

Surface characterization of borated γ -alumina by using proton affinity distributions

Caracterización de la superficie de γ -alúminas modificadas con boro usando distribuciones de afinidad protónica

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Abstract

Borated aluminas with different boria contents (2, 3, 5 and 8 wt.% B_2O_3) were prepared to be used as supports for hydrotreating CoMo catalysts. The borated aluminas were characterized by proton affinity distributions (PAD) to obtain information about changes caused by boron introduction in the surface hydroxyl groups. The later being the sites by means of Mo and Co are anchored to the support. Two new peaks, which cannot be attributed to alumina hydroxyl groups, were found in the PAD profiles of borated aluminas. These two new peaks increased with increasing boria loading, even, in the PAD profile of the alumina with 8 wt.% B_2O_3 almost no other peaks were present. By comparing PAD profiles with FT-IR spectra of both the OH stretching ($3900-3400\text{ cm}^{-1}$) and the skeletal (under 2000 cm^{-1}) regions, it was possible to assign these new peaks to hydroxyls linked to trigonal and tetrahedral borated species, respectively. Thus, it could be inferred that boria OH groups progressively replaced alumina ones with increasing boria content forming a cover layer. Trigonal borated species were always predominant, however the relative population of tetrahedral species increased with increasing boria content.

----- *Keywords:* Alumina, boron, proton affinity distribution (PAD), infrared, hydroxyls

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Resumen

Alúminas modificadas con diferentes contenidos de boro (2, 3, 5 y 8 % en peso de B_2O_3) fueron preparadas con el objeto de ser usadas como soporte de catalizadores de hidrotreatmento CoMo. Estos soportes fueron caracterizados mediante distribución de afinidad protónica (DAP) obteniendo información sobre los cambios causados por la introducción de boro en los grupos hidroxilos superficiales. Estos últimos son los sitios donde posteriormente se anclarán el Mo y el Co al soporte. En las curvas DAP de las alúminas modificadas con boro se encontraron dos nuevos picos, los cuales no pueden ser atribuidos a hidroxilos de la alúmina. Estos nuevos picos se hacen más grandes al aumentar el contenido de boro en la alúmina, hasta el punto, que en la curva DAP de la alúmina con 8 % de B_2O_3 son prácticamente los únicos picos presentes. Comparando las curvas DAP de las alúminas modificadas con boro con sus respectivos espectros infrarrojo, en las regiones de hidroxilos ($3900-3400\text{ cm}^{-1}$) y esquelética (debajo de 2000 cm^{-1}), fue posible asignar los nuevos picos que aparecen en las curvas PAD de las alúminas modificadas con boro, a grupos hidroxilos unidos a especies de boro trigonal y tetragonal, respectivamente. Por tanto, del análisis de los PAD de alúminas modificadas con boro se puede inferir que los grupos OH de la alúmina son reemplazados por OH ligados a especies de boro. Las especies de boro trigonales fueron siempre predominantes, sin embargo la concentración relativa de compuestos tetraédricos aumenta con el contenido de boro.

---- *Palabras clave:* Alúmina, boro, distribución de afinidad protónica (DAP), infrarrojo, hidroxilos

Introduction

Borated aluminas have been used as effective catalysts for reactions such as skeletal isomerization of n-butenes, m-xylene isomerization, Beckmann rearrangement, toluene disproportionation and selective oxidation of ethane [1-4]. They also have been used as supports for Re in methathesis of functionally substituted alkenes [5] and as support for CoMo and NiMo hydrotreating catalysts [6-12]. Recently, Saih and Segawa [6] showed that the hydrodesulfurization (HDS) activity of dibenzothiopehe and 4,6-dimethyldibenzothiophene over $CoMo/B_2O_3(x)-Al_2O_3$ exhibit a maximum for B_2O_3 loadings around 3–5 wt%. Flego et al. [12] tested different CoMo catalysts supported in mixed oxides of Al with B, Zr, Si and Mg and found that with the catalysts supported on the mixed oxide Al-B the highest HDS activity was obtained as well as a decrease in the hydrogenation (HYD) of butenes. We have also found that borated

aluminas supported CoMo catalysts of 2-3 wt.% boria contents improve the selectivity (HDS/HYD of internal olefins) in the hydrotreatment of synthetic FCC naphtha [8]. The improvement in the selectivity was linked to an increase in Brønsted acidity and acidity strength as well as to the fact that boron causes changes in Co and Mo coordination and morphology [8, 13]. Thus, in order to explain the changes in the CoMo phase, it is necessary a proper characterization of the borated alumina is necessary to understand how Co and Mo are anchored to its surface.

Proton affinity distribution (PAD) is a technique which has been used successfully to obtain an accurate description of the processes that result in the binding of ionic ligands to substrates used as catalysts supports [14-17]. In this approach, an analysis of the heterogeneity of proton binding sites at the oxide/solution interface could be achieved using PAD measurements [14-17].

In bare alumina these proton binding sites correspond to the surface hydroxyls [14-17]. Very accurate information about the distribution of different hydroxyls groups in alumina and alumina doped with small ions (Na^+ , F^-) have been obtained [14, 15, 17]. This technique has also been used to obtain information about the binding of more complex ion such as PdCl_4^{2-} and $\text{Pd}(\text{NH}_3)_4^{2+}$ [14, 15]. Recently, in our group, this technique was used to characterize the surface of different commercial aluminas and of Pt catalysts supported on these [18]. Combining PAD with other techniques it was found that Pt dispersion could be associated with a specific interaction between Pt and the hydroxyl groups of the alumina [18]. Additional advantages of the PAD technique are its low cost and its simple implementation in the laboratory; because the only apparatus needed to obtain the potentiometric data is an automatic titrator.

Consequently, in the present paper borated aluminas were prepared and characterized using PAD profiles to obtain information about the changes in surface hydroxyls caused by boron introduction, taking into account that these are the sites where Mo and Co are considered to be anchored if we used borated aluminas as the support for hydrotreating catalysts. From our knowledge, PAD profiles have not been used in the borated alumina system. Thus, a detailed interpretation of the PAD profiles of borated aluminas was needed. This interpretation was made by comparing PAD profiles of the borated aluminas with its corresponding IR spectra of the OH stretching and skeletal regions

Experimental

Preparation of catalysts

Boron modified aluminas (2, 3, 5 and 8 wt.% B_2O_3) were prepared by the incipient wetness impregnation of $\gamma\text{-Al}_2\text{O}_3$ (*Procatalyse*) with a methanol solution of H_3BO_3 in the appropriated concentration. After impregnation, solids were dried under airflow at 393 K for 12 h and, finally, air calcined at 773 K for 4 h. The supports prepared

in that way were named as AB(x), where x represents the B_2O_3 wt.%. An unmodified $\gamma\text{-Al}_2\text{O}_3$ *Procatalyse* was used as a reference catalyst for comparison purposes. In preliminary experiments, it was found that the characterization results of an alumina impregnated only with methanol were quite similar to that of the unmodified alumina. Thus, the election of the unmodified alumina as a reference is valid for our purposes.

Characterization of catalysts

The B content was analyzed by the inductively coupled plasma (ICP) technique. An ICP AES Thermo Jarrell Ash Iris apparatus was used. Proton affinity distribution (PAD) measurements were used to determine the particular surface characteristics of the pure alumina and boron modified aluminas. This characterization was carried out by potentiometric titration, using the procedure described by Schwarz et al. [14]. A Titroline Alpha (SCHOTT, ± 0.001 pH units) equipped with a magnetic stirrer was used to perform titration measurements. All experiments were done using either 0.1 N HNO_3 or 0.1 N NaOH solutions. The samples (0.5 g) were first equilibrated with a neutral electrolyte (50 mL of 0.1 M NaNO_3 solution) under constant but gentle stirring. The titrations went continuously through a series of pseudo equilibrium states, and a large number of data was collected by adding 0.05 mL of titrant at a constant rate and reading the pH values every 90 s. In the case of titration with HNO_3 the final pH was 3 and in the case of titration with NaOH the final pH was 11. The proton consumption function was calculated from the balance equations and then converted into proton binding isotherms [14, 15]. The method proposed by Rudzinski and Jagiello [19] to calculate affinity distributions from proton binding isotherms was used as a model for these calculations.

FTIR spectra of dehydrated supports in the OH ($3400\text{-}3900\text{ cm}^{-1}$) and skeletal region ($800\text{-}1800\text{ cm}^{-1}$) were recorded with an IFS55 equinox spectrometer (Brücker) equipped with a DTGS detector using 100 scans and a

resolution of 4 cm^{-1} . Supports powders were pressed (3 tons) into self-supported wafers (15 mg, 13 mm diameter) and placed in a homemade IR cell. Previously to take the respective IR spectra samples were dehydrated under vacuum ($< 1.10^{-5}$ mbar) at 773 K for 2 h and after left under vacuum all night.

Results and discussion

Figure 1 shows PAD curves of AB(x) supports as well as the one of bare $\gamma\text{-Al}_2\text{O}_3$. In the case of bare $\gamma\text{-Al}_2\text{O}_3$, it can be observed the presence of OH groups type IA, IB, IIA and III [16, 17] of Knözinger and Ratnazamy [20] classification. The OH groups type III are the most acidic and they correspond to OH groups coordinated with three Al^{3+} cations in octahedral interstices [20]. Type I OH groups are terminal ones coordinated to a single either tetrahedral (IA OH groups) or octahedral (IB OH groups) Al^{3+} cation [20]. These are the most basic OH groups [20]. Whereas, type IIA OH groups are of character intermediate acidic and these consist of bridging OH groups which link an octahedral and a tetrahedral Al^{3+} cation [20]. It is observed that in bare $\gamma\text{-Al}_2\text{O}_3$ the more acidic type III and IIA OH groups predominate, nevertheless, an important quantity of type IA and IB OH groups are present too.

On the other hand, with the introduction of B on the alumina surface it is observed that the alumina OH groups disappear, especially those corresponding to the more basic OH groups (IA and IB), which are practically consumed after the introduction of 2 wt.% B_2O_3 . At the same time, it can be observed that with increasing boron content two new peaks appear. One peak at pH ca. 3.8, in the limit zone between groups III and IIA appears and another one at pH ca. 9.9 in the left side of the pH region corresponding to OH groups type IB, which is only observed clearly in the PAD curve of AB(8). Concerning the first one, because of its intermediate position, this peak cannot be attributed either to OH groups type III or IIA of alumina and it seems to correspond to a new OH group linked to boron cations. Regarding the peak ca. pH = 9.9, this cannot be assigned

to group IB of alumina because, according to literature [1, 3, 4, 6], basic OH sites are the sites where B is anchored on the alumina surface and these are the first in disappear, thus it will be logical to think that this peak is also due to new OH linked to borate species.

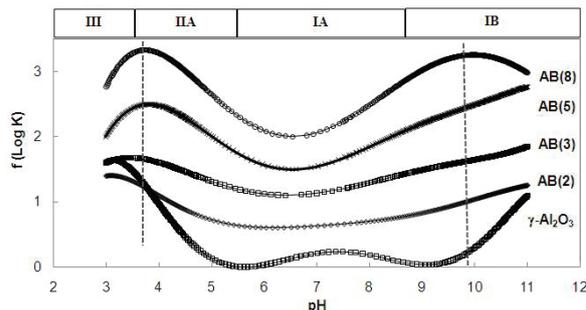


Figure 1 Proton affinity distribution function of the boron modified aluminas

To try to interpret the apparition of these new peaks in the PAD of boron modified aluminas, IR spectra of the OH region of AB(x) supports were obtained and they were compared with the bare $\gamma\text{-Al}_2\text{O}_3$ IR spectrum. These spectra are shown in figure 2. For bare $\gamma\text{-Al}_2\text{O}_3$ the same OH groups observed in the PAD in figure 1 are also observed: IB (3790 cm^{-1}), IA (3770 cm^{-1}), IIA (3735 cm^{-1}) and III (3680 cm^{-1}) [20]. As its PAD profile, the more prominent peaks correspond to OH groups type III and IIA. In accordance with observed in the PAD profiles of AB(x) boron introduction causes a decrease in all the alumina OH groups, especially in the more basic ones (IA and IB). It is observed that the peak corresponding to OH group type III of alumina (3680 cm^{-1}) was progressively replaced by a new peak at ca. 3695 cm^{-1} . Indeed, in the spectrum of AB(8) this is the only peak observed. This peak has already been reported by other authors [1, 2, 4-6], who concluded that it is due to OH groups linked to B species, because its frequency compares well with the $\nu(\text{OH})$ of free BOH groups such as those of H_3BO_3 in N_2 cryogenic matrices (3668.5 cm^{-1}) or on the surface of silica impregnated by boria (3703 cm^{-1}). Thus, this fact confirms that new OH groups linked to borate species are generated

on the borated alumina surface with increasing boron content as we have supposed to explain our PAD results. However in PAD profiles of borated aluminas (Figure 1) we observed two new peaks different from that of bare alumina, meanwhile in the IR of the OH stretching region only one new peak appears. Consequently, there is something missing in our explanation of PAD profiles. A possible explanation is that the IR peak located ca. 3695 cm^{-1} is due to OH groups linked not only to one single borate species but to a variety of them which could react with protons in two different ways during the potentiometric titration. Thus, a look into the possible borate species existing in borated alumina surface is still needed.

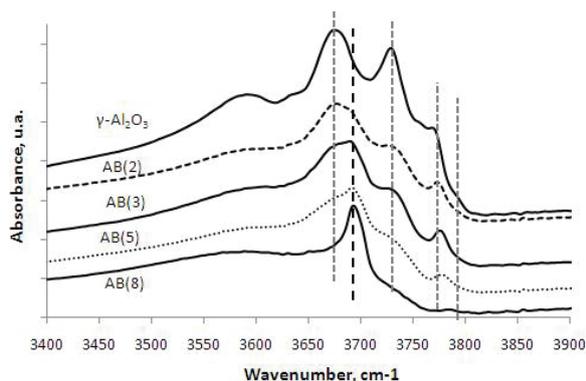


Figure 2 IR spectra of boron modified aluminas in the OH region

In some previous works [1-3, 5, 21] it has been evidenced, by using B^{11} MAS-NMR, that there are two borate species coexisting in borated alumina surface: BO_3 trigonal species and BO_4 tetrahedral species. These species have been properly quantified in these works and it has been concluded that trigonal borated species are the main species at low content of boria and increased with increasing boria loading [2, 3, 5, 21]. However, tetrahedral borated species (BO_4) also appears with increasing boria loading and its relative content increased with boria loading [2, 3, 5, 21]. Sato et al. [2] has shown that at boria contents above 2 wt.% these BO_4 species are formed. The differentiation between trigonal and tetrahedral borated species have also been

shown in a more qualitatively way by using IR [4, 21]. In this sense, in boron oxide compounds, broad bands in the region $1500\text{--}1200\text{ cm}^{-1}$ are typically due to the asymmetric B-O stretching modes of BO_3 species. Tetrahedral borate species are instead characterized by complex absorptions due to asymmetric and symmetric BO_4 stretchings in the region $1100\text{--}900\text{ cm}^{-1}$. In figure 3, the FT-IR spectra of the prepared borated aluminas in the skeletal region are presented. Two strong and broad peaks at ca. 1225 and 1400 cm^{-1} are observed along with another small peak at ca. 1025 cm^{-1} . According to the above stated [4, 21], the broad peaks could be attributed to BO_3 species and the small one to BO_4 species. The higher intensity and broadness of the peaks at ca. 1225 and 1400 cm^{-1} indicates that BO_3 species are prevalent. Both kinds of peaks increased with increasing boria content as well as with the relative concentration of BO_4 species.

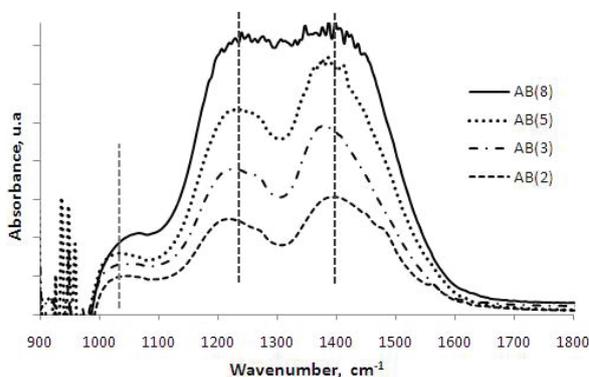


Figure 3 IR spectra of boron modified aluminas in the skeletal region

Flego et al. [1] have shown schematically that hydroxyls associated with borate species could be linked to both trigonal and tetrahedral species. These authors have shown seven different forms of how surface hydroxyls could be linked to borate species. However, in these schemes they have shown that hydroxyls linked either to trigonal or tetrahedral borates are always linked to one single B atom, different to the case of hydroxyls linked to Al^{+3} ions which can be linked to 1, 2 or 3 of these. Consequently, if

we classify surface borated hydroxyls according to their net charge, in a similar way to what Knözinger and Ratnazamy [20] used to classify alumina surface hydroxyls, we will obtain only two kinds of surface borated hydroxyls; those linked to trigonal and tetrahedral species. The net charge on the hydroxyl anion was calculated in the same way as Ratnazamg [20] as the sum of the negative charge of the hydroxyl and the sum of the strengths of the electrostatic bonds (cation charge divided by its coordination number) to the hydroxyl anion from adjacent cations. Thus, the net charge of an OH linked to borate trigonal species is zero meanwhile that of an OH linked to borate tetrahedral species is -0.25. IB and IA OH type groups of alumina have net charges of -0.5 and -0.25 respectively, and they are in the right side of the PAD profiles, meanwhile groups IIA and III have net charges of 0.25 and 0.5 respectively, and they are located in the right side of the PAD profile. Thus, in analogy with the assignation of peaks in alumina PAD profiles we assign the new peak appearing in alumina borates PAD at ca. pH = 3.8 to trigonal borated species, whereas that appearing at ca. 9.9 was assigned to tetrahedral borate species. Thus, according to our identification of peaks in the PAD profile of borated aluminas, using this technique in addition to the appearance of a new OH group linked to borate species, it will be also possible to distinguish between the groups linked to trigonal borated species and those linked to tetrahedral ones.

Consequently, if we interpret the PAD profiles as already stated, we can conclude that with increasing boron concentration, alumina OH are progressively consumed and new boria OH appear. There are two kinds of boron hydroxyls; those linked to trigonal borate species and those linked to tetrahedral ones. Trigonal borated species always predominated in the interval of boria content used during the present work (0-8 wt.%), however tetrahedral species were present even at the lowest boria content used (2 wt.%) and their relative concentration increased as already found in previous literature reports [2,

3, 5, 21]. In the range 2-5 wt.%, we observed a mixture of boria and alumina hydroxyls, but in AB(8) practically the only OH groups observed were those of boria. The first alumina groups being consumed were the most basic ones (IA and IB), but after 2-3 wt.% boria, when these groups were almost totally consumed, the acidic OH groups (IIA and III) were also consumed. Thus, as already proposed by other authors [1, 5] we inferred that a polymeric boron cover layer was progressively formed over the alumina surface with increasing the boron loading. The formation of this polymeric cover layer would account for the decrease in the total number of hydroxyls with increasing boria loading. The OH of some of the monomeric boria species would condense to form an oxygen bridge which link one monomeric species with the one next to it to finally form the cover layer [1, 5]. Thus, if we need to support a metal on the surface of borated aluminas according the content of boria in the support this metal would be attached either to a mixture of boria and alumina hydroxyls or to boria hydroxyls only.

The characterization of the OH groups existing in borated aluminas along with the knowledge of the relative quantity of boron in a given coordination is important to give an explanation to the changes observed in the performance of catalysts containing boria. For instance, it is well known that the increase in the relative content of borated tetrahedral species is related with the increasing strength of the acid sites as well as with the increase in the amount of Brönsted acid sites [2, 5, 21]. In a previous work [8] we have reported that with increasing boria content in alumina supported CoMo both the concentration of Brönsted acid sites and the strength of the acid sites were increased. This fact was very important because the changes in acidity generated increases in acid type olefin reactions, like isomerization and cracking, which competed with HDS and the HYD of olefins. It was found that in the range 2-3 wt.% boria content, cracking was less promoted than skeletal isomerization and than the isomerization of the double bond

from external to internal position reaction [8]. Consequently, within this range an increase in the selectivity HDS/HYD of internal olefins was found [8]. Such change in selectivity is highly desired in the HDS of FCC naphtha, because internal olefins are the olefins with the highest concentration in FCC naphtha and they make a great contribution to the octane [22].

On the other hand, the knowledge of the ratio of hydroxyls linked to borated species to that of hydroxyls linked to Al is important to explain the changes in the dispersion and distribution of species of supported metals like in the case of supported CoMo catalysts. For instance, we have observed changes in the Raman spectra of CoMo supported on borated aluminas [13]. These changes suggest that with increasing boria content the relative population of surface polymeric molybdenum compounds ($\text{Mo}_7\text{O}_{24}^{6-}$ and $\text{Mo}_8\text{O}_{26}^{4-}$) increases, in detriment of the population of monomeric compounds. Also it was observed that the size of these polymeric compounds increases. This fact is explained because when increasing boria content Mo ions should anchor to borated OH instead of alumina ones during the impregnation process. Thus, from one side, Mo is stronger bonded to Al than to B atoms [6, 9-11] and from another point of view, the increase in boria content causes an increase in the local PZC, which is the cause of a displacement of the equilibrium between monomeric and polymeric Mo species [9-11].

Conclusions

Proton affinity distributions profiles of borated aluminas gave us important and reliable information about the distribution of the different hydroxyls existing on its surface either attached to Al or B. These profiles were interpreted in detail and properly by comparing them with their corresponding IR spectra in the OH stretching and skeletal regions and by analogy with the alumina PAD profile interpretation used by other authors before. Thus, the new peaks appearing in the borated aluminas PAD profile were attributed to OH groups linked to trigonal borated species and

tetrahedral ones. Both of these OH boria species appear even for the alumina with the lowest content of boria (2 wt.%) and trigonal borate species were always predominant. However, the relative concentration of tetrahedral borate species increased with increasing boria content. Boria hydroxyls progressively replaced alumina ones with increasing boria content until formation of a cover layer. The replacement of alumina hydroxyls by boria ones and the progressive formation of a cover layer would account for the changes observed on the surface properties of CoMo catalysts supported on borated aluminas in comparison with the catalyst supported on bare alumina.

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