Characterization of the aluminas formed during the thermal decomposition of boehmite by the Rietveld refinement method

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Boehmite synthesized through a sol-gel route from a non-conventional raw material, as an aluminum waste, was calcined at temperatures between 500 to 1500°C. Quantification of crystalline phases was performed by the Rietveld refinement of the XRD patterns. γ-Al_2O_3 is formed at 500ºC, and up to 1000°C, is the dominant phase. At temperatures ranging from 1000 to 1400°C it was observed the appearance of a four-phases region. The complete transformation into α-Al_2O_3 lasts until 12 h at 1400°C or at higher temperatures. The presence of an amorphous phase in calcined samples was confined by direct comparison with a standard of pure α-Al_2O_3.

Keywords: boehmite, calcination, transition aluminas, corundum, Rietveld refinement

Introduction

Aluminum oxides or aluminas (Al_2O_3) are low cost materials extensively used in numerous industrial applications, for example as catalyst support, in electronic-device fabrication, as material for implants in bio-medical application, as refractory material, as abrasive and thermal wear coatings, etc.[1, 2] The wide variety of these applications results from the structural features of its modifications (the so called transition aluminas, as well as its thermodynamically stable alpha alumina (α-Al_2O_3) or corundum), which determine state of the oxide surface.

Aluminas are mainly prepared by calcinations of precursor aluminum hydroxides, which can be in crystalline and gelatinous forms.[3-5] Basically, the crystalline forms consist of three aluminum trihydroxides $Al(OH)_3$ (gibbsite, nordstrandite and bayerite) and two aluminum oxyhydroxides AlOOH (boehmite and diaspore). These crystalline hydroxides can be found in the nature, mainly obtained from bauxite, or prepared synthetically in a number of ways. From either origin, when these hydroxides and oxyhydroxides are heated, they start to undergo compositional and structural changes until all of the material is converted into α-alumina. Several "transition" aluminas are produced during this process, which are designated as oxides, although it is not certain that all are anhydrous.[6-10] The term "transition" rather than "metastable", reflects the fact that the phase transition between them is irreversible and occurs only on increasing the temperature and/or time of the thermal treatment. In the case of boehmite, conversion into α-Al_2O_3 involves a complex transformation sequence of transitional aluminas: Boehmite/amorphous $Al_2O_3 \rightarrow \gamma$-$Al_2O_3 \rightarrow \delta$-$Al_2O_3 \rightarrow \theta$-$Al_2O_3 \rightarrow \alpha$-$Al_2O_3$.[11, 12] Nevertheless, the transition sequences depend strongly on the chemical routes in synthesis, atmospheric conditions,

degree of crystallinity, heating rates, impurities, moisture, alkalinity, the thermal history of the material, etc.

A wide variety of experimental and computational methods have been used to describe the structures of transition aluminas over the last half century. However, no definitive consensus has been reached on issues such as the arrangement of vacancies and the structures of transition aluminas are under certain amount of debate. The structures of these transition aluminas are traditionally considered to be based on a face-centered cubic (FCC) array of oxygen anions.[10, 11] The structural differences between these forms only involve the arrangement of aluminum cations in the interstices of an approximately cubic close-packed array of oxygen anions. Gamma alumina (γ-Al_2O_3) has a tetragonally distorted defect spinel structure with vacancies on part of the cation positions (two cubic structures inside a bigger lattice).[13] Paglia et al.[9] have reported a gamma-prime (γ'-Al_2O_3) phase also to occur. It is a phase similarly structured as the gamma phase but with slight uncertainty in the structure. Delta alumina (δ-Al_2O_3) has a tetragonal superstructure of the spinel lattice with a triple cell of γ-Al_2O_3.[6] Finally, theta alumina (θ-Al_2O_3) has the monoclinic structure of β-Ga_2O_3 and it is also related to the spinel structure.[14, 15]

In previous paper,[16,17] the conversion of a boehmite, synthesized by a sol-gel route from a non-conventional raw material, as a waste from aluminum industry, into α-alumina at 1300 and 1400ºC, was studied by X-ray diffraction (XRD), transmission electron microscopy (TEM) and Fourier transformed infrared spectroscopy (FTIR). In most of previous works, the phase identification after a thermal treatment of boehmite has been performed by XRD diagrams using a search-match program supported by JCPDS cards. As reported by Boumaza et al.,[18] matching the XRD pattern with the JCPDS data base did not allow to unambiguously characterizing the phases present when the samples contain several transition aluminas due to systematic peak

overlap. Specifically, these authors cannot prove by XRD the formation of θ-Al_2O_3 during thermal treatment of boehmite[18]. Thus, they used the simultaneous analysis of XRD patterns and IR spectra to characterize the transition alumina phases. However, this information is not precise enough to determine the properties associated to resulting material, and hence, for its technological application, it is necessary to quantify the phase fraction of the different aluminas. This problem could be overcome by using the Rietveld analysis, which has been widely reported as one of the most suitable technique for identification and quantification of crystalline phases in multiphase systems from the XRD pattern.[19,20] As this method fits the whole diffraction pattern, all reflections, overlapping or not, are used in the fitting process, and the complex severely overlapped patterns of samples with several transition aluminas can, in principle, be analyzed. Besides, variations in peak positions due changes in lattice parameters by the presence of impurities, and peak broadening associated to microstructural details (crystallite size and microstrain), are explicitly included. Thus, the Rietveld method allows extract information simultaneously about the unit cell and crystal structure, microstructure (crystallite size and microstrain), quantitative phase analysis of phases, etc., of the measured sample.[21]

The main goal of this work is to evaluate the use of XRD data and the Rietveld refinement method for the identification, quantification, and calculation of the structural of the various transition aluminas and corundum formed by the dehydration of as-obtained boehmite in air at temperatures ranging from 500 to 1500ºC. The main limitation is the expertise required to develop an appropriate initial structural model, to identify inconsistent results for the phases present, physically meaningless values of the line broadening, interpret correctly the corresponding figures of merit, and to detect in difference plots the presence of any additional phases not considered in the refinement. As these limits are clearly identified and structural

parameters could easily be refined or constrained to known values to reflect variations typically found in transition aluminas, it would become possible to characterize aluminas mixtures using only a Rietveld analysis. The combination with of other supplementary techniques like Raman spectroscopy, Infrared spectroscopy, and TEM would be no longer needed for industrial quality control. Finally, corundum and transitional aluminas can coexist with amorphous or low crystallinity component(s) after boehmite calcination process of boehmite. As an amorphous phase do not produce visible peaks in the X-ray diffraction diagram, increasing only the background, it cannot be detected directly by XRD. In this work, the absolute phase composition was determined by direct comparison with a standard of pure α-Al_2O_3 measured separately, but under the same conditions. For this goal, integrate intensity of the individual Bragg peaks of corundum was calculated using a combination of Pawley's fitting for corundum and Rietveld method for transitional aluminas.

Experimental procedure

Characterization techniques

A sample of the alumina precursor, boehmite, was obtained by a sol-gel process of an aluminum waste as raw material as previously reported.[17] Chemical analysis of boehmite was carried out by X-ray fluorescence (XRF, Panalytical Axios wave-length-dispersive X-Ray spectrometer) on a powdered sample compressed in a cold 150 MPa isostatic press in order to obtain a 37 mm diameter disk. The thermal transformation of boehmite into alumina was followed by simultaneous thermogravimetric/differential thermal analysis (TG/DTA) in a TA Instrument model SDT-Q 600. Analyses were performed in N_2 atmosphere, up to 1300ºC, at a

heating rate of 20ºC/min. According to the results of this analysis, around 2 g of boehmite was heated at 20ºC/min in air in an Eurotherma Furnace AB Model SF-2, at different temperatures ranging between 500 and 1500ºC, for 2, 7 and 12 hours. A batch was also performed at 1400ºC, 7 h in nitrogen atmosphere. Identification of the crystalline phases after this treatment was conducted by X-ray diffraction. Measurements were carried out with a SIEMENS D5000 diffractometer equipped with X-ray Cu tube and a diffracted beam monochromator. A current of 30 mA and a voltage of 40 kV were employed as tube setting. Operational conditions were selected to obtain XRD diagrams of sufficient quality: sufficient counting statistics, narrow peaks and detection of small diffraction peaks of minor phases. XRD data were collected over a 2θ range of 20-105º with a step width of 0.02º and a counting time of 10 s/step. The phase present in the XRD patterns were identified using the JCPDS data base and the DIFFRACplus EVA software by Bruker AXS.

XRD pattern refinement method

It is well known that the Rietveld method is a powerful tool for calculation of structural parameters from diffraction patterns of polycrystalline bulk materials recorded in Bragg-Brentano geometry. In this work, instrument functions were empirically parameterized from the profile shape analysis of a corundum sample measured under the same conditions. The version 4.0 of Rietveld analysis program TOPAS (Bruker AXS) for the XRD data refinement was used in this study. The refinement protocol included also the major parameters like, background, zero displacement, the scale factors, the peak breadth, the unit cell parameter and texture parameters. The quality and reliability of the Rietveld analysis was quantified by the corresponding figures of merit: the weighted summation of residual of the least squares fit, $R_{wp,}$ the statistically expected

least squares fit, R_{exp}, the profile residual, R_p, and the goodness of fit (sometimes referred as chi-squared), GoF[18]. Since $GoF = R_{wp} / R_{exp}$, a $GoF = 1.0$ means a perfect fitting.

The room temperature structures used in the refinement were an appropriated combination of metastable structures including γ, δ and θ aluminas, as well as its stable α-alumina phase. The crystal structure of α-alumina or corundum has been determined by different authors.[22, 23] It has a trigonal structure, with space group $R\overline{3}c$ and cell parameters a = 0.4754 nm and c = 1.299 nm at 300K. The rhombohedral cell contains two formula units where oxygen anions occupy 18c Wyckoff positions, whereas the aluminum cations are located at 12c positions. This means that every aluminum atom is coordinated octahedrally to six oxygen atoms, and two thirds of the octahedral interstices are occupied with Al cations to maintain electrical neutrality.

The structural models for the metastable aluminas used in the analysis were based on the crystal values reported in references. The γ-Al_2O_3 has been described as defect spinel structures using the $Fd\overline{3}m$ space group.[24, 25] It is commonly accepted that this alumina contains oxygen ions in 32e Wyckoff positions, while aluminum cations (to satisfy Al_2O_3 stoichiometry) are distributed over 16d octahedral and 8a tetrahedral sites. However, there is a large confusion regarding this distribution, and in addition many authors suggest that some Al cations can occupy 16d, 16c, 8a, 8b, and 48f sites in the $Fd\overline{3}m$ space group, which are not occupied in the normal spinel structure.[11, 15, 26]

The structure of δ-Al_2O_3 has also been described as based on the spinel structure. However, it is believed to be a superlattice built by piling up three spinel units, with the Al cations occupying 13+1/3 of the octahedral sites and all the tetrahedral sites of the conventional spinel structure.[7, 11] Repelin et al.[8] have applied a least-squares fitting procedure to described the

X-ray data from δ-Al$_2$O$_3$ by the $P\overline{4}m2$ space group and lattice parameters a = 0.560 nm and c = 2.3657 nm.

Finally, θ-Al$_2$O$_3$ is a structural isomorph of β-Ga$_2$O$_3$. This structure is monoclinic, with space group C2/m[7, 15]. The lattice parameters are: a = 1.1795 nm, b = 0.291 nm, c = 0.5621 nm and β = 103.79°[27]. This unit cell contains 20 atoms (four Al$_2$O$_3$ units), with the oxygen atom distribution close to a FCC lattice and the aluminum cations equally distributed between octahedral and tetrahedral sites.

After the calcination process of boehmite, corundum and transitional aluminas can coexist with amorphous or low crystallinity component(s). This may make the Rietveld-based quantitative analysis inapplicable, or at best, may reduce its precision. While the Rietveld method may still result in reliable weight ratios among the crystalline components in the sample, it is important to know the absolute weight fractions that include the content of the amorphous part of the specimen. The absolute phase composition of calcined samples can be determined by the Rietveld refinement using the atomic structure of corundum and transitional aluminas described before, and a known amount of a standard material. However, in order to avoid mixing a standard with the specimen, the diffraction patterns of both, a standard of pure α-Al$_2$O$_3$ and the specimen were measured separately, but under the same conditions. Intensity of the standard diffraction peaks and the intensity of the same Bragg peaks of analyzed specimen were used to calculate the weight fraction of α-Al$_2$O$_3$ as follow:

$$W_{corundum} = \frac{I_{(hkl)\ specimen}}{I_{(hkl)\ s\tan dard}} \qquad (1)$$

In order to increase the accuracy of the analysis, the integrated intensity of diffraction peaks with an intensity ratio higher than 15% of the strongest Bragg peak were used in this calculation:

$$W_{corundum} = \frac{\sum\limits_{(hkl)} I_{(hkl)\,specimen}}{\sum\limits_{(hkl)} I_{(hkl)\,s\tan dard}} \qquad (2)$$

Finally, the weight fractions of corundum obtained from the Rietveld refinement are normalized to match the content of the corundum obtained from (2). The weight fractions of transitional aluminas were recalculated using the following expression:

$$W_i = W_i^R \frac{W_{corundum}}{W_{corundum}^R} \qquad (3)$$

And the weight fraction of the amorphous component (W_A) is determined from the difference:

$$W_A = 1 - \sum_{i=1}^{N} W_i \qquad (4)$$

The main difficulty in quantification of the X-ray diffraction peaks intensities of corundum in the specimens arise from the overlapping of some diffraction peaks with peaks of transitional aluminas. Thus, integrate intensity of the individual Bragg peaks of corundum peaks

was calculated using a combination of Pawley's fitting for corundum and Rietveld method for transitional aluminas.

Results and discussion

Characterization of boehmite

The as-synthesized precursor boehmite was first semiquantitatively analyzed for determining the elemental composition by XRF. As shown in Table I, only the concentration of Fe_2O_3 and SiO_2 are meaningful (up to 0.5%) among the secondary constituents. The major phase present in this precursor was confirmed to be boehmite by matching the XRD pattern with the JCPDS card 021-1307. Figure 1 shows a quite good Rietveld refinement of the boehmite XRD profile within an orthorhombic crystal structure with space group Cmcm (R_{exp} = 5.20, R_{wp} = 6.63, R_p = 5.16, and GoF = 1.28), and it gives as results lattice parameters of a = 2.876 nm, b = 12.207 nm, and c = 3.750 nm, and a crystallite size of 2 nm.

A typical TG and DTA curves of boehmite is shown in Fig. 2. TG curve shows a continuous mass loss from room temperature up to nearly 1000ºC, with bad-defined inflexions, which can be better distinguished in its derivative curve (DrTG). In this curve it can be observed that total dehydration of boehmite to form alumina occurred in three steps:

a) The first mass loss takes place up to 264ºC corresponds mainly to the dehydration of water molecules weakly bound to form a dry boehmite. It represents about 12.6% of the total mass loss and it is associated with an endothermic peak in DTA curve centered at 141ºC

(integration peak 285.4 µVs/mg). According to Tsukada et al.[28] this loss corresponds to interlayer/absorption water.

b) The second mass loss represents 14.2% of the total mass, and occurs between 264 and 491°C. This endothermic effect (65.09 µVs/mg), centered at 380°C is attributable to the dehydroxylation of boehmite.[28-30] This value is slightly lower than the theoretical mass loss of 15% for the thermal decomposition of boehmite into γ-Al_2O_3,[31] which would indicate that there is still certain amount of remnant hydroxyl groups.

c) Between 535 and 900°C, takes place a final small mass loss of about 2.2%, which is observed as a very broad and endothermic peak on the DTA curve (78.21 µVs/mg) which was centered to 735°C. It corresponds with the elimination of residual hydroxyls. Since the dehydration process is complete after this step, the transition alumina must contain some amount of OH groups.[28] Accordingly, the total mass loss reached 30.3% corresponds to a boehmite of stoichiometry $AlOOH \cdot 0.8H_2O$.[17]

Finally, although there is not mass loss, DTA curve shows an exothermic peak between 1090 and 1181°C (24.5 µVs/mg), with maximum centered at 1143°C, which correspond to the abrupt transition from metastable aluminas to α-Al_2O_3.[32]

Characterization of aluminas

According to TG/DTA analyses, and in order to obtain the phase γ-alumina, boehmite was calcined at 500 and 600°C for 7 h. XRD patterns of both samples are similar and consist of very broad, overlapping peaks and significant background. The XRD pattern of sample calcined at 500°C is presented in Fig. 3a. The major phase observed in this diffractogram correspond to γ-Al_2O_3 (JCPDS card 050-0741), which is formed by progressive dehydration and elimination of

hydroxyl groups. The most important features of the XRD profiles can be accounted by the Rietveld refinement using the crystallographic data for the γ-Al_2O_3 reported by Shirasuka et al.[33] since R_{exp} = 5.31, R_{wp} = 6.26, R_p = 4.87, and GoF = 1.18. As observed in Fig. 3a, XRD patterns exhibit broad and diffuse profiles, indicating the presence of small crystalline grains and compositional fluctuations typical of a complex and disordered crystallographic structure. This was associated to the varying occupation among the tetrahedral and octahedral sites by Al ions within the spinel structure, as reported by many authors.[11] Rietveld analysis using the double-Voigt method gives a crystallite size of 2.5 nm. This size is of similar to the crystallite size of the precursor boehmite.[34] The transformation of boehmite into γ-Al_2O_3 in this temperature range is pseudomorphic, involving atom displacements within only a single boehmite crystal. As a consequence, derived transitional aluminas will have a crystallite size that depended on the precursor crystal dimensions. The crystallite size and lattice parameters of the calcined samples after Rietveld refinement of the XRD patterns are collected in Tables II and III.

In the material calcined at 850°C for 7 h, the occurrence of additional diffraction peaks become evident, indicating that γ-Al_2O_3 is partially converted to δ-Al_2O_3 (JCPDS card 01-088-1609). Transformation of $\gamma \rightarrow \delta$ on heating has been reported in some studies of phase transformation between metastable aluminas.[11] Figure 3b shows the Rietveld refinement based on a mixed γ-and δ-Al_2O_3 phase analysis (R_{exp} = 5.55, R_{wp} = 7.52, R_p = 5.82, and GoF = 1.36). It can be observed that the diffraction patterns of both phases are similar, indicating that the structure of δ-alumina is close to that of γ.

In XRD pattern of sample obtained at 1000°C (Fig. 4a), the presence of α-Al_2O_3 along with the other transitional aluminas is observed. None of the diffraction patterns obtained from samples calcined at temperatures ranging from 1000 to 1400°C correspond to a pure alumina

phase, and they show a mix of four phases: γ-, δ-, θ- (JCPDS card 035-0121), and α-Al_2O_3 (JCPDS card 046-1212). No measurable effect due to the transition transformations from γ-Al_2O_3 to other metastable alumina polymorphs was observed on the TG and DTA curves of Fig.1. As transformations of γ- into δ- and θ-alumina proceeds pseudomorphically, by the cation migration from octahedral to tetrahedral sites, it requires only small amounts of energy that can be hardly detected in DTA experiments.[35-37] Besides, as the structural changes involved in the transformations γ→δ→θ→α occur very gradually, they will proceed continuously, leading to the appearance of a four phases region in this temperature range. This multi-phases region is maintained even at 1400°C for short calcination time (2 and 7h), as shown in Fig. 4b and c. As reported by Boumaza et al.,[18] unambiguous identification of alumina phases coexisting in these samples it is not possible only by matching the XRD pattern with the JCPDS data base. This problem can be overcome by using the Rietveld analysis, which makes possible the decomposition of experimental XRD pattern in terms of the of the diffraction patterns calculated from the crystal structures of the component alumina phases. As shown in Fig 4a, b and c, the Rietveld refinement reveals the existence of θ-Al_2O_3 by several non overlapping peaks, for instance at 32.8 and 47.7°.

Assuming that the sum of those crystalline phases was 100%, the concentration distribution (in wt%) among the different aluminas determined using the Rietveld refinement is listed in Table IV. From the results shown in this table, it could not be excluded that all metastable alumina phases can transform directly into alpha. It is widely reported that the formation of corundum from boehmite is complete at temperatures above 1200°C.[32] On the other hand, Bye et al.[38] have demonstrated that presence of Fe increases the rate of conversion of metastable alumina into α-Al_2O_3. However, in this study a transformation over 90% is not

observed until 1400°C. The complete transformation of transitional aluminas into α-Al_2O_3 lasts until approximately 12h at 1400°C or at higher temperatures. Those samples contain in addition some Fe_2AlO_4 (JCPDS card 034-0192), and also mullite (JCPDS card 015-0776) in some cases, as shown in Table IV. When calcinations of sample are performed in an inert atmosphere, it is observed the decrease of conversion rate of transitional phases into corundum. Thus, as shown in Table IV, for the same temperature (1400ºC) and time (7 h) of heating, the sample calcined in N_2 contains 22.7% of γ-Al_2O_3, and this phase is not observed in sample calcined in air.

Aluminum and oxygen atoms movement during the transformations $\gamma \rightarrow \delta \rightarrow \theta \rightarrow \alpha$ produces aluminas with larger crystallite dimensions. As shown in Table II, crystallite size of a metastable alumina polymorph presents, within the error limits, a similar crystallite size independently of the calcination time and/or temperature. As metastable aluminas changes to α-Al_2O_3, the crystallite size increases, this means that, the gaps between the chains and the crystal defects are gradually reduced, and finally disappear. When all transitional aluminas are converted into α-Al_2O_3, it was observed a crystallite size that cannot be measured with reasonable accuracy with conventional diffractometers, since crystallite size lead to broadening similar to the instrumental broadening.

As shown in Table III, Rietveld refinement also showed that the unit cell parameters of the different alumina remains effectively constant, within the limits of the experimental uncertainty, with the time-temperature conditions of its formation. The unit cell parameters found for θ by Rietveld refinement compare well with those found by Willson et al.[7]. The α-Al_2O_3 obtained from the Rietveld refinement of the XRD patterns has a greater lattice parameter (a = 0.4766 nm, c = 1.3009 nm) than that of JCPDS file 46-1212 (a = 0.4758 nm, c = 1.299 nm) and a similar c/a ratio (c/a = 2.730). This difference on crystallographic parameters has been attributed

by Boumaza et al. [39] to microstructural changes that frequently accompany phases transformations.

In the other hand, the presence of an amorphous coexisting with corundum and transitional aluminas in calcined samples was confirmed comparing the corresponding XRD patterns with that of a standard of pure α-Al_2O_3 measured under the same conditions. The weight percent of each phase modified by applying the empirical corrections described previously varies between 15-20%. These amorphous oxides would be originated from portions of the original boehmite powders containing trace impurities that did not transform into crystalline phases by calcinations. The amorphousness could be attributable to elements such as phosphor and silicon coming from the raw material used to synthesize boehmite.

Conclusions

Alumina, Al_2O_3, was produced by calcinations of a precursor boehmite obtained from an aluminum waste through a sol-gel process. Progressive dehydration and elimination of hydroxyl groups from the boehmite below 500°C led to its transformation into γ-Al_2O_3. Conversion of γ- into the stable α-Al_2O_3 occur very gradually, leading to the appearance of other transitional alumina species like δ- and θ-Al_2O_3 during calcinations at temperatures ranging from 1000 to 1400°C. The complete transformation of transitional aluminas into α-Al_2O_3 lasts until approximately 12h at 1400°C or at higher temperatures in air atmosphere. Unambiguously determination of the phases present in calcined samples by XRD can only be performed using the Rietveld refinement, due to systematic diffractions peak overlap of the different transition

alumina phases. On the other hand, direct comparison of diffraction patterns of a standard of pure α-Al_2O_3 and calcined samples, both measured under the same conditions, is required to determine the presence of an amorphous component.

Acknowledgment

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Figure Captions

Fig .1. XRD pattern and Rietveld refinement analysis of initial boehmite showing scale observed (open points) and calculated (red solid line) intensity. The differences between experimental data and the fitted simulated pattern is plotted as a continuous green line at the bottom.

Fig. 2. TG/DrTG and DTA curves of boehmite.

Fig. 3 Observed (open circles) and calculated (red solid line) XRD pattern of boehmite calcined for 7h at a) 500 and b) 850ºC after the Rietveld refinement. The differences between experimental data and the fitted simulated pattern is plotted as a continuous green line at the bottom.

Fig. 4 Selected part of 2θ from 30 to 50º showing on an enlarged scale observed (open circles) and calculated (red solid line) XRD pattern of boehmite calcined a) at 1000ºC for 7h and at 1400ºC for b) 2, c) 7, and d) 12h after the Rietveld refinement. The differences between experimental data and the fitted simulated pattern is plotted as a continuous green line at the bottom and the contribution of the component phases in different colors.

Table Legend

Table I. Results of the XRF semi-quantitative analysis (normalized to 100 wt. %) of initial boehmite and after calcination at 1500°C for 7 hours.

Table II. Crystallite size (nm) of the calcined samples after Rietveld refinement of the X-ray diffraction patterns.

Table III. Lattice parameters (nm) of the calcined samples after Rietveld refinement of the X-ray diffraction patterns.

Table IV. Composition of the calcined samples after Rietveld refinement of the X-ray diffraction patterns.