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Surface characterization of Ba-β-alumina

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The surface properties of a Ba-β-alumina sample (Ba : Al ratio 1 : 12) very stable to sintering (15 m^2/g after calcination at 1670 K for 10 h) have been investigated by FT-IR spectroscopy of adsorbed probe molecules (water, pyridine and CO_2) and by measuring the isoelectric point. The surface has a medium-strong basic character, justified by the preferential exposition of Ba–O-containing "mirror planes", parallel to 0001 planes, on the surface of plate-like particles. This behavior has been associated to the resistance to sintering, typical of this material, possibly originated by the difficulty of the very big Ba^{2+} ions to migrate into the spinel-type alumina blocks. This should imply the blocking of the crystal growth along the crystallographic *c* axis.

Keywords: barium-β-alumina; surface characterization; surface characterization of Ba-β-Al_2O_3; hydroxy-groups on Ba-β-Al_2O_3 surface; pyridine adsorbed on Ba-β-Al_2O_3; isoelectric point of Ba-β-Al_2O_3; FT-IR spectra of Ba-β-Al_2O_3

1. Introduction

High-temperature methane catalytic combustion technology is receiving much attention in recent times in order to limit NO_x emission with waste gases from power stations [1]. This technology needs the developments of new catalytic materials with high thermochemical stability in oxygen and steam atmospheres up to 1400°C [2]. Among the most promising support materials for such gas-turbine combustion catalysts are the Ba-β-aluminas proposed by Arai et al. [3]. In fact, these materials are proven to be extremely resistant to sintering at high temperature, retaining surface areas of near 10 m^2/g after prolonged heating at 1600°C [3]. La-β-aluminas were also proposed and show similar performances [4]. These materials could be used as the supports for noble metal catalysts: alternatively, aluminum in their structure can be substituted by trivalent transition metal cations like Cr^{3+},

Fe^{3+} or Mn^{3+}, to produce noble-metal-free combustion catalysts that can be directly extruded as monoliths [5,6].

β-aluminas constitute a family of ion conducting compounds with a general formula $M_2O{\cdot}nAl_2O_3$, where M is a monovalent cation, in the most common case [7]. The stoichiometry of "ideal" Na-β-alumina is $NaAl_{11}O_{17}$ [8,9], with $n = 11$ in the above general formula, although Na excess is frequently present. Its layered structure is constituted by spinel-type blocks having the formula $[Al_{11}O_{16}]^+$ (whose structure is closely related to those of transitional aluminas, like θ-Al_2O_3) separated by mirror planes where mobile and exchangeable Na^+ ions are located together with oxygens bridging between spinel blocks. Similar structures also form with other very large cations like K^+, Ba^{2+}, Pb^{2+} and La^{3+} [7].

It has recently been demonstrated that two distinct Ba-β-alumina phases exist: (i) the so-called Ba-poor phase, with composition near $0.82BaO{\cdot}6Al_2O_3$, with the same structure as "ideal" Na-β-alumina but with defects to compensate the excess charge of Ba^{2+} with respect to Na^+ [10]; and (ii) the so-called Ba-rich phase, with composition near $1.31BaO{\cdot}6Al_2O_3$, where interstitial Ba ions are also located into the "spinel blocks" [11]. An intermediate structure, assumed to be constituted by the interplay of the two phases, can also occur, generating materials that are very stable to sintering [12].

In spite of their wide applications and the large amount of work devoted to the surface properties of different aluminas and metal aluminates [13,14], few is known on the surface properties of β-aluminas. The surface properties of these materials are expected to be relevant in relation to their use for the preparation of supported metal combustion catalysts (whose behavior is sensitive to the acid–base nature of the support) and in order to have an indication of the reasons of their resistance to sintering. In the present paper the results of a surface characterization study of a Ba-β-alumina sample highly resistant to sintering is reported.

2. Experimental

2.1. PREPARATION OF THE SAMPLE

The Ba-Al-O sample with nominal atomic ratio Al/Ba = 12 was prepared according to the precipitation method in aqueous medium reported in ref. [6]. $Ba(NO_3)_2$ (Fluka) was completely solved in hot water ($T = 330$ K) under vigorous stirring. The resulting solution was acidified (pH = 1) with HNO_3 and subsequently $Al(NO_3)_3{\cdot}9H_2O$ (Fluka) was added. The solution was poured under vigorous stirring at constant temperature ($T = 330$ K) into a $(NH_4)_2CO_3$ solution. The formation of a white precipitate was observed. The slurry was then aged at 330 K for about 3 h; the pH of the slurry varied in the range 7.5–8. The precipitate was filtered, washed and dried at 330 K overnight. Analysis by atomic absorption for Ba and Al contents in mother liquors and washing waters indicated that the precipitation occurred in a quantitative way. Chemical analysis of the dried samples confirmed that the actual Al/Ba ratio corresponds to the nominal one (12 : 1). The sample was then calcined at 1670 K for 10 h (heating rate 60 K/h, cooling rate 100 K/h).

2.2. CHARACTERIZATION OF THE SAMPLE

XRD analysis was performed with a Philips PW 1050-70 vertical goniometer using Ni-filtered Cu Kα radiation. TEM micrographs were recorded with a Jeol JEM 2000EX instrument. The surface area was measured by means of nitrogen adsorption at the liquid nitrogen temperature with a conventional BET apparatus. The FT-IR spectra have been recorded using a Nicolet Magna 750 Fourier transform instrument. For the region 4000–350 cm^{-1} a KBr beam splitter has been used with a DTGS detector, while for the FIR region (600–50 cm^{-1}) a "solid substrate" beam splitter and a DTGS polyethylene detector have been used.

For bulk characterization studies, KBr pressed disks (IR region) or polyethylene pressed disks (FIR region) were used. For surface characterization studies the pure powder was pressed into self-supporting disks and was treated in conventional IR cells connected to outgassing/gas manipulation apparatuses.

The measurement of the isoelectric point has been carried out using a mass titration method [15] based on the measurement of the H^+/OH^- exchange properties of the solid surface in acid and basic medium. In a typical experiment 100 ml of KCl 1 M (pH = 5.54) were added with HCl 0.1 M, for the acid branch of the curve, or KOH 0.1 M, for the basic one, to fix the pH at 3 and 11 respectively. Subsequently, 2 g of the Ba-Al-O (Al/Ba = 12) sample were suspended in the obtained solution. The experiment consists in varying the pH of the solution and evaluating the amount of HCl or KOH 0.1 M added to bring the pH at fixed values and to keep it constant for 1 h. The experiment has been performed on a blank solution in the same conditions. The isoelectric point was determined as the pH value corresponding to the zero value of the differences between the amount of the titrating solution added to the suspension and to the blank solution.

3. Results

A detailed XRD analysis, reported previously [12], suggested that the sample under investigation is monophasic and possesses a structure intermediate between those of the Ba-rich and the Ba-poor Ba-β-alumina phases, likely originating by an intergrowth of domains of the two phases. The FT-IR/FT-FIR spectrum of this sample in the skeletal region is shown in fig. 1, and can be compared with those reported in the literature for Na-β-alumina and other isomorphous compounds. In the spectrum of our preparation we observe at least 22 maxima above 300 cm^{-1} and four well resolved bands in the region 300–50 cm^{-1}.

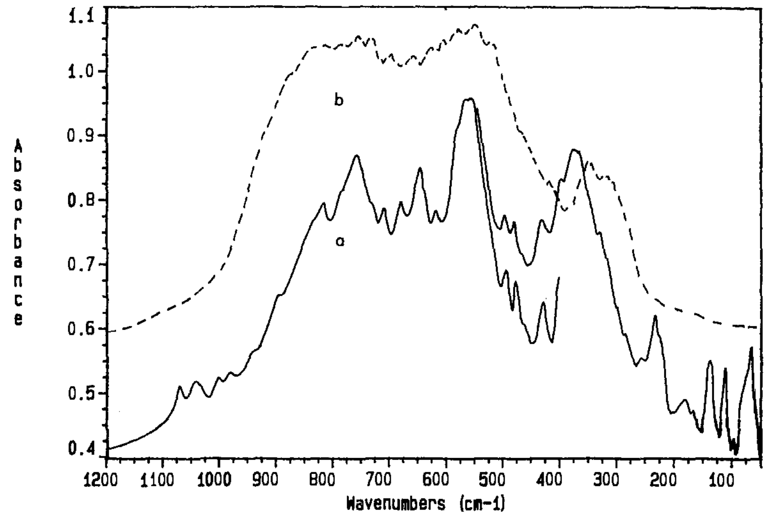

Fig. 1. FT-IR/FT-FIR spectra of Ba-β-Al_2O_3 (a) and θ, δ-Al_2O_3 (b).

To separate the vibrational modes associated to Al–O bonds of the spinel blocks from those of the cations lying in the mirror planes we can compare the spectrum of our Ba-β-alumina with that of an ordered defective spinel-type alumina, θ-Al_2O_3, possibly containing also traces of δ-Al_2O_3 (fig. 1b). In both cases a strong absorption with a number of maxima occurs in the region 1100–300 cm^{-1}, but bands are observed in the region 300–50 cm^{-1} only in the case of Ba-β-alumina. So, the bands in the region 1100–300 cm^{-1} are due to the Al–O vibrational modes of the spinel-type blocks. According to Colomban and Lucazeau [16] the two modes associated to the vibrations of the oxygen ions bridging between spinel blocks are expected in the region 300–100 cm^{-1}. Consequently, we can assign the two strong bands at 139 and 234 cm^{-1} to the movements of such bridging oxides (211 and 270 cm^{-1} in Na-β-alumina [16]). We assign the bands at 67, 75 and 82 cm^{-1} to the partially superimposed in-plane and out-of-plane vibrational modes of the Ba^{2+} ions in the mirror planes in two slightly different environments and the sharp peak at 112 cm^{-1} to lattice vibrations involving interstitial Ba cations. These assignments are based on the comparison of the skeletal spectra of our sample with those of Ba-rich and of Ba-poor Ba-β-alumina phases, as discussed in detail elsewhere [17].

The morphology of the samples has been investigated by transmission electron microscopy. Typical TEM micrographs (fig. 2) show particles with nearly hexagonal contour, 100–500 nm wide. The results of XRD analysis by Rietveld refinement [12] evidenced a pronounced shape anisotropy, with crystallite dimension along the *c* axis eight times smaller than that of the *ab* plane. This morphology, according to the crystal density of 4.075 g/cm^3, agrees with the experimentally measured surface area of our specimen, 15 m^2/g. These data suggest that our particles are similar to those of Machida et al. [3,5,18], characterized by the same composition and close surface areas, described to be thin plate-like.

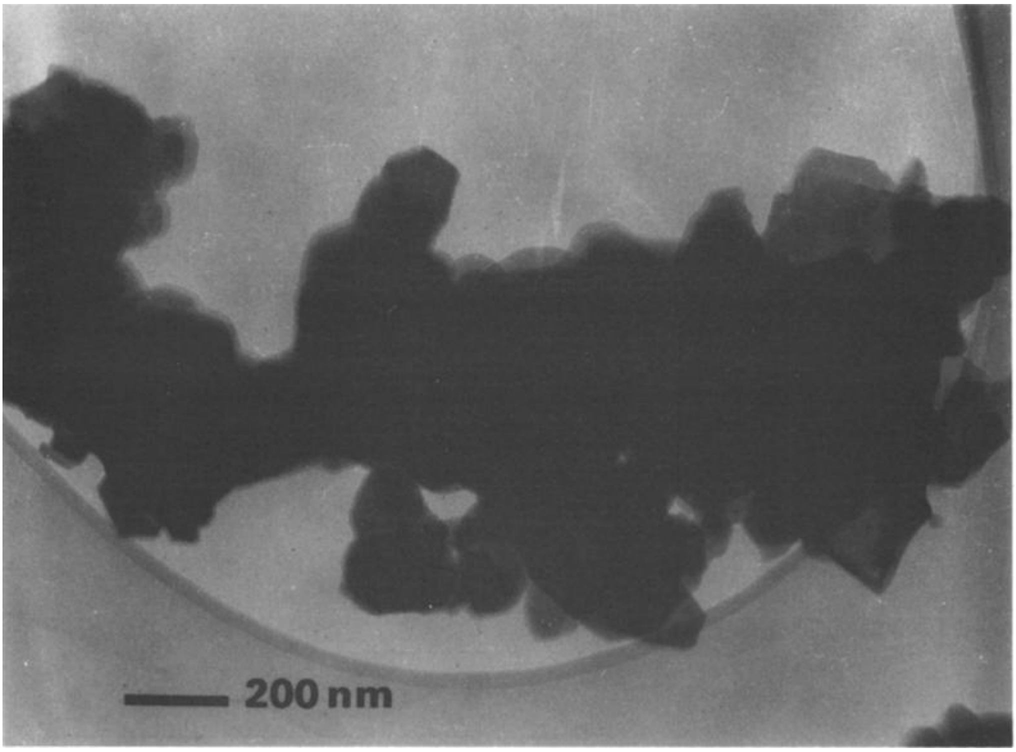

Fig. 2. TEM micrograph of the Ba-β-Al_2O_3 powder sample.

The FT-IR spectra of a pressed disk of pure Ba-β-alumina (fig. 3) show a cut-off limit near 900 cm^{-1}, as well as four strong bands in the region 1100–900 cm^{-1}, corresponding to the highest frequency bands detected in the spectrum of the KBr pressed disk. A broad absorption is also found in the region 1700–1300 cm^{-1} that decreases in intensity by increasing the outgassing temperature to disappear when the sample is outgassed at 773 K. This absorption (fig. 3) presents a maximum near 1630 cm^{-1}, due to adsorbed molecular water, already desorbed at 373 K, and components at 1520 and 1400 cm^{-1}, more resistant to outgassing and restored by contact with CO_2 gas. These features, due to surface carbonate species, do not correspond, neither for the position and shape, nor for the thermal stability, to those of $BaCO_3$. This means that Ba is not segregated but is totally in the β-alumina structure, in contrast to its tendency to segregate as $BaCO_3$ in other Ba-containing materials like $BaTiO_3$ [19] and YBCO superconductors [20]. The observed bands are, instead, due to carbonate species adsorbed on the β-alumina surface.

Above 1800 cm^{-1} the absorption baseline grows due to the wavelength dependence of radiation scattering. The OH stretchings of the surface species arising from adsorbed water typically fall in the region 3800–3000 cm^{-1}. After outgassing at 473 K, when molecular water is already desorbed, two broad and strong compo-

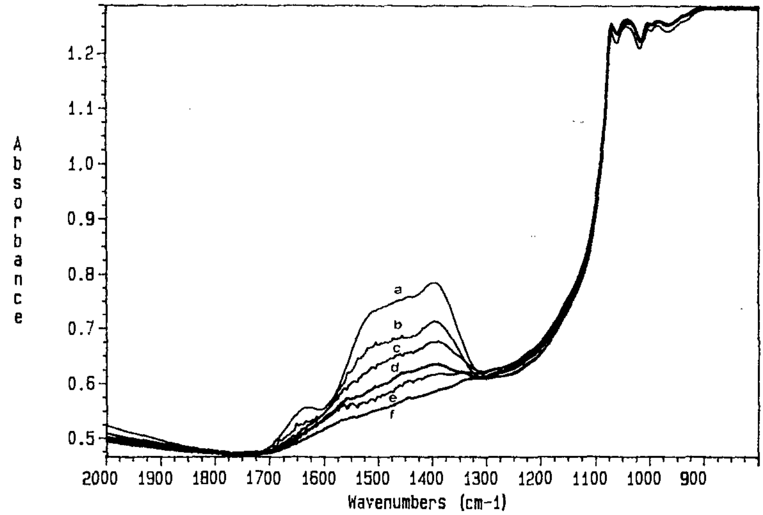

Fig. 3. FT-IR spectra (carbonate region) of a pressed disk of Ba-β-Al_2O_3 after outgassing at 300 K (a), 373 K (b), 473 K (c), 573 K (d), 673 K (e) and 773 K (f).

nents are found near 3540 and 3380 cm^{-1}, due to H-bonded hydroxy-groups (fig. 4). In the region 3800–3600 cm^{-1} sharp and weak components are still observed after outgassing at 773 K, due to surface free hydroxy-groups. Two different sharp components are observed at 3700 cm^{-1}, most intense after outgassing at 473 K, and at 3722 cm^{-1}, most intense after outgassing at 773 K. An extremely weak feature is also found at 3787 cm^{-1} after outgassing at 773 K. To have better information on the surface hydroxy-groups we isotropically exchanged them with

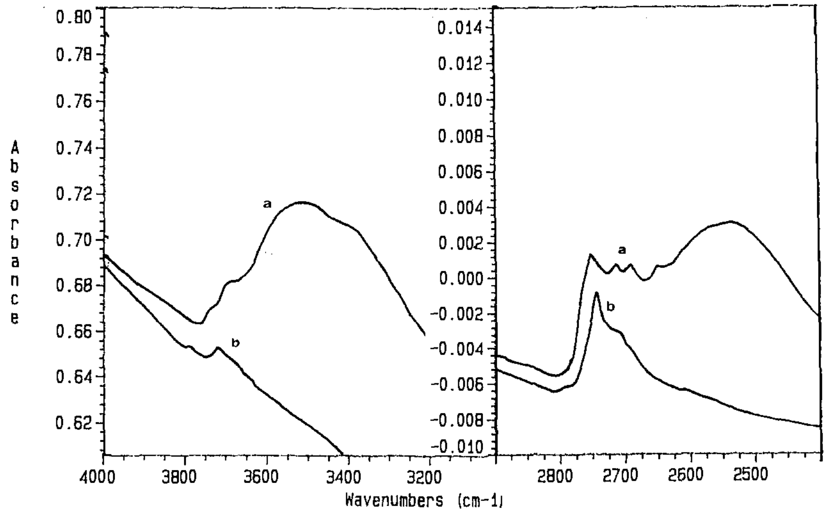

Fig. 4. FT-IR spectra (OH and OD stretching regions) of Ba-β-Al_2O_3 pressed disks put into contact with water vapour (left) and heavy water (right) vapours and then outgassed at 473 (a) and 773 K (b).

D_2O at 473 K and we later outgassed again at 773 K. We find new bands due to OD stretching of surface free deuteroxy-groups, with maximum at 2745 cm^{-1}, sharp, with a second component at 2715 cm^{-1}, which correspond to the OH stretchings at 3722 and 3700 cm^{-1}. An extremely weak feature near 2790 cm^{-1} could correspond to that found at 3787 cm^{-1} in the spectrum of the non-deuterated sample. The spectrum differs significantly from those of the surface OH's of spinel-type aluminas, characterized by four strong bands at 3790, 3770, 3730 and 3680 cm^{-1}, independently of the specific phase (γ, η, δ or θ-Al_2O_3 [13,14]).

To have information on the surface acidity of the Ba-β-alumina sample, we also performed experiments on the adsorption of he basic probe molecule pyridine. The spectra of adsorbed pyridine are reported in fig. 5. They show the strong and most sensitive bands associated to the 8a and 19b ring vibrational modes centered at 1594 and 1443 cm^{-1}, moderately shifted upwards with respect to the liquid-phase values (1583, 1439 cm^{-1}). Outgassing at increasing temperature causes the higher frequency band to slightly shift further to 1597 cm^{-1}. These spectra strongly differ from those of pyridine adsorbed on spinel-type pure aluminas, that are characterized by much stronger shifts of the more sensitive bands with respect to the liquid-phase values. In the case of pyridine adsorbed on transitional aluminas, in fact, ν8a is observed split at 1625, 1615 cm^{-1} and ν19b is found above 1450 cm^{-1} [14].

In contrast, the position of these bands on our Ba-β-alumina sample agrees with those typical for pyridine adsorbed on basic surfaces, like alkali earth oxides [21], as well as on Ba compounds like $BaTiO_3$ [19].

The picture of the surface character of Ba-β-alumina, as obtained by the above spectroscopic measurements, looks similar to that reported previously for Ca-

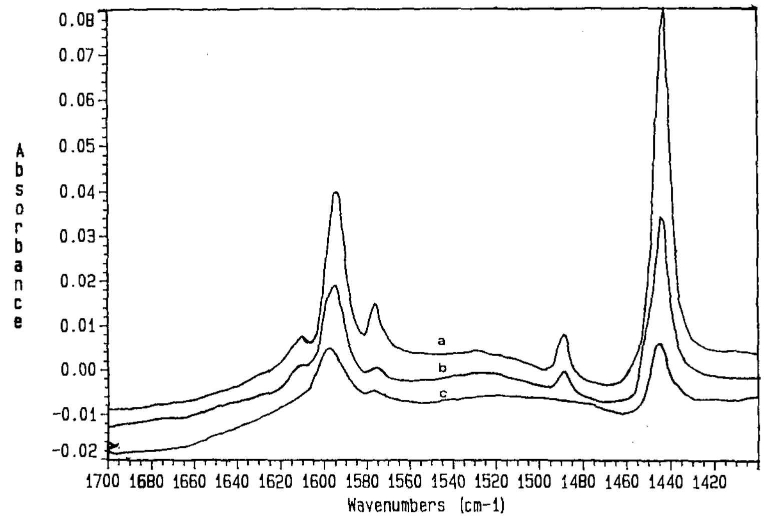

Fig. 5. FT-IR spectra of pyridine adsorbed on a Ba-β-Al_2O_3 pressed disk previously activated at 773 K. After pyridine adsorption, outgassing at 300 K (a), 423 K (b) and 573 K (c).

doped γ-Al_2O_3 [22], for which it has been demonstrated that Ca^{2+} ions accumulate at the surface and produce a dramatic perturbation of the alumina surface, inducing a strong basic character.

To further investigate the acid/basic nature of the surface of the Al/Ba = 12 sample, measurements of the isoelectric point have been performed. The basic and acid branch of the measurement are reported in fig. 6. A value of $pH_{iso} = 9.5$ is observed that further evidences the basic character of the Ba-β-alumina surface. This value is significantly higher than that reported for the defective spinel-type γ-Al_2O_3 (8.8 [23]), confirmed also by our own experiments, and mostly, than that of non-defective spinel aluminates like $CoAl_2O_4$ and $NiAl_2O_4$ (both 2.65 [24]).

4. Discussion

The data reported above indicate that Ba-β-alumina shows a very weak Lewis acidity that can be associated to coordinatively unsaturated exposed Ba^{2+} ions. No traces are found for coordinatively unsaturated Al^{3+} ions similar to those typically observed on the surface of transitional aluminas, whose structure is definitely similar to that of the spinel blocks of Ba-β-alumina. Similarly, also the spectrum of the surface hydroxy-groups is not similar to those typical of spinel-type aluminas and aluminates. The detection of surface carbonates stable to outgassing up to 773 K and the isoelectric point of 9.5 characterize the surface of Ba-β-alumina as a definitely, although not extremely, basic material. These results suggest a predominance of the basic character of the BaO component with respect to the acidic char-

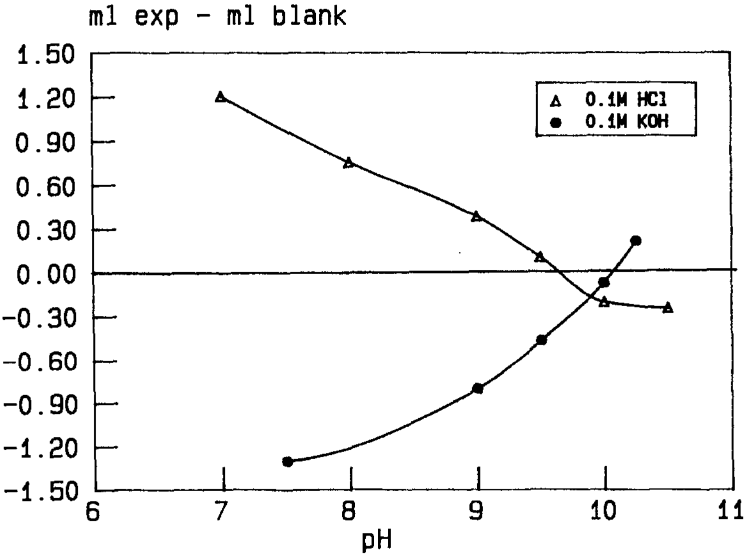

Fig. 6. Isoelectric point measurement by mass titration (see experimental section).
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acter of spinel-type aluminas, in contrast to the nominal predominance of the Al_2O_3 component according to the nominal formula $BaO{\cdot}6Al_2O_3$. However, a segregation of barium out of the β-alumina structure is excluded. A similar complete masking of the surface properties of a spinel-type alumina was shown previously by surface doping of γ-Al_2O_3 by 3% w/w of CaO [22]. XRD Rietveld analysis of our specimen evidenced that the crystallites have a plate-like shape characterized by a strong anisotropy, according to an inhibition of the crystal growth along the crystallographic *c* axis. This agrees with the morphology as it appears from TEM micrographs, which show particles with a nearly hexagonal contour.

These results allow us to propose that the preferential exposition at the crystallite surface of planes parallel to (001) is most likely. These faces, likely similar to the so-called "mirror planes" where ionic conduction occurs, should only contain coordinatively unsaturated Ba^{2+} ions and oxygen ions. This preferential exposition is likely responsible for the basic properties of the surface (typical of Ba oxide compounds) that, in view of the low bulk Ba-content of this compound, can hardly be explained assuming a statistical exposure of different crystallographic planes.

The experimental data reported here and their interpretation provide support to the mechanism of sintering resistance of these materials hypothesized elsewhere [12] on the basis of the following arguments: (i) the strong connection between high surface area and crystal shape anisotropy, indicating that lack of sintering originates from inhibition of crystal growth along the *c* axis; (ii) the humpering of Ba diffusion along the *c* axis associated with the difficulty of the extremely large Ba^{2+} ions to migrate into the oxide cubic close packing of non-cationic deficient spinel-type blocks; (iii) the impossibility, for energetic and electrostatic reasons, for the crystal structure to allocate adjacent Ba-containing planes. Consequently, the sintering resistance may arise from the difficulty of crystallites with Ba-containing planes exposed at the surface to coalesce along the *c* direction. This mechanism should result in the preferential exposure of Ba^{2+}–O^{2-} couples directly bonded to the alumina blocks at the crystallite surface, giving rise to a definite, although not extreme, basic character to this solid.

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