room temperature on a glass disc placed on a rotating holder in order to avoid eventual preferential orientations. The X-ray beam, emitted by a fixed source, reached the sample rotating around its holder axis. By reflection, the diffracted beam was detected by a scintillation counter. For a diffraction angle of  $\theta$  corresponded a  $2\theta$  moving of the counter on the diffractometer circle. The recordings were made with a measure step of  $0.2^\circ$  in a domain from  $2\theta = 5^\circ$  to  $2\theta = 75^\circ$  and with an integration time of 30 s.

### **XPS**

The spectra were recorded on an AEI ES200B spectrometer. The X-ray source was an aluminum anode ( $E = 1486.6$  eV) excited under a power of 300 W (12 kV, 25 mA). The samples were grinded in an agate mortar and then pressed on indium before being introduced in the analysis chamber under a vacuum inferior to  $4.10^{-8}$  Torr. The obtained information was both qualitative and quantitative<sup>55</sup>. Further, the three-dimensional thick binary oxide model was used to interpret spectra intensity variations as it is suitable and very convenient to characterize bulk samples prepared by the sol-gel method. This model allows following the boron distribution (or repartition) within the alumina matrix.

## **NMR**

### **MAS-NMR**

Like for the xerogels<sup>1,54</sup>, the MAS-NMR spectroscopy was used in order to characterize the local environment of the aluminum and boron species in / on the calcined samples. The spectra were recorded on a Brüker ASX 400 spectrometer working at 104.229 MHz (<sup>27</sup>Al) and 128.33 MHz (<sup>11</sup>B). The <sup>27</sup>Al spectra were recorded at a rotation frequency of 15000 Hz, with a pulse length of 0.8 μs and a repetition time between two acquisitions of 3 s; the reference at 0 ppm was taken for Al(H<sub>2</sub>O)<sub>6</sub><sup>3+</sup>. The <sup>11</sup>B spectra were recorded with a rotation frequency of 14500 Hz, with a pulse length of 10 μs and a repetition time of 10 s, the reference at 0 ppm being taken for BF<sub>3</sub>.OEt<sub>2</sub>.

### **MQ-MAS NMR**

In order to confirm the assignment of the aluminum species peaks (in particular of the pentahedral aluminum species), a MQ-MAS NMR spectra (2D NMR) was recorded using an experimental method described elsewhere<sup>56</sup>.

### **BET specific surface area (SSA) measurements**

The SSAs of the calcined oxides were determined using the one point BET method on a Quantasorb Junior (Ankersmit) after degassing the samples under primary vacuum at 250°C for 2 h.

## **Results and discussion**

### **Composition of the oxides**

The B / Al atomic ratios, determined by X fluorescence, are reported in Figure 1 as a function of the theoretical ones (ratios used during the sol-gel synthesis). Up to B / Al ~ 0.15 the measured B / Al ratio was equal to the expected one. In contrast, at higher B loadings

( $B / Al > 0.15$ ), the measured  $B / Al$  ratios of the calcined oxides became significantly less than the theoretical ones. It is remarkable that this transition ratio ( $B / Al = 0.15$ ) corresponds to the limit between domains II and III, as defined for the dried xerogels. Indeed, in the dried xerogels, when the  $B / Al$  ratio was higher than 0.15, the results suggested that  $BO_3$  chains started to emerge from the host matrix, progressively dislocating the boehmite mother structure. In addition it has been previously observed several times that near  $500^\circ\text{C}$ , boron oxides or polymeric  $BO_3$  like chains are volatile<sup>14,57,58</sup>, in good agreement with the Giellisse *et al.* diagram<sup>59</sup> (Figure 2) that shows that  $B_2O_3$  is fusible near  $470^\circ\text{C}$ . Therefore, the results presented in Figure 1 suggest that a part of the boron oxo-species present as  $BO_3$  chains of different lengths in the xerogels volatilizes during the calcination step at  $500^\circ\text{C}$ . Then, the actual  $B / Al$  ratio becomes inferior to the desired one. Note that when  $B / Al > 0.15$ , the  $BO_3$  chains in the xerogels are sufficiently long for crossing the host matrix. The value of 0.15 for the  $B / Al$  ratio seems to be a key value for this kind of solids as all the characterization techniques used later in the present work exhibit a change of behavior from this ratio.

#### **Texture of the solids (SSA)**

The SSAs of the calcined oxides are reported in Figure 3. While the SSAs are constant at a value of about  $500 \text{ m}^2.\text{g}^{-1}$  up to  $B / Al = 0.15$ , a clear and net increase is observed for higher boron loadings, for which the SSAs are about  $650 \text{ m}^2.\text{g}^{-1}$ , irrespective of the boron amount. As recalled above, this 0.15 value corresponds to the beginning of domain III in the xerogels. From this ratio,  $BO_3$  chains start to crossover the boehmite matrix. Then, the boehmite host structure is progressively dislocating by the  $BO_3$  chains development. In addition, as the  $BO_3$  chains (partly) volatilizes during the calcination step (B deficit observed in Figure 1 for  $B / Al > 0.15$ ), further dismembering of the solid structure during calcination with formation of smaller particles can explain such a SSA increase.



## Structure

### X-Ray diffraction

The X-ray diffractograms of the calcined mixed oxides are presented in Figure 4. In addition, in Table 1 are gathered the characteristic features of standard boron and boron-aluminium oxides that might be formed. Unfortunately, it is quite difficult to unambiguously interpret the diffractograms of Figure 4 as the solids appear to be poorly crystallized, with rather weak and broad peaks. Thus, the peaks in the dotted rectangles could be either attributed to mixed oxides ( $A_9B_2$ ,  $A_2B$ ) or  $H_3BO_3$  or  $B_2O_3$  or a combination of them in a poorly crystallized state. Further, for  $B / Al = 0$ , the features are, as expected, characteristic of a poorly crystallized sol-gel  $\gamma$ -alumina<sup>60</sup>.

The peak near  $2\theta = 45^\circ$  corresponding to diffraction on the alumina (113) plane is shifted to higher angles when the boron loading increases up to the ratio  $B / Al \sim 0.15$  and then stabilizes at  $2\theta \sim 50^\circ$ . This is again the ratio of  $B / Al = 0.15$  that seems to be a critical structural limit for the calcined oxides. The progressive shift of this peak suggests that when boron is introduced, the host network is progressively modified to accept the  $BO_3$  entities in its structure. Then, in the  $B / Al$  range from 0.15 to 0.38, the alumina (113) plane diffraction remains present at a constant  $2\theta$  value of about  $50^\circ$ , suggesting that a given mixed phase is present for the solids. As this mixed phase imposes constraints related to its genesis on the alumina lattice, the alumina peak is shifted, which is characteristic of an epitactic organization ( $A_9B_2$ - or  $A_2B$ -like phase might be formed over / through an  $Al_2O_3$  framework). Then, for  $B / Al > 0.38$  (beginning of domain IV of the xerogels), the alumina (113) plane peak is no more observable and the spectra are constituted essentially of very broad features that can be attributed to boron-alumina mixed oxides. The solids have then not any more a pseudo-epitactic character, but can be rather described as ‘real’

bulk random mixed oxides.

## NMR

The  $^{27}\text{Al}$  NMR spectra of the calcined mixed oxides are presented in Figure 5. They are very different from those obtained for xerogels with a remarkable increase in the intensity of the peaks attributed to tetrahedral ( $\sim 60$  ppm) and pentahedral ( $\sim 40$  ppm) aluminum species. Moreover, the spectra shape evolves sensibly with the boron loading. For B / Al atomic ratio between 0 and 0.184, the relative proportion of each species does not change significantly, while starting from B / Al = 0.263 a modification of the global shape of the spectra is observed with a drastic increase in the intensity of the peaks of tetrahedral and pentahedral aluminum species. It is remarkable to note that the spectra of high boron loadings samples are similar to that obtained for an  $\text{A}_9\text{B}_2$  phase<sup>61</sup>. Further, in order to check if the peak observed near 30 ppm is effectively due to pentahedral species and not to shifted tetrahedral species, a MQ-MAS spectrum of one selected sample has been recorded (Figure 6). This permitted to clearly identify the presence of pentahedral aluminum species according to a methodology described elsewhere. This presence means that the peak near 30 ppm is not due to tetrahedral aluminum species which have been shifted by the proximity of boron atoms (B-O-Al bonds) as it was suggested by other authors for solids prepared by coprecipitation. In addition, in the dried xerogel state, the creation of pentahedral aluminum species was also observed from B / Al = 0.26. Their presence was presumably a consequence of an extreme distortion of the system that could not be considered any more as a boehmite modified with B atoms, but rather as a mixed oxide precursor. Then, calcination transformed this system into a more organized mixed oxide in which pentahedral aluminum species are more abundant.

The  $^{11}\text{B}$  NMR spectra of the calcined mixed oxides are presented in Figure 7. Their shapes are also clearly different from those obtained for the dried xerogels. Indeed, while on the dried

xerogels a broad band with a small shoulder at low ppm was observed ( $\text{BO}_3$  species and  $\text{BO}_4$  species respectively), a doublet is observed in the calcined solids. For  $\text{B} / \text{Al} \geq 0.263$ , the low ppm peak exhibits clearly a sharp feature at its top part. As stated in the previous paper, the signal due to the  $\text{BO}_3$  species was modified by a quadrupolar interaction. While in the case of the dried xerogels, this interaction intensity was not strong enough to generate an apparent splitting of the signal (only a broadening was observed), in the case of the calcined solids the quadrupolar interaction becomes sufficiently strong to make apparent the peak splitting. The NMR spectra have been simulated and, as expected, the low ppm part of the  $\text{BO}_3$  doublet contains a component due to  $\text{BO}_4$  species. To reveal this feature, the spectra are first simulated with the QUASAR software in the same way as for the dried xerogels considering only the presence of  $\text{BO}_3$  species. For all the samples, a significant simulation misfit is always observed on the low ppm part of the simulated  $\text{BO}_3$  doublet. Then, by subtracting each experimental spectrum with the corresponding  $\text{BO}_3$  simulated spectrum, the peak due to  $\text{BO}_4$  species is revealed and can be further separately simulated. Furthermore, the simulated parameters obtained separately for the  $\text{BO}_3$  and the  $\text{BO}_4$  components are subsequently input together to finely simulate each global spectrum and a difference equal to only  $\pm 1\%$  is obtained for the new parameters when compared with the values obtained for the separated simulations. The simulations allow to determine the quadrupolar interaction intensity and the real chemical shift of each species as well as the  $\text{BO}_4 / \text{BO}_3$  ratio. The results are presented and discussed separately for the low boron and the high boron loadings:

*i) Low boron loadings (domains I and II of xerogels)*

The calculated “true” chemical shifts of the boron species are modified after calcination when compared with those obtained for the corresponding dried xerogels. The chemical shift of the

BO<sub>3</sub> species increased from 16 ppm to 17.5 ppm when the dried xerogels were calcined, while it decreased in the same time from 2 ppm to 1.1 ppm for the BO<sub>4</sub> species (Figure 8). In addition, the quadrupolar interaction on the BO<sub>3</sub> species increased from 2.3 MHz (dried xerogels) to 2.7 MHz upon calcination (Figure 9), which reflects an increase in the distortion of the local environment of the BO<sub>3</sub> species that are compelled to fit up in an organized oxide structure. For the BO<sub>4</sub> species, the quadrupolar interaction is about 0.4 MHz up to about B / Al = 0.08 and then seems to become very small. In fact for 0.08 < B / Al < 0.15, the BO<sub>4</sub> species quantity is quite low (Figure 10) and the simulation misfit is not sensitive to the quadrupolar interaction intensity applied on the BO<sub>4</sub> species signal in a reasonable range. Then, the simplex algorithm converges artificially to a value close to 0. Forcing the software to apply a value of 0.4 MHz did not change significantly the results when simulating the spectra of the solids with 0.08 < B / Al < 0.15. Therefore, the variations of the quadrupolar interaction intensity as a function of the B / Al atomic ratio in the full range of studied compositions are arbitrary linked (Figure 11). The value of 0.4 MHz obtained for the low boron loadings is in good agreement with the value extrapolated for “isolated” BO<sub>4</sub> species (Al-(OAl)<sub>3</sub>BO<sub>4</sub> species) in the dried xerogels.

**ii) High boron loadings (domains III and IV of the dried xerogels)**

For high loadings, the quadrupolar interaction on the BO<sub>3</sub> species remains constant at about 2.7 MHz (for B / Al > ~ 0.15 in Figure 11). In contrast, the quadrupolar interaction on the BO<sub>4</sub> species increases from 0.4 to 0.9 MHz for B / Al = 0.15 (which corresponds again to the interface between the domains II and III of the dried xerogels). From B / Al = 0.15, the dried xerogels started to be crossed by BO<sub>3</sub> chains that became sufficiently long and, as aforementioned, it is well known that BO<sub>3</sub> species organized in chains can volatilize at relatively low temperatures<sup>14,57,58</sup>. According to Giellise *et al.* (Figure 2) the temperature of fusion of B<sub>2</sub>O<sub>3</sub> is about 450°C; further, Handbook of Chemistry and Physics<sup>62</sup> indicates that the ebullition

temperature of this compound is of about 1860°C. Although no numerical values were found for the B<sub>2</sub>O<sub>3</sub> superficial vapor tension, Maljuk *et al.*<sup>63</sup> annealed pure B<sub>2</sub>O<sub>3</sub> in an Al<sub>2</sub>O<sub>3</sub> crucible at 1240°C (12 h, air) and found that the volatility of boron oxide was equivalent to nearly 1.2 wt.% per day. This suggests that volatilization of well-crystallized boron oxide is not so effective. Nevertheless, in our case, two points have to be taken into consideration: (i) we are not in presence of a well-defined B<sub>2</sub>O<sub>3</sub> structure but rather in presence of BO<sub>3</sub> chains more or less dissolved into a boehmite matrix; (ii) the system is calcined from the dried state, which means that it is not yet so well organized into a real mixed oxide and then very unstable. Then, evaporation of boron oxide might occur at the earlier stage of calcination procedure for which the oxidic species entanglement is not so structured and thus can be easily subjected to heat decompositions. Further, boehmite conversion into alumina involves structure reorganization with H<sub>2</sub>O molecules liberation. In addition, Buyevskaya *et al.*<sup>64</sup> who studied partial oxidation of propane over boria-alumina proposed that the observed activity decrease with the time on stream was due to volatilization of BO<sub>3</sub> species during the reaction and their conversion into boric acid due to the presence of H<sub>2</sub>O in the feed gas. This is in good agreement with our assumption. Then, considering the B / Al composition results (loss of boron upon calcination, Figure 1) and the increase in the SSA (Figure 3) starting at B / Al = 0.15, the morphological change induced by calcination with volatilization of (a part of) BO<sub>3</sub> chains can be schematically illustrated in Figure 12 on which dislocation of the boehmite sheets is presented. Before calcination, surface BO<sub>4</sub> species are present on the top parts of the sheets of the host boehmite structure and it can be supposed that most of them are likely to remain after calcination (and rehydration). After calcination, some BO<sub>3</sub> species that were in the inner part of the matrix (hatched triangles in Figure 12(a)) are now on the top of the newly created surfaces and can therefore undergo hydration and become BO<sub>4</sub> species. As these latter BO<sub>4</sub> species were inner BO<sub>3</sub> species in the

xerogel, they might be still strongly strained in the new surface layer (epitactic growth as discussed from the XRD results). Therefore, their local environment is different from the one of the initial  $\text{BO}_4$  species. These latter species exhibited a quadrupolar interaction intensity of about 0.4 MHz, and the creation of the new type of  $\text{BO}_4$  species from  $\text{B} / \text{Al} > 0.15$  is responsible of an increase in the apparent global quadrupolar interaction intensity up to about 0.9 MHz. Further, as for the dried xerogels, the  $\text{BO}_3$  chemical shift do not seem to be significantly modified when the  $\text{B} / \text{Al}$  ratio changes (Figure 13). In contrast, the simulated chemical shift of the  $\text{BO}_4$  species peak seems to slightly increase from  $\text{B} / \text{Al} = 0.15$ , which is in good agreement with the above discussion. Indeed, it is very likely that most part of the  $\text{BO}_4$  species for  $\text{B} / \text{Al} > 0.15$  are not of the same type as the ones for  $\text{B} / \text{Al} < 0.15$ .

Finally, Figure 14 presents the  $\text{BO}_4$  species quantity as a function of the  $\text{B} / \text{Al}$  atomic ratio. Three parts can be distinguished. In the first part, corresponding to domains I and II of the dried xerogels, the  $\text{BO}_4$  percentage decreases linearly. In the second part, from  $\text{B} / \text{Al} \sim 0.13$  to  $\text{B} / \text{Al} \sim 0.50$ , which corresponds substantially to domain III of the dried xerogels, the  $\text{BO}_4$  species percentage increases up to  $\text{B} / \text{Al} \sim 0.26$  and then stabilizes from  $\text{B} / \text{Al} \sim 0.26$  to  $\text{B} / \text{Al} \sim 0.50$ . Finally, in the third part, corresponding to domain IV of the dried xerogels, the percentage of  $\text{BO}_4$  species increases drastically. These values, limiting the different composition parts, are in good agreement with the values of the Giellisse *et al.* diagram (Figure 2). Indeed, according to this diagram, while alumina and the  $\text{A}_9\text{B}_2$  phase are formed for  $0 < \text{B} / \text{Al} < 0.18$ , for  $0.18 < \text{B} / \text{Al} < 0.43$  the two  $\text{A}_9\text{B}_2$  and  $\text{A}_2\text{B}$  phases coexist and for  $\text{B} / \text{Al} > 0.43$ ,  $\text{B}_2\text{O}_3$  and the  $\text{A}_2\text{B}$  phase are both present. Furthermore, these limits are also in very good agreement with the XRD results, i.e. that the alumina is first modified by the presence of inner  $\text{BO}_3$  chains for  $0 < \text{B} / \text{Al} < \sim 0.15$  and then for  $\text{B} / \text{Al} > 0.15$  an epitactic-like mixed oxide phase is

progressively created. Then, for  $B / Al > 0.381$ , the system loses totally its 'alumina-like' character as the alumina XRD features completely disappear from the diffractograms.

## XPS

Figure 15 represents the XPS chemical shift of the B 1s core level as a function of the bulk  $B / Al$  ratio while Figure 16 represents evolution of its full width at half maximum (FWHM). The binding energies reported in Figure 15 are calculated by reference to the Al 2p level at 74.8 eV, the value generally obtained for  $\gamma$ -alumina. As a remark, the observed O 1s binding energy is constant at a value of  $531.9 \pm 0.1$  eV, the FWHM being of  $3.3 \pm 0.1$  eV irrespective of the  $B / Al$  ratio. As observed in Figure 15, up to  $B / Al = 0.18$ , a value which is close to the transition between domains II and III observed on the dried xerogels, the B 1s binding energy increases quite linearly and then decreases progressively for higher  $B / Al$  ratios. For low  $B / Al$  ratios, boron is supposed to be randomly dispersed in the alumina matrix, meaning that a mixed phase is locally formed, in good agreement with the Gielisse *et al.* diagram (Figure 2). Therefore, the observed binding energy for very low  $B / Al$  ratios (192.4 ~ 192.6 eV, Figure 15) is close to the one of a model  $A_9B_2$  phase (192.5 eV). Then, for  $B / Al > 0.05$ ,  $BO_3$  chains progressively developed in the dried xerogels and a part of them remained after calcination. Therefore, the  $BO_3$  species are locally more and more surrounded by other  $BO_3$  entities, as it is the case for  $H_3BO_3$  or  $B_2O_3$  solids that contains exclusively  $BO_3$  chains. Thus, the B 1s binding energy progressively increases when increasing the  $B / Al$  ratio up to about 0.2 with a value of 193 eV, to be compared with the value commonly observed for  $H_3BO_3$  (193.2 eV) or  $B_2O_3$  (193.5 eV). Further for  $B / Al > 0.15$ , as represented in Figure 12, calcination induces cleavage caused by volatilization of  $BO_3$  chains sufficiently long for crossing the boehmite matrix. Then, new B oxo-species are created on the new surfaces (hatched species in Figure 12). In other words, for  $B / Al > 0.15$  the system becomes progressively a 'real' mixed phase with B and Al species 'randomly' distributed

at the particle level. Consequently, the B 1s binding energy progressively decreases to approach again the value observed for an  $A_9B_2$  phase (192.5 eV) when B / Al increases.

The shape of Figure 16 (FWMH of the B 1s peak) is very similar to the one obtained for the calculated percentage of  $BO_4$  (Figure 14) and it is then likely that the FWHM is influenced by the percentage of  $BO_4$  in the solids. Indeed, while the XPS resolution is not sufficient to separate the peaks of the different B species, the B 1s peak appears plus or minus broadened due to a certain distribution in the binding energies of the respective species. Moreover, unlike the case of the NMR spectra that have been recorded at atmospheric pressure without any pretreatment (except for the experiment used to verify the disappearance of the  $BO_4$  peak after dehydration; a result not shown here), the XPS spectra are taken after degassing the samples under very low pressures, and the  $BO_4H$  species are converted into  $BO_3$  species by dehydration prior to the measurement. Therefore, the observed binding energies are the ones of bulk  $BO_3$  species and surface  $BO_3$  species (that can undergo the aforementioned hydration/dehydration process). As their environment differs only slightly, their binding energy might be therefore rather close, unlike if the surface ones were  $BO_4$  species (electronic influence of the fourth oxygen atom). This slight difference is reflected in the FWHM of the peak. This result is in very good agreement with the QASAR simulations results. It appears interesting to note that modification of the local environment of atoms which induces changes in the binding energy of core level(s) has already been reported in the literature for mixed oxides other than boron-alumina. For example, the Ti  $2p_{3/2}$  line shifts from 458.5 eV for Ti in octahedral coordination as in  $TiO_2$  to about 460.0 eV for Ti in tetrahedral coordination in mixed  $TiO_2$ - $SiO_2$  aerogels with low Ti content. In the latter case, the Ti atoms are mainly surrounded by O-Si linkages<sup>65</sup>.

Finally, in order to check about the homogeneity of the solids, the B / Al ratio are calculated from the XPS results using the three-dimensional thick binary oxide model described elsewhere.



In this model, calculations of atomic ratio from XPS are obtained by integrating the differential equation relative to the XPS intensity of a given line versus the position in the solid of atom emitting photoelectrons from 0 (uppermost surface layer) to  $\infty$  (sample “thick” relative to the mean free path of the photoelectrons). Such an investigation permits to probe elements in a solid depth to about 10 nm. The fact that the B / Al calculated ratio from XPS peak intensity [B / Al (XPS)] are very close to bulk ratio as measured by X-ray fluorescence (Figure 17) indicates that the samples of that system exhibit a good B-Al homogeneity: the B / Al surface ratio (0-10 nm) is representative of the B-Al bulk ratio.

## Conclusions

The calcined boria-alumina mixed oxides with different B / Al atomic ratio have been characterized by various complementary techniques that show consistent results, further validating *a fortiori* the model proposed for the corresponding dried xerogels.

For B / A < 0.15, the solids are composed of a  $\gamma$ -alumina host matrix locally modified with BO<sub>3</sub> species. The random distribution of BO<sub>3</sub> species modifies progressively the alumina original network and the XRD peak attributed to the (113) plane of  $\gamma$ -alumina progressively shifts to higher  $2\theta$  when B / Al increases.

For B / Al > 0.15, the structure of the solids drastically changes. Indeed, in the corresponding dried xerogels, BO<sub>3</sub> chains are developing and progressively cross the host matrix. The sufficient long BO<sub>3</sub> chains are (partly) volatilized during calcination and the measured B / Al ratio of the calcined oxides become significantly lower than the theoretical one, while in contrast an excellent correlation is obtained for B / Al < 0.15. Volatilization of the BO<sub>3</sub> chains leads to a dislocation of the initial system and the specific area of the solids increases noticeably for

calcined samples with B / Al higher than 0.15. Then, new exposed surfaces are created, which exhibit boron oxo-species that were previously members of core BO<sub>3</sub> chains. The creation of these new BO<sub>3</sub> species (hydrated into BO<sub>4</sub> species in the ambient atmosphere) that are incrustated in the surface of the solids is accompanied with an increase in the quadrupolar interaction intensity (calculated by simulating the <sup>11</sup>B MAS-NMR spectra) observed on the BO<sub>4</sub> species. When the longer BO<sub>3</sub> chains have been volatilized, the B remaining oxo-species are well distributed in the network with supposedly a non-negligible part incrustated in the cleaved surface. The solids can then be considered as mixed phases according to the following arguments:

- The XPS results have shown that for B / Al < 0.15 the B 1s binding energy progressively increases with the boron loading (organization into longer and longer BO<sub>3</sub> chains), while for B / Al > 0.15 it progressively decreases to become closer and closer from the B 1s binding energy observed for a mixed 9Al<sub>2</sub>O<sub>3</sub>.2B<sub>2</sub>O<sub>3</sub> phase;

- The shape of the <sup>27</sup>Al MAS-NMR spectra becomes similar to the one obtained in previous literature for the above-mentioned 9Al<sub>2</sub>O<sub>3</sub>.2B<sub>2</sub>O<sub>3</sub> phase, especially for B / Al > 0.184.

- The XRD diffractograms progressively lose the features of  $\gamma$ -alumina, especially for B / Al > 0.263, while the shift of the peak due to the diffraction on the (113) plane of the  $\gamma$ -alumina stops from B / Al ~ 0.156, indicating the formation of a defined mixed phase (supposedly epitactic-like growth).

Further, the software simulations allowed to calculate the ratio BO<sub>4</sub> / BO<sub>3</sub> (ratio between 'surface BO<sub>3</sub> species' and 'bulk BO<sub>3</sub> species'). Results are in good agreement with the creation of new exposed surfaces from B / Al = 0.15. In addition, the wt.% of BO<sub>4</sub> species in the oxides as a function of the B / Al ratio is reported in Figure 18. It is remarkable that the limits that can be distinguished are in excellent agreement with either the limits defined for the dried xerogels

and also of the phase diagram previously proposed by Gielisse *et al.* As a final remark, the quantity of  $\text{BO}_4$  species is a very important parameter. Indeed, as discussed above, these species are surface species and therefore boron species that are accessible to molecules in the case of catalytic reactions. Further, the presence of  $\text{BO}_3$  chains is also a very important parameter in the point of view of catalytic applications. Indeed, while these chains can volatilize for rather low temperatures, possibly leading to a loss of the properties initially brought by the B atoms in the system, it is also known that the catalytic system can auto-repair by replenishment through the migration of the bulk B species to the solid surface. Thus, in order to avoid undesirable volatilization of the active species while keeping the auto-reparation property, it seems preferable to work with solids that contain reasonably short  $\text{BO}_3$  chains. In other words, mixed oxides with rather well distributed boron species might be good candidates. Considering the solids of the present study, for  $\text{B} / \text{Al} < 0.15$  short  $\text{BO}_3$  matrix chains are present and might be volatilized for sufficient times on stream during catalytic applications. In contrast, for  $\text{B} / \text{Al} > 0.15$ , the solids progressively tend to exhibit the structure of mixed oxides, especially for  $\text{B} / \text{Al} = 0.381, 0.484$  and particularly for 0.728 for which characteristic  $^{27}\text{Al}$  MAS-NMR spectrum features are obtained. Actually, some of the solids presented in this work have been used for example as catalysts for the vapor phase Beckmann rearrangement of the cyclohexanone-oxime<sup>66</sup>. The results fit very well with the conclusions of the present study as the catalyst with  $\text{B} / \text{Al} = 0.728$  exhibits a lifetime about twice higher than that of the ones with  $\text{B} / \text{Al} = 0.013, 0.062$  and 0.280. In addition, the sol-gel boria-alumina catalysts showed longer lifetime than those of solids prepared by conventional impregnation. This can be attributed to a higher stability of the boron species within the catalyst structure ( $\text{BO}_4$  species incrustated in the cleaved surfaces). Furthermore, in another study boria-alumina carriers prepared using the method proposed in the present work have been subsequently impregnated with solutions

containing Co and Mo species and then submitted to a sulfidation procedure to use them as HDS catalysts<sup>67</sup>. Thiophene and dibenzothiophene (DBT) hydrodesulfurization (HDS) reactions exhibited a maximum for B / Al ~ 0.05 (corresponding to end of domain I of the xerogels), for which a local maximum of acidity was observed by NH<sub>3</sub> adsorption / desorption experiments on the bare oxide carriers.

### Acknowledgements

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### Figures captions

Figure 1. Measured B / Al atomic ratio in the calcined oxides as a function of the theoretical one (xerogel composition).

Figure 2. Gielisse *et al.* phase diagram (adapted from Ref. 59). A = Al<sub>2</sub>O<sub>3</sub>, B = B<sub>2</sub>O<sub>3</sub>, A<sub>9</sub>B<sub>2</sub> = 9Al<sub>2</sub>O<sub>3</sub>.2B<sub>2</sub>O<sub>3</sub>, A<sub>2</sub>B = 2 Al<sub>2</sub>O<sub>3</sub>.B<sub>2</sub>O<sub>3</sub>.

Figure 3. Specific surface areas of the calcined samples.

Figure 4. Diffractograms of the calcined samples.

Figure 5. <sup>27</sup>Al NMR spectra of the calcined samples.

Figure 6. <sup>27</sup>Al MQMAS spectrum of one calcined sample (B / Al = 0.138).

Figure 7. <sup>11</sup>B NMR spectra of the calcined samples.

Figure 8. Observed and calculated boron chemical shift for calcined samples (low boron loadings).

Figure 9. Quadrupolar interaction frequency for calcined solids (low boron loadings).

Figure 10. %BO<sub>4</sub> defined as  $\{B(BO_4)\} / [B(BO_4) + B(BO_3)] \times 100$  on calcined solids (low boron loadings).

Figure 11. Quadrupolar interaction frequency for boron species and for all the boron loadings.

Figure 12. Schematic representation of a sheet of boehmite host structure (xerogel) and of the same sheet after calcination ( $\gamma$ -alumina sheet) for B / Al > 0.15.

Figure 13. Chemical shifts of boron species in the calcined solids.

Figure 14. %BO<sub>4</sub> defined as  $\{B(BO_4)\} / [B(BO_4) + B(BO_3)] \times 100$  on calcined solids (full range of boron loadings).

Figure 15. Chemical shift of B 1s level as a function of the bulk B / Al ratio.

Figure 16. Evolution of the FWHM of the B 1s level peak as a function of the bulk B / Al ratio.

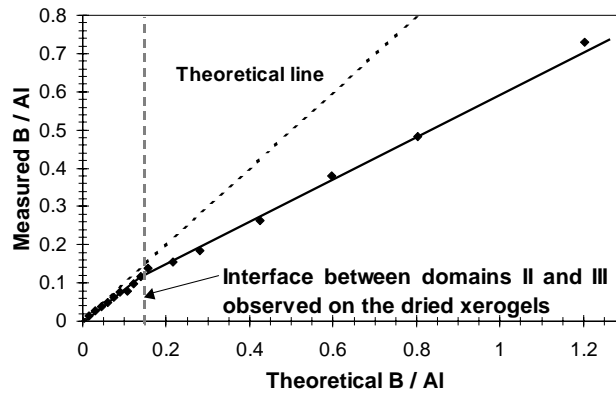
Figure 17. B / Al ratio as determined by XPS as a function of the B / Al bulk ratio.

Figure 18. Amount of boron in tetrahedral coordination calculated in BO<sub>4</sub> wt.% in B-Al<sub>2</sub>O<sub>3</sub> as a function of the B / Al ratio.

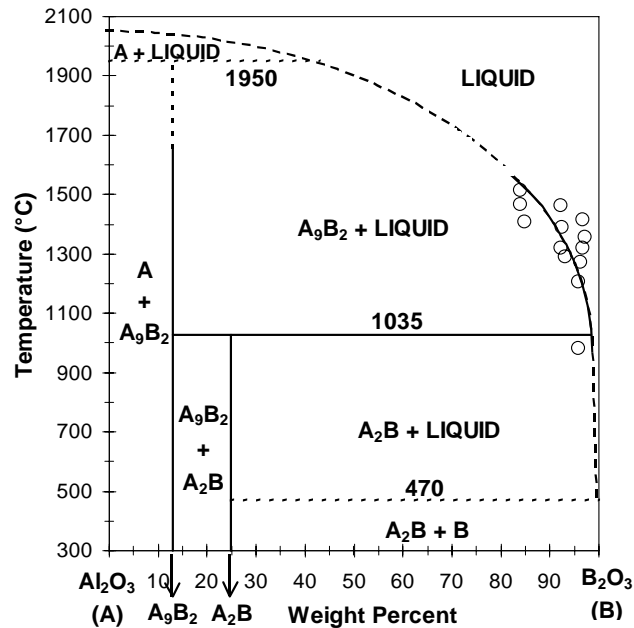
## Tables and figures

Table 1. Main XRD peaks observed for selected borica and borica-alumina mixed compounds

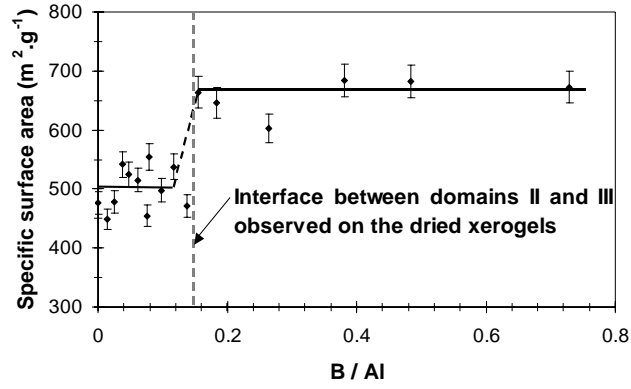
| Compound  | ASTM    | Main features (2θ) (relative intensity) |            |            |           |
|-----------|---------|---|------------|------------|-----------|
|           |         |   |            |            |           |
| $B_2O_3$  | 13-0570 | 27.8° (100)                             | 14.6° (35) | 23.4° (25) |           |
| $H_3BO_3$ | 30-0199 | 28° (100)                               | 14.6° (30) | 15° (20)   |           |
| $A_2B$    | 47-0319 | 16.4° (100)                             | 26.1 (78)  | 41.5 (51)  |           |
| $A_9B_2$  | 32-0003 | 16.5° (100)                             | 20.4° (50) | 26.4° (40) | 33.3 (40) |



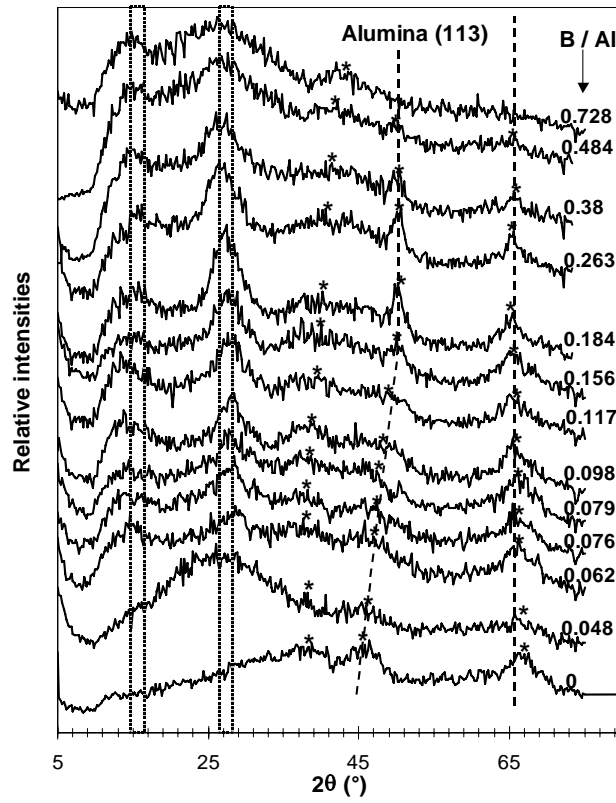
(Fig. 1)



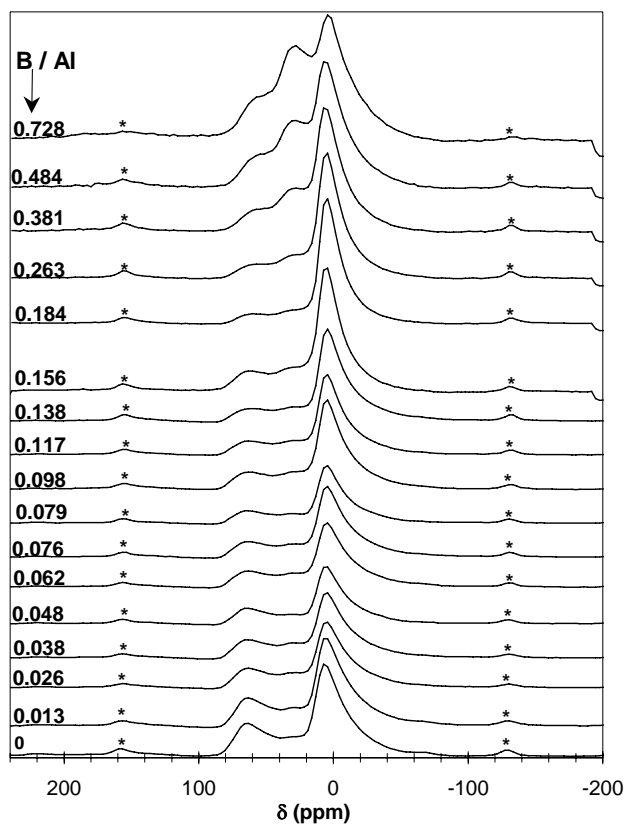
(Fig. 2)



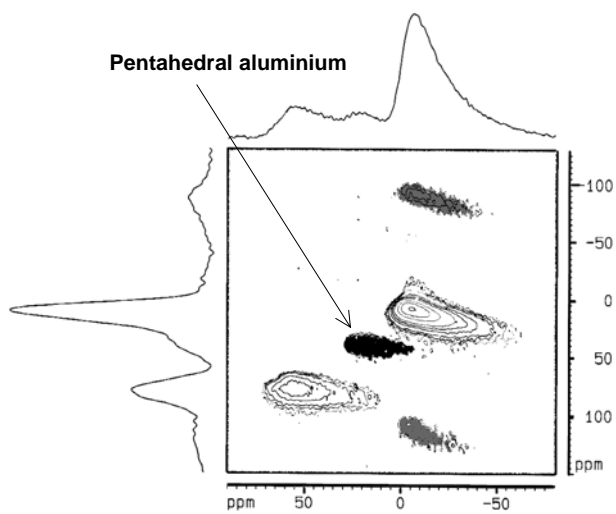
(Fig. 3)



(Fig. 4)

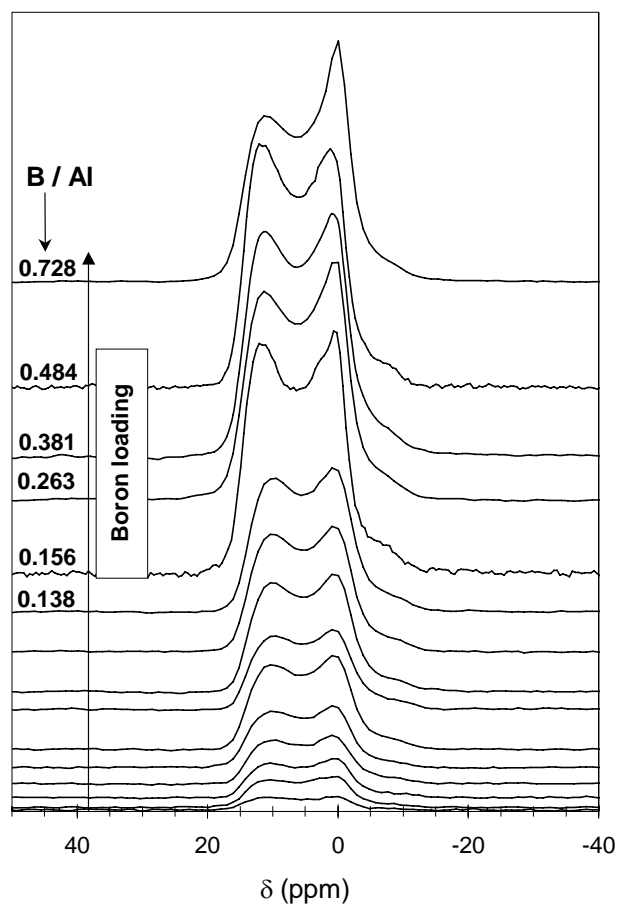


(Fig. 5)

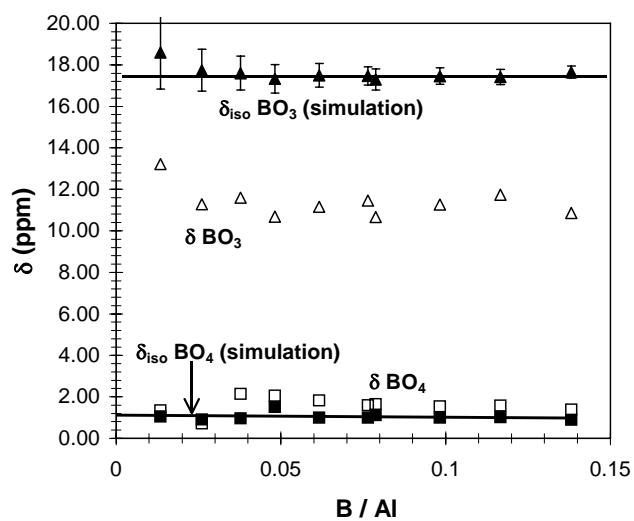


(Fig. 6)

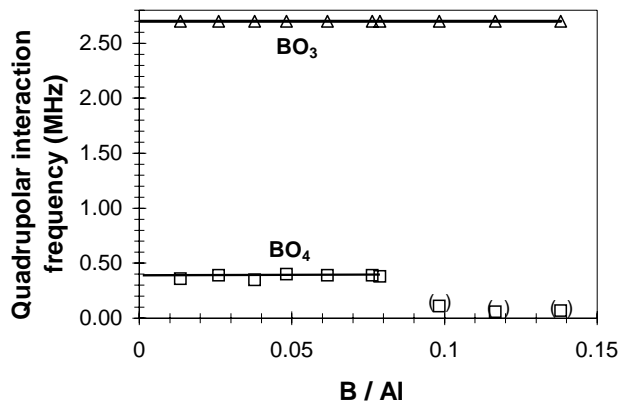




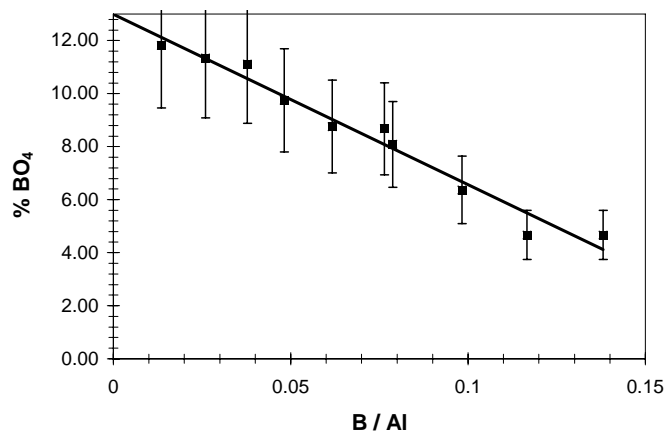
(Fig. 7)



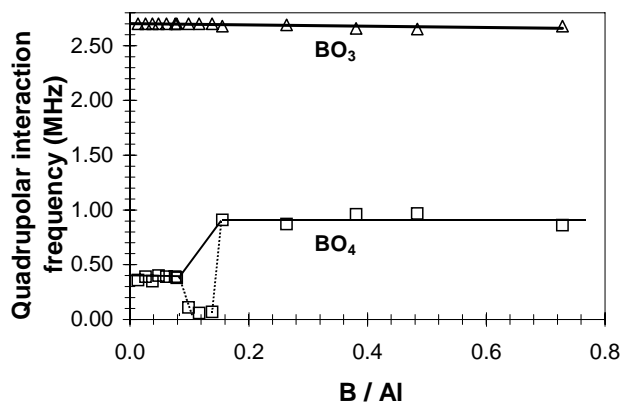
(Fig. 8)



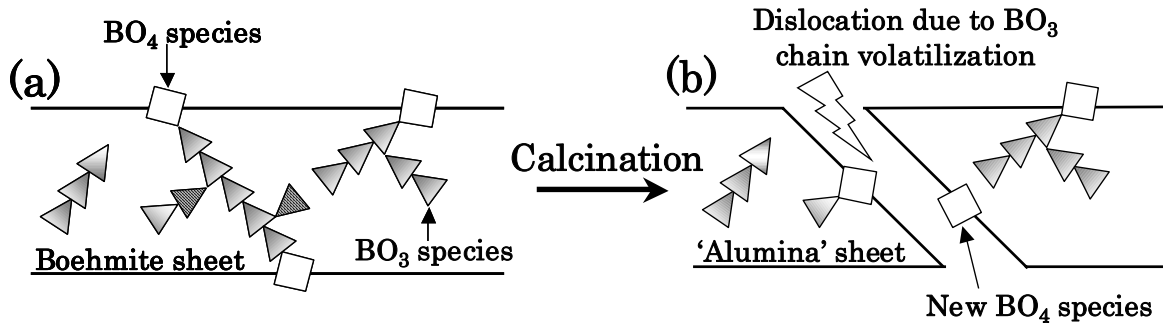
(Fig. 9)



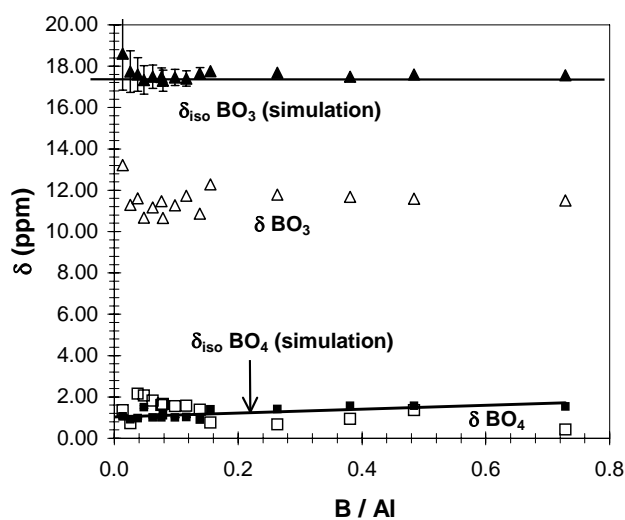
(Fig. 10)



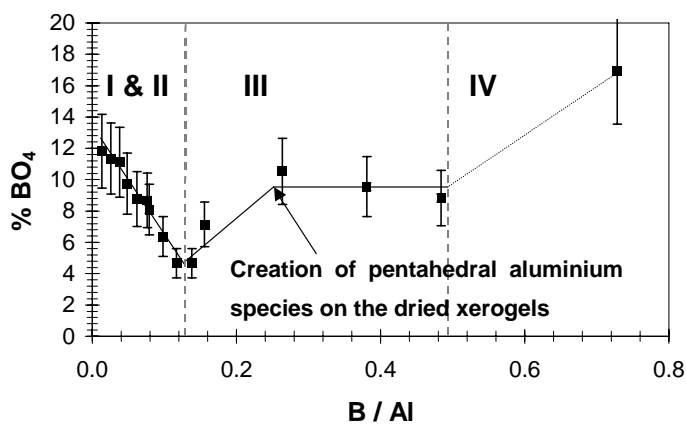
(Fig. 11)



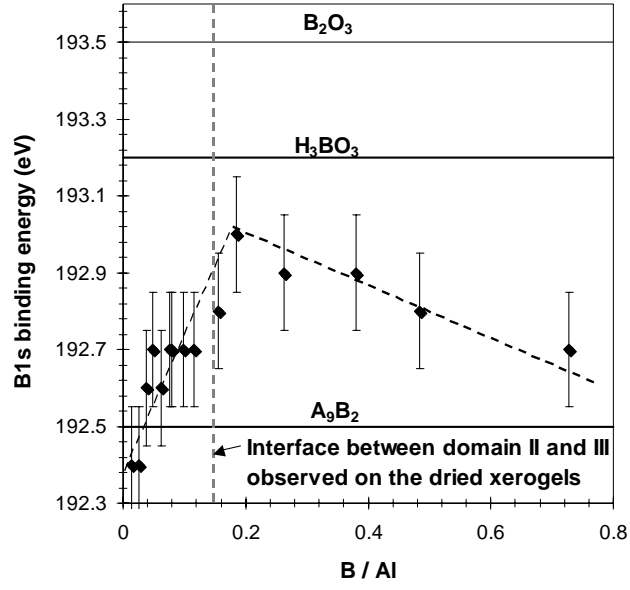
(Fig. 12)



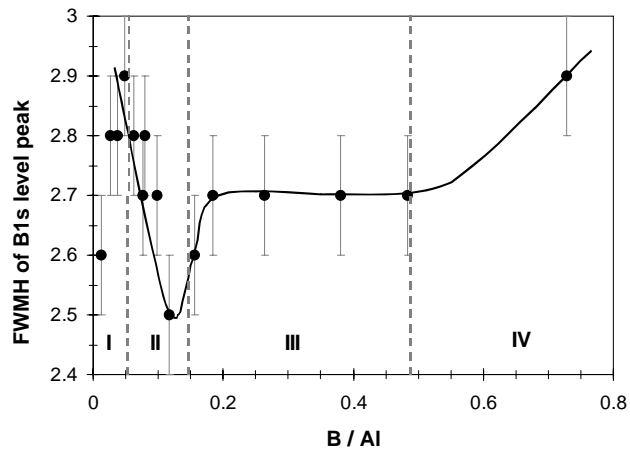
(Fig. 13)



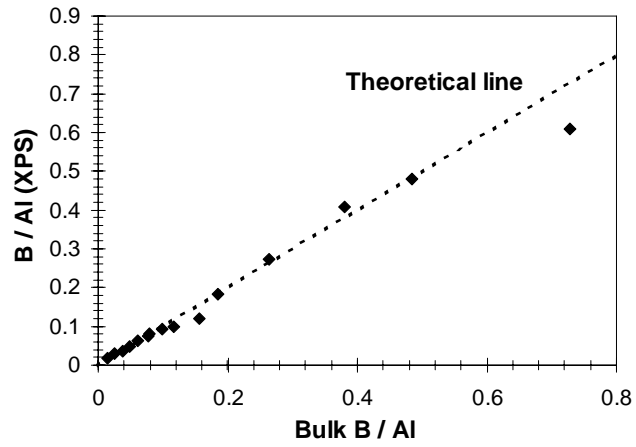
(Fig. 14)



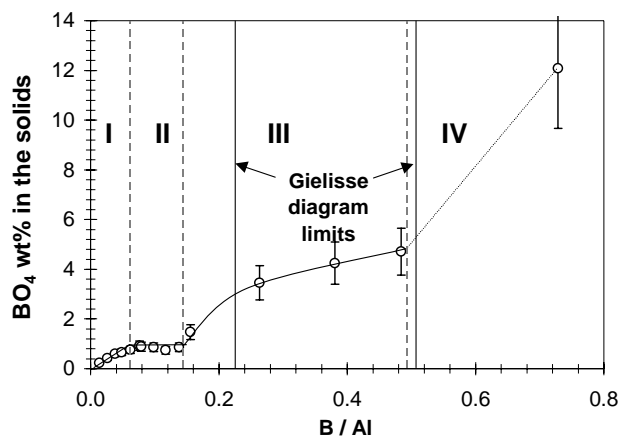
(Fig. 15)



(Fig. 16)



(Fig. 17)



(Fig. 18)

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