Boron alumina: qualitative investigation of the surface acidity by FTIR measurements of CO adsorption

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Abstract

The aim of this work was to determine the nature and the strength of surface acid sites present on boron alumina surface. From the results obtained by FTIR of CO adsorbed at $-135\text{ }^{\circ}\text{C}$, it can be concluded that the boron alumina has a Brönsted acidity due to the OH groups. These Brönsted acid sites are stronger than those of γ -alumina but in much smaller quantities due to its lower specific surface area. Similarly, it is noted that the boron alumina exhibits a single OH type with a single band around 3701 cm^{-1} . This band represents a single configuration of OH species linked to boron and this species is disturbed by the adsorption of the CO probe molecule whereas on alumina we notice the presence of four OH species linked to aluminum. Only one of which is disturbed by the adsorption of CO with a decrease in the intensity of this band and the increase in the intensity of a band present at lower frequency.

Keywords Boron alumina · γ -Alumina · FTIR · CO adsorption · Brönsted acidity · Lewis acidity

1 Introduction

Boron alumina ($\text{Al}_{18}\text{B}_4\text{O}_{33}$ or $9\text{Al}_2\text{O}_3 \cdot 2\text{B}_2\text{O}_3$) is well known as ceramic material that possesses excellent electrical conductivity and chemical inertness properties at high temperatures [1–3]. It is also known as a thermostable light-weighted ceramic (density = 2.9 kg dm^{-3}) that can be used as refractory materials up to $1700\text{ }^{\circ}\text{C}$ [4, 5]. In fact, such ceramic is known as reinforcing material due to its high mechanical resistance along with an extreme chemical resistance in oxidizing conditions and a low thermal expansion coefficient ($4.2 \times 10^{-6}\text{ K}^{-1}$) which makes it resistant to thermal shocks [6–10]. All these properties made such ceramic a good candidate to be used in different industrial field such as nanoelectronics, nanomechanics and nanocomposites.

Moreover, boron alumina has been studied widely due to its relative low cost and good properties. The structure

of boron alumina is orthorhombic with parameters $a = 1.500\text{ nm}$, $b = 0.768\text{ nm}$ and $c = 0.530\text{ nm}$. Furthermore, the elementary mesh of this material contains sites in tetrahedral (AlO_4) and octahedral (AlO_6) symmetry [6–12]. In addition, it has been shown to have acidity due to the substitution of Al^{3+} with B^{3+} in the alumina-based structure leading to an enhancement of surface acidity of the solid [6, 7].

Various technics can be used in order to study the surface acidity of a material. Hassan et al. have studied the surface acidity of different materials such as TiO_2 and $\text{SnO}_2/\text{TiO}_2$ nanoparticles using two different methods: Potentiometric titration and FTIR spectroscopy of pyridine probe molecules adsorption [13, 14].

Since boron alumina acidity are not well defined. Therefore, the aim of this present article is to investigate the acidity of boron alumina by FTIR spectroscopy of CO probe molecules adsorption at low temperature and to compare

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it to γ -alumina known as amphoteric oxide with both weak Brönsted and Lewis acidity [15–22].

2 Experimental

2.1 Solid preparation

Alumina used in this study is γ - Al_2O_3 (Rhodia SPH 569) with a specific surface area of $140 \text{ m}^2/\text{g}$. Boron alumina was prepared by wet impregnation method. A flask was filled with 150 mL of distilled water in which H_3BO_3 boric acid (Aldrich, 99.5%) was dissolved at 60°C for 1 h using a laboratory dissolution apparatus with an automatic magnetic stirrer (ZONWON). Then the required amount of γ -alumina was added to the flask and the slurry was mixed at 60°C for 1 h. The water was then removed at 60°C under reduced pressure. The obtained solid was dried overnight at 120°C , crushed and calcined at 1100°C during 12 h under O_2 .

2.2 Physicochemical characterisations

Chemical composition of boron alumina was determined by inductively coupled plasma atomic emission spectroscopy, ICP-AES.

Phase determination was performed using X-ray diffraction. X-ray diffractograms were recorded with a SIEMENS D500 diffractometer using Cu K α 1 radiation ($\lambda = 1.5406 \text{ \AA}$ Ni filtered). Diffraction data were recovered from 10° to 70° in 2θ angles with a step of 0.02° and a count time of 16 s. Data were compared to JCPDS files.

Specific surface areas were measured from N_2 adsorption at 77 K. The experiences were performed in a TRISTAR 3000 equipment. Samples were desorbed at 300°C for 2 h under vacuum (10^{-2} Pa) prior to measurement.

Infrared spectroscopy (FTIR) has been used to monitor the adsorption of CO on solids. In fact, the adsorption of molecular probes makes it possible to obtain information on the nature of the adsorption sites. Therefore, the solids were compressed under a pressure of 4 t/cm^2 in order to have a pellet of 18 mm in diameter and of weight from 20 to 50 mg. The pellet was then placed in a sample holder itself introduced into a Pyrex glass cell with calcium fluoride (CaF_2) windows which allows different treatments as well as the adsorption of the molecular probe. The temperature of the sample was measured using a K-type thermocouple. The cell was connected by a pumping system allowing a limit pressure of approximately 10^{-6} Torr to be reached.

Before probe molecules adsorptions, pellets were subject to a rise in temperature under vacuum from room temperature to 400°C at $5^\circ\text{C}/\text{min}$. Then, after having spent 1 h

under vacuum at 400°C , they undergo a pretreatment under oxygen flow for 1 h in order to remove all the impurities then under vacuum for 1 h. After this step, the pellets were quickly cooled to room temperature. Then, liquid nitrogen were introduced in the tube surrounding the Pyrex glass cell in order to reach a temperature of -135°C . The probe molecule used during this study was CO because it has the advantage of selectively bonding to surface metal atoms [22]. Moreover, carbon monoxide has received a great deal of attention due to its suitability for both qualitative and quantitative analysis. Its small size, basicity, non-reactivity at low temperature make it ideal for investigation of samples with both Brönsted and Lewis acid sites [22, 23]. The suitability of CO as probe molecule for the investigation of surface acidity, capable of differentiating between sites of very similar acid strength was reported in many previous studies [22, 23]. Its adsorption was carried out at -135°C under a different CO gas pressure (10; 5; 2.5; 1.3; 0.6; 0.3; 0.1; 0.08; 0.04; 0.02; 0 Torr).

3 Results and discussion

Chemical analysis revealed the composition corresponding to boron alumina with Al/B weight ratio of 10.9 close to the theoretical value of 11.2 (Table 1).

The specific surface area obtained for boron alumina was $24 \text{ m}^2/\text{g}$. The X-ray diffractogram obtained at room temperature for boron alumina (Fig. 1) reveals a well crystallized phase for boron alumina phase (JCPDS 32-0003) with the presence of diffraction peaks at $2\theta = 16^\circ, 20^\circ, 26^\circ, 34^\circ, 36^\circ$ and 62° [1].

Before CO adsorption experiments, infrared spectra were recorded at room temperature under vacuum in the range of $4000\text{--}1000 \text{ cm}^{-1}$ with a resolution of 4 cm^{-1} using a spectrometer Nicolet Magna 550.

Figure 2 reports spectra of alumina and boron alumina recorded at room temperature in the spectral range of $4000\text{--}1000 \text{ cm}^{-1}$ with a resolution of 4 cm^{-1} .

In the OH stretching region ($3900\text{--}3300 \text{ cm}^{-1}$), we notice the presence of four bands around 3760, 3734, 3682 and 3586 cm^{-1} corresponding to the OH species on alumina while on the spectrum of boron alumina, we note the presence of a single band around 3700 cm^{-1} corresponding to a single OH species which would be linked to boron. Moreover, the boron alumina spectrum presents around 1400 and 1260 cm^{-1} two wide and extremely intense bands that could

Table 1 Elemental composition of boron alumina

Boron alumina	%Al	%B	Al/B
Theoretical	45.9	4.11	11.20
Experimental	44.7	4.08	10.9

Fig. 1 X-ray diffraction of boron alumina **Fig. 2** FTIR spectra of alumina and boron alumina under vacuum at room temperature

be, according to Yang et al., attributed to B–O vibrations [24]. We also note the presence of two bands around 2652 and 2278 cm⁻¹ which could be the harmonics of the bands located around 1100–1300 cm⁻¹ [15, 24–27].

In order to better examine these bands and in particular the bands present between 500 and 1600 cm⁻¹, a dilution with KBr was made by mixing 3 mg of boron alumina with 150 mg of KBr. The solid was then compressed under pressure (4 t/cm²) in order to have a pellet of 153 mg.

Figure 3 reports FTIR spectrum of boron alumina diluted with KBr in the spectral range 1600–400 cm⁻¹. The spectrum exhibits different absorption bands. We notice the presence of three absorption areas corresponding to three types of Metal–Oxygen patterns. All the bands located between 1600 and 800 cm⁻¹ are linked to the different vibrations of B–O bonds in the triangular planar [BO₃] and tetrahedral [BO₄] units [28]. Furthermore, all the bands located between 400 and 800 cm⁻¹ are assigned to the

Fig. 3 FTIR spectrum of boron alumina diluted with KBr under vacuum at room temperature

stretching vibrations of $[\text{AlO}_6]$ and $[\text{AlO}_4]$ groups and the bending vibrations of O–B–O in $[\text{BO}_3]$ and $[\text{BO}_4]$ units [15, 26, 28]. According to the bibliography, the bands between 1200 and 1500 cm^{-1} are due to the B–O bonds non-bridging stretching vibrations in $[\text{BO}_3]$ and to the symmetric stretching relaxation of B–O in triangle $[\text{BO}_3]$ units and the bands between 800 and 1200 cm^{-1} are due to the stretching vibrations of B–O bonds in $[\text{BO}_4]$ [28]. In our case, we see the presence of four bands around 1278, 1334, 1395 and 1426 cm^{-1} which can be explained by the presence of four different environments for B–O in $[\text{BO}_3]$ [27]. In a study by El Hakam et al. [16] concerning boron alumina with different boron concentrations, the authors observe different bands between 1200 and 1500 cm^{-1} around 1271, 1334 and 1427 cm^{-1} whose intensity increases with the boron concentration which means that these bands can be attributed to the formation of the boron alumina phase. As hypothesis, we can say that in the pure and crystallized phase, there are four different types of planar triangular $[\text{BO}_3]$ represented in Fig. 4.

Moreover, according to the bibliography, the bands between 810 and 640 cm^{-1} are attributed to the angular deformation (bending vibrations) of O–B–O in $[\text{BO}_3]$ and $[\text{BO}_4]$ while the bands between 750 and 950 cm^{-1} and between 500 and 650 cm^{-1} are attributed respectively to the stretching vibration of Al–O in tetrahedral $[\text{AlO}_4]$ and octahedral $[\text{AlO}_6]$ units respectively [15, 26, 28].

After CO adsorption experiments, infrared spectra were recorded at -135°C . Since CO is σ -donor and π -acceptor,

CO can be adsorbed at room temperature on electron deficient transition metals but cannot be adsorbed on an inert support [27, 29, 30]. For this reason, it is necessary to work at low temperature (-135°C) in order to adsorb CO on alumina and boron alumina. Moreover, CO molecule has a permanent dipole moment, which should give it a force of interaction with the hydroxyl groups OH on the surface of the support at low temperature and lead to a disturbance of the vibrations $\nu(\text{OH})$ [27, 29, 30].

The spectral changes obtained by adsorption of different CO pressures at low temperature on alumina and boron alumina have been represented in Figs. 5, 6, 7 and 8. Each figure has been divided into two regions: $\nu(\text{CO})$ between 2250 and 2050 cm^{-1} and $\nu(\text{OH})$ between 4000 and 3300 cm^{-1} .

The infrared spectrum of $\gamma\text{-Al}_2\text{O}_3$ (Fig. 5) shows the development of a band $\nu(\text{CO})$ at 2152 cm^{-1} moving gradually up to 2157 cm^{-1} with the increase in CO pressure. This band is attributed to the adsorption of CO on an OH groups assigned to Brönsted acid sites [22, 23, 25, 30]. We notice also a lower intensity band around 2190 cm^{-1} attributed to the adsorption of CO on surface tricoordinated Al^{3+} ions, which are therefore Lewis acid sites [22, 23, 30]. The displacement of wavenumbers $\nu(\text{CO})$ towards the high frequencies compared to CO gas phase frequency $\nu(\text{CO})_{\text{gas}}$ (2143 cm^{-1}) is allotted to a reinforcement of the electronic density of the orbital σ of CO in another term it is assigned to the strengthening of the bond strength between CO and OH [30]. In fact, since CO is σ -donor, it

Fig. 4 Different types of BO_3 according to Flego and Parker [15]

Fig. 5 Spectral evolution of physisorbed CO on $\gamma\text{-Al}_2\text{O}_3$ as a function of CO pressure at low temperature (-135°C)

supplies electrons to OH, which strengthens the bond between CO and OH and transforms CO into CO^+ . The electronic density which is in the doublet σ of CO decreases and this reinforces the CO bond whose length decreases and passes from 1.13 to 1.11 Å so that the energy of the CO

bond increases and therefore the frequency which linked to energy increases [31–33]. Similarly, it is noted after adsorption of 10 Torr of CO that the surface is not yet saturated with CO because for higher pressures of 10 Torr there is always an increase in the intensity of the strip around

Fig. 6 Spectral evolution of hydroxyls on γ - Al_2O_3 as a function of CO pressure at -135°C

Fig. 7 Spectral evolution of physisorbed CO on boron alumina as a function of CO pressure at low temperature (-135°C)

2152 cm^{-1} . This means that there is a large amount of OH group on the surface of the alumina.

Figure 6 shows the spectrum of alumina under vacuum at -135°C . Before CO adsorption (0 Torr), we notice the

presence of four bands at 3758, 3729, 3679 and 3584 cm^{-1} corresponding to the vibrations of hydroxyl bands (OH species) in different configurations on the surface. These bands can be assigned to isolated OH groups coordinated

Fig. 8 Spectral evolution of hydroxyls on boron alumina as a function of CO pressure at -135°C

to various numbers of Al^{3+} lattice ions [33–35]. According to the model of Knözinger and Ratnasamy, the two bands at 3758 and 3729 cm^{-1} represents OH species with strong basicity, the band around 3679 cm^{-1} represents the OH species of low basicity and the band around 3584 cm^{-1} represents the acidic OH species [34]. The bands present at lower wavenumbers correspond to bridged OH species and are more acidic [33–37].

In addition, Usman et al. also find four bands for alumina around 3772, 3727, 3677 and 3580 cm^{-1} . These authors separate these OH species into very basic OH species (3772 and 3727 cm^{-1}), basic OH species (3677 cm^{-1}) and an acidic OH species (3580 cm^{-1}) [27].

After adsorption of CO, in the region between 3300 and 4000 cm^{-1} , we notice that the band present around 3729 cm^{-1} decreases in intensity with the increase of the CO pressure and was accompanied with the appearance of a new band at lower wavenumbers around 3638 cm^{-1} representing acid OH species. The intensity of this band increases with increasing CO pressure. As for the the band around 3729 cm^{-1} corresponds to an OH species disturbed by the adsorption of CO. In fact, the adsorption of CO on this OH species weakens the OH bond and therefore the OH bond energy decreases which increase the Brönsted acidity of this species and this is what explains the appearance of a band at a lower frequency. We can say that this disturbed OH species corresponds to the species on which CO is adsorbed and therefore is connected to the characteristic CO band which is found around 2152 cm^{-1} . These

two bands characterize the formation of a surface complex between CO and OH [36, 37].

The FTIR spectra obtained by adsorption of increasing pressures of CO at low temperature on the boron alumina are represented in Figs. 7 and 8. In Fig. 7, we observe a spectrum very different from that of alumina with a single band. First of all, it is noted that the boron alumina has very few tricoordinated B^{3+} ions (Lewis acidity). Thus, for the first increments, we observe the appearance of a very weak band at 2184 cm^{-1} attributed to the adsorption of CO on a small number of tricoordinated B^{3+} species. This can be due to the low specific surface area of boron alumina. For CO pressures greater than 0.6 Torr, we notice a disappearance of this band and the appearance of a band $\nu(\text{CO})$ at 2172 cm^{-1} gradually shifting towards lower wavenumbers (2163 cm^{-1}) with the increase of CO pressure. This band is attributed to the adsorption of CO on an acid OH group corresponding to Brönsted acidity. Similarly, we note that the position of this band is localized towards higher frequencies than the frequencies obtained with alumina, which means that these OH groups have a stronger Brönsted acidity than those of alumina. Similarly, the intensity of this band is approximately five times lower than that obtained with alumina and it is noted that after adsorption of 5–10 Torr of CO, the surface becomes saturated with CO since after adsorption of 5 Torr CO, we obtain roughly the same spectrum as the one obtained after adsorption of 10 Torr CO. This ultimately means that the quantity of OH groups existing on the surface

and having this Brönsted acid character is fewer than the quantity of OH groups existing on alumina. This may be due simply to the difference between the specific areas of alumina and boron alumina.

Figure 8 represents the evolution of hydroxyls on boron alumina as a function of CO pressure at -135°C in the frequencies range between 4000 and 3300 cm^{-1} . As we can see, this spectrum of boron alumina are different from those of alumina. We notice on the spectrum of boron alumina, the presence of a single band of low intensity compared to the alumina which is around 3701 cm^{-1} and which represents a single OH species. After the adsorption of CO at low temperature, we note that the intensity of this band decreases slightly with the increase in CO pressure and also the appearance of a second much larger band between 3500 and 3600 cm^{-1} . Since CO is σ -donor, it is adsorbed on this OH species, which decreases the strength of the OH bond therefore the energy of the OH bond decreases so that the frequency of the bond decreases. The weakening of the OH bond results in a displacement of $\gamma(\text{OH})$ towards the low frequencies.

All this explains the decrease in the intensity of the band around 3701 cm^{-1} and the increase in the intensity of the band around 3600 cm^{-1} which represents the species B–OH disturbed by a change of environment [36, 37]. The two bands around 3701 and 2163 cm^{-1} characterize the formation of a surface complex between CO and OH [30]. These two bands are both of low intensity because of the presence of a small amount of OH groups having a Brönsted acidity on the surface of the boron alumina.

It is noted that the intensity of the CO adsorption band on the OH sites of the boron aluminate is higher than the intensity of the CO adsorption band on the tricoordinated boron ions, which shows that the boron alumina has stronger Brönsted acidity. Similarly, the intensity of this band is approximately five times lower than that obtained by adsorption of CO on the OH groups in the case of alumina, which shows a small amount of OH sites present on the surface of boron alumina.

4 Conclusion

Boron aluminate has been characterized by FTIR for the study of its structure and acidity. FTIR spectroscopy by probe molecules adsorption made it possible to obtain information on the nature of the adsorption sites and to distinguish between Brönsted acidity and Lewis acidity. From the results of this study showed that boron alumina has stronger Brönsted acid sites than $\gamma\text{-Al}_2\text{O}_3$, but in small quantities which is due to the difference between the specific areas.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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