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High surface area α-alumina preparation by using urban waste

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Abstract

A new method for preparing high surface area α-alumina from urban waste is proposed. The method consists of the precipitation of a precursor that contains bohemite mixed with a linear polymer and subsequently the thermal decomposition of the precursor by heating in nitrogen and air to 1200 °C. The resulting α-alumina consists of nanocrystals of about 100 nm aggregated into larger particles with relatively high surface area (12 $m^2 g^{-1}$) and a significant macropore volume of 0.545 cm^3 g. Methods of X-ray diffraction (XRD), scanning electron microscopy (SEM), high-resolution transmission electron microscopy (HRTEM) and selected area electron diffraction (SAED) were used to characterize microstructure of prepared materials. Results of differential thermal analysis, thermogravimetry and emanation thermal analysis characterized the thermal behaviour of α-alumina precursors.

Keywords: α-Alumina preparation; Surface area; Urban waste; Microstructure characterization; Thermal behaviour

1. Introduction

Alumina has a significant importance from the technological point of view, with applications in electronics, optoelectronics, wear protection, refractories, catalysis (both as catalytic supports and as catalysts) in petroleum refining, automotive emission control, and hydrogenation [1–5]. Fine powders of alumina are of most interest for preparing ceramics with improved hardness and wear resistance or for their application in membranes or catalytic materials [1,3,5,6]. Additionally, obtaining high crystallographic and dimensional stability alumina with high specific surface area is of great importance to membranes or catalytic processes involving high temperatures and, specially, to their regeneration. Thus, for example, for clean combustion catalytic processes, efficiency is restricted by the temperature that the catalyst can withstand before a structural collapse happens.

Although corundum, α-Al_2O_3, is the thermodynamically stable phase at standard pressure and temperature conditions, most of the preparation methods for high surface area alumina yield metastable phases such as −χ, −θ, −γ, −δ, due to the lower surface energy of these phases as compared with that of corundum [7]. Nevertheless, these metastable phases are not useful for applications that require high temperatures while they are transformed into corundum by further heating, usually, above 1100 °C. This heating treatment produces sintering and specific surface area reduction. Thus, the direct preparation of α-Al_2O_3 at low temperatures has been considered of interest. The only hydroxide that can be directly transformed into α-Al_2O_3 is diaspore. Diaspore is usually prepared under hydrothermal conditions and its topotactic conversion into corundum takes place at temperatures as low at 450 °C, yielding high surface area α-Al_2O_3. Nevertheless, surface area of these aluminas decreases sharply when samples are heated at temperatures above 700 °C [8].

Some research works focused on sol–gel methods. Thus, α-Al_2O_3 with 11 $m^2 g^{-1}$ specific surface area has been prepared from carboxylates at 975 °C [9], but this specific surface area falls drastically to 1 $m^2 g^{-1}$ when heated at 1200 °C. Starting

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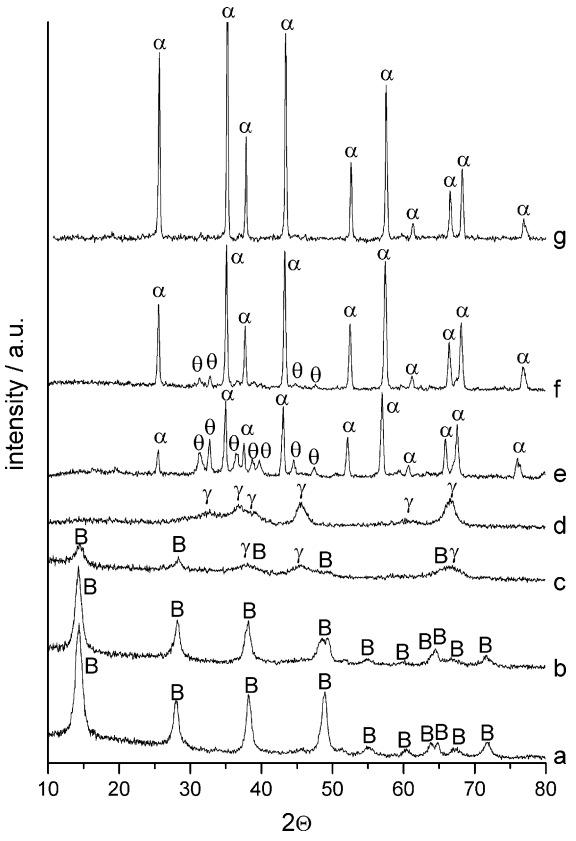

Fig. 1. High temperature X-ray diffraction measurements of alumina precursor in air at different temperatures: (a) 25 °C, (b) 300 °C, (c) 350 °C, (d) 900 °C, (e) 1150 °C, (f) 1200 °C and (g) 1200 °C for 30 min. B: bohemite, γ: γ-alumina, θ: θ-alumina, α: α-alumina.

from aluminium sec-butoxide [10], 33 $m^2\ g^{-1}$ specific surface area aluminas have been achieved, but these aluminas consist of α–θ or α–κ mixture phases, and their specific surface areas also falls when the complete transformation into α-Al_2O_3 takes place.

Other methods include calcination of emulsion precursors that yields α-Al_2O_3 at 1000 °C with about 15 $m^2\ g^{-1}$, but this specific surface area cannot be retained at high temperatures [11,12]. Wang et al. [13,14] proposed calcining carbon-covered γ-Al_2O_3 in oxygen flow at 800 °C to obtain α-Al_2O_3 with a specific surface area of about 8 $m^2\ g^{-1}$. The use of colloidal crystals as templates have been reported for the preparation of macroporous α-alumina [15]. Alumina nanopowders with surface areas as high as 34 $m^2\ g^{-1}$ have been produced from synthetic Bayer liquor, but the resulting samples are a mixture of α and γ phases [16]. The heterogeneous precipitation of boehmite on θ-Al_2O_3 has been also proposed as a procedure to prevent aggregation during its transformation into α-Al_2O_3 [17].

The aim of this work was to propose a new method for preparation of high porosity α-alumina stable up to high temperatures. The method used an urban waste aluminium alloy acidic solution as starting material.

2. Materials and methods

Alumina investigated in this work was prepared by using an urban waste aluminium alloy acidic solution as raw material. This solution was prepared by dissolving in a 5 M HCl solution a number of drinking cans and aluminium foil from urban waste. The resulting solution was filtered to remove the insoluble fraction. The initial composition of this solution was analysed by inductively coupled plasma–atomic emission spectroscopy (ICP–AES), showing the following results: aluminium: 75,600 g l^{-1}; iron: 3900 g l^{-1}; and magnesium: 800 mg l^{-1}.

The alumina precursor was prepared as follows: the acidic solution was added dropwise with a burette into a 50 vol.% lineal polymer (bisphenol-A-eplichloridrine) solution dissolved on ethanol. Hexamethylenetetramine was used as co-precipitation agent. The addition was performed at 40 °C with continuous agitation up to pH 6. The resulting gel was homogenized with distillate H_2O by hot agitation. Then it was vacuum filtered, and the resulting paste was washed with hot distillate H_2O and filtered again; finally, it was dried.

The thermogravimetry (TG) and differential thermal analysis (DTA) of the precipitated samples were carried out by using a SETARAM Labsys TG–DTA instrument at a heating rate of 5 K min^{-1}, both in air and nitrogen flows (100 $cm^3\ min^{-1}$).

Emanation thermal analysis (ETA) measurements were performed on heating in air and nitrogen, respectively, at a heating rate of 5 K min^{-1}, using a modified NETZSCH DTA-ETA 404 instrument. The ETA involves measurements of radon release rate from samples previously labelled by ^{220}Rn atoms. The ^{220}Rn atoms are incorporated into the sample to a maximum depth of 80 nm due to recoil energy (85 keV $atom^{-1}$), which the atoms gained by the spontaneous α-decay. The evolution of the radon release rate or emanation rate (E) with temperature serves to evaluate the radon mobility and transport properties and characterizes the microstructure development of the samples under ''in situ'' conditions of heating [18–22].

The X-ray diffraction patterns of the precipitates and alumina powders were obtained by a SIEMENS D5000 powder diffractometer with a Ni filter, using Cu Kα radiation.

The porous structure of the samples was characterized by N_2 adsorption–desorption at 77 K, and CO_2 at 273 K performed in an Omnisorp 100cx equipment (Coulter). Samples were previously outgassed during at least 8 h at 150 °C. From the N_2 isotherm, the apparent surface area (A_{BET}) was determined applying the BET equation [23], the micropore volume (V_{DR}) were calculated using the CO_2 adsorption data and the Dubinin–Raduchkevich method [24].

Macropore volume was measured using a Porosimeter 4000, Carlo Erba Instruments, by the mercury intrusion porosimetry method, based on the Washburn equation:

$$Pr = -2\gamma \cos\theta \quad (1)$$

where $\gamma = 480$ din/cm is the surface tension of mercury and $\theta = 141.4°$ is the contact angle between mercury and the material.

Transmission electron micrographs (HRTEM) were obtained by using JEOL JEM 3010 operated at 300 kV (LaB6 cathode). Copper grid coated with a holey carbon support film was used to prepare samples for the TEM

observation. A powder sample was dispersed in ethanol, and the suspension was treated in an ultrasonic bath for 2 min.

Scanning electron micrographs (SEM) were obtained by using Philips XL30 CP microscope equipped with energy-dispersive X-ray (EDX), Robinson, SE, and BSE detectors. Particle size distribution has been obtained from micrographs using about 200 particles.

3. Results and discussion

High temperature X-ray diffraction measurements of precursor in air and nitrogen are shown in Figs. 1 and 2. The X-ray diffraction patterns at room temperature shows the presence of bohemite as the only crystalline phase. On heating in air (Fig. 1), bohemite remains as the only phase up to 300 °C. At 350 °C, bohemite is partially converted into γ-alumina, while at 400 °C bohemite totally disappears and only γ-alumina is detected. In the range from 400 °C to 900 °C, γ-alumina is the only identified phase, but at higher temperature some peaks assigned to θ-alumina are observed. Thus, up to 1100 °C, a mixture of γ-alumina and θ-alumina is observed. As temperature increases to 1150 °C, both θ-alumina and α-alumina are the present phases. At higher temperatures, the intensities of the θ-alumina peaks decrease while those of the α phase increase. Eventually, when the sample is heated at 1200 °C for 30 min, α-alumina is the only present phase.

For the heating the precursor in nitrogen, the high temperature X-ray diffraction (Fig. 2) showed similarities with the case when heated in air. Thus, the original bohemite also converts firstly into γ-alumina above 300 °C, similarly to the behaviour in air. Nevertheless, when the precursor was heated in nitrogen, a new κ phase mixed with the γ one is detected at 900 °C and remained up to 1150 °C; such phase is not observed when the heat treatment was performed in air. The presence of κ phase has been mostly reported for materials prepared by chemical vapour deposition; although it has been also produced by heat treatments of hydrated aluminas under vacuum [25–30]. Thus, the different conditions, inert or oxidizing atmosphere, determined the presence of the κ-alumina as intermediate phase. At 1200 °C, the κ-alumina was not detected while γ and θ were the only present phases, except for tiny reflections corresponding to α-alumina. Treatments of about 3 h at 1200 °C are requested to obtain pure α-alumina.

The chemical composition of the resulting α-alumina, as obtained from ICP–AES measurements, show that the material is constituted mainly by Al_2O_3 (99.62%) with a small amount of Fe_2O_3 (0.29%) and MgO (0.08%).

TG–DTA curves of the alumina precursor sample when measured in air and nitrogen are reported in Figs. 3 and 4, respectively. For the measurements on heating in air flow, the TG results demonstrated a mass loss of about 7.2% at temperatures below 175 °C, corresponding to water desorption. This process is accompanied by an DTA endothermic effect. In the range from 175 °C to 720 °C, the TG results demonstrated several overlapping mass loss effects that correspond to a total weight loss of 35.1, no further mass loss was observed on sample heating to higher temperatures. Thus, this mass loss could be attributed to the polymer combustion and to the alumina formation from the precursor. In the DTA curve, these processes are recorded by at least two thermal effects: one exothermic at 310 °C and another endothermic at 439 °C. The DTA curve also demonstrated an exothermic effect at about 1207 °C corresponding to the final transformation into α-alumina.

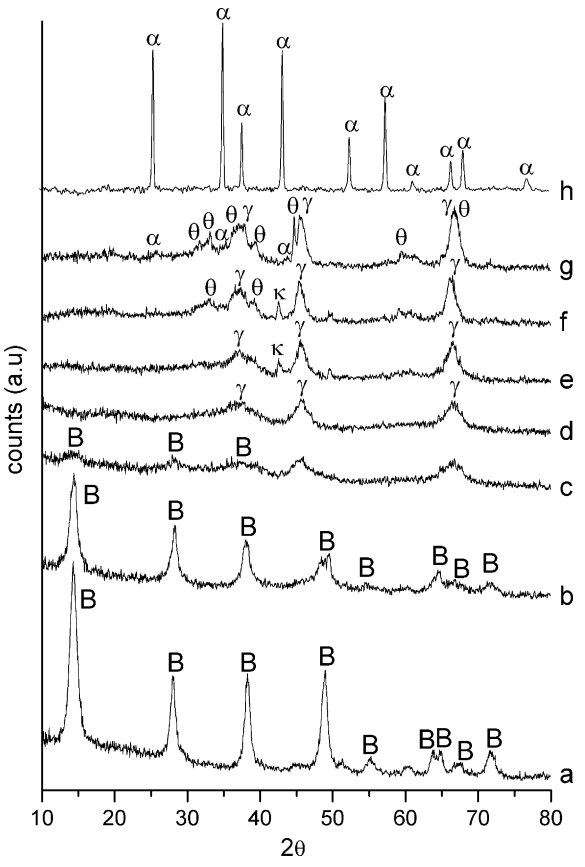

Fig. 2. High temperature X-ray diffraction measurements of alumina precursor in nitrogen at different temperatures: (a) 25 °C, (b) 300 °C, (c) 350 °C, (d) 600 °C, (e) 900 °C, (f) 1150 °C, (g) 1200 °C and (h) 1200 °C for 3 h. B: bohemite, γ: γ -alumina, κ: κ-alumina, θ: θ-alumina, α: α-alumina.

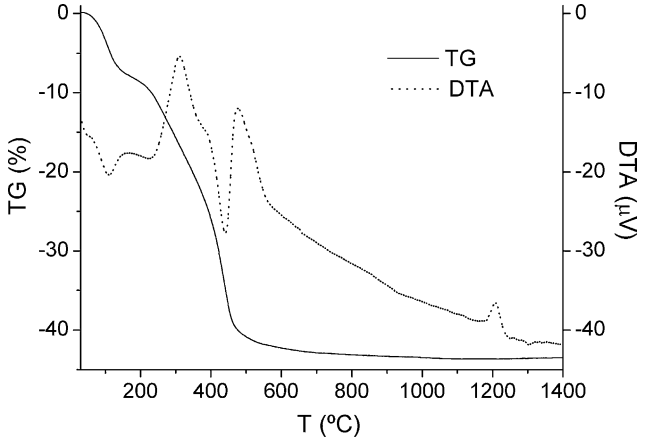

Fig. 3. Results of thermogravimetry (TG) and differential thermal analysis (DTA) of the alumina precursor measured on heating in air.

Table 1
Surface characterization of samples heated at 1200 °C.

Sample	BET (N_2) surface area ($m^2\ g^{-1}$)	DR (CO_2) surface area ($m^2\ g^{-1}$)	DR (CO_2) micropore volume ($cm^3\ g^{-1}$)	Macropore volume ($cm^3\ g^{-1}$)
Heated in air	9.2	9.5	0.0035	0.489
Heated in nitrogen followed by heating in air at 800 °C	12.0	11.0	0.0042	0.545
Without polymer and heated in air	6.3	6.2	0.0024	0.204

TG and DTA results of the alumina precursor on heating in nitrogen flow (Fig. 4), showed the small weight loss and an endothermic peak below 175 °C corresponding to water desorption. For temperatures higher than 175 °C, several overlapping mass losses were observed on heating up to 920 °C, while the DTA results showed an endothermic effect; the mass loss in this range was 28%. It is worth to note that the mass loss of the sample on heating in nitrogen (28%) is smaller than that in air (35.1%) due to the fact that on heating in nitrogen a pyrolysis of the sample took place, while on heating in air a combustion process took place. At higher temperatures, the DTA results obtained on the sample heating in nitrogen showed a broad exothermic effects above 1200 °C; it was not so well defined as for the DTA measurement in air.

Fig. 5 depicts the emanation thermal analysis results measured on heating the alumina precursor from 400 °C to 1300 °C in air and nitrogen, respectively .The ETA method is a sensitive method suitable to characterize structure and microstructure development of the samples under in situ conditions of heating [18–22]. The results presented in Fig. 5 showed following differences in the thermal behaviour of the alumina precursor sample on heating in air and nitrogen flow, respectively.

The increase of the emanation rate, *E*, measured on heating above 1000 °C indicated a higher radon diffusion mobility in sample on heating in air (Fig. 5, curve a) than on heating in nitrogen (Fig. 5, curve b). The maxima of the emanation rate values were observed at 1148 °C and 1210 °C for the sample heated in air and nitrogen, respectively, being followed by a significant decrease in the emanation rate, *E*. This behaviour corresponds to the crystallization of the α-alumina, as confirmed by high temperature X-ray patterns (Fig. 2), indicating that the crystallization of α-alumina takes place at a slightly higher temperature on sample heating in nitrogen than on heating in air.

The decrease in the emanation rate, *E*, observed on the ETA curves in Fig. 5 characterized healing of structure irregularities and annealing of the grain boundaries during the crystallization of the sample.

The results of surface area obtained from N_2 adsorption–desorption at 77 K, CO_2 adsorption at 273 K and from mercury porosimetry measurements are summarized in Table 1. The results correspond to the properties of the sample obtained in air (1200 °C, 30 min) and of the sample prepared in nitrogen (1200 °C, 3 h) and subsequently heat treated in oxygen (800 °C, 1 h) in order to remove the remaining carbon. Additionally, for the sake of comparison, the data corresponding for the sample obtained without polymer additive and decomposed in air (1200 °C, 30 min) have been also included.

Results summarized in Table 1, showed that the polymer additive caused an increase in the surface area of the materials both as measured using the B.E.T. method and the Dubinin–Radushkevich method (CO_2). In a similar way, both the micropore volume, as obtained from the CO_2 adsorption data, and the macropore volume, determined from mercury porosimetry results, indicated that the use of the polymer additive caused an increase in both parameters. These results suggest that the polymer additive acts as a template that enhances the surface area of the resulting α-aluminas. Decomposition atmosphere also plays a role in the texture of the resulting materials as obtained for the polymer containing precursor. Thus, when the sample is decomposed in nitrogen

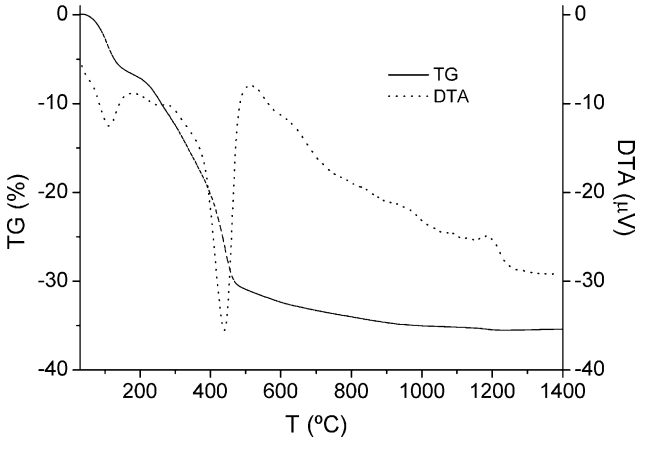

Fig. 4. Results of thermogravimetry (TG) and differential thermal analysis (DTA) of the alumina precursor measured on heating in nitrogen.

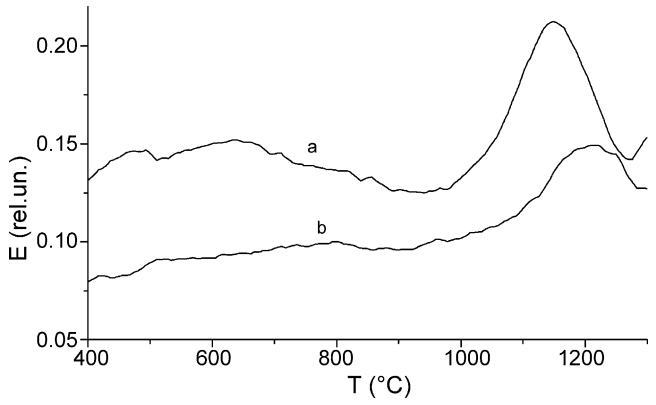

Fig. 5. Emanation thermal analysis (ETA) results of the alumina precursor measured in the range from 400 °C to 1300 °C on heating in air (a) and nitrogen (b).

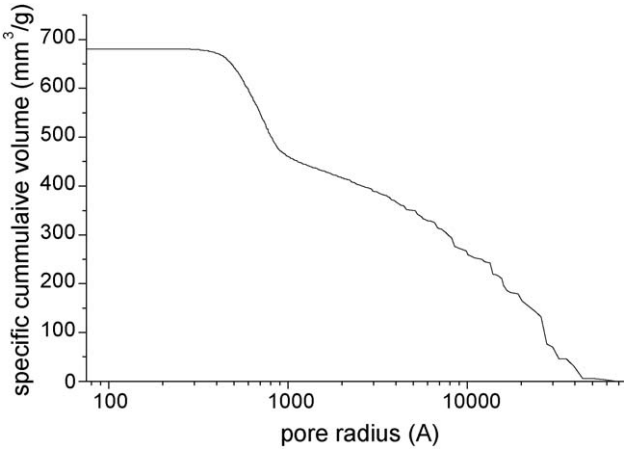

Fig. 6. Cumulative curve of intrusion of mercury, for the sample obtained from the polymer containing precursor decomposed by heating in nitrogen.

and the remaining carbon is later on thermally removed, the resulting α-alumina showed larger surface area as well as larger micropore and macropore volumes. This behaviour can be attributed to the remaining carbon that prevents particles from sintering even when heated up to 1200 °C. The further heating in air at 800 °C removes the carbon leaving empty pores in the material.

Fig. 6 shows the cumulative curve of intrusion of mercury, for the alumina sample prepared by heating of the alumina precursor in nitrogen. As it is a powdered sample, the intrusion takes place at low pressures as mercury penetrates the large interparticles voids. Additional intrusion occurs at higher pressures into pores within particles. The slight slope between 3500 Å and 900 Å indicates a small amount of porosity in this radius range. At 900 Å intrusion commences into a range of pores with 900–300 Å radii, while no further intrusion takes

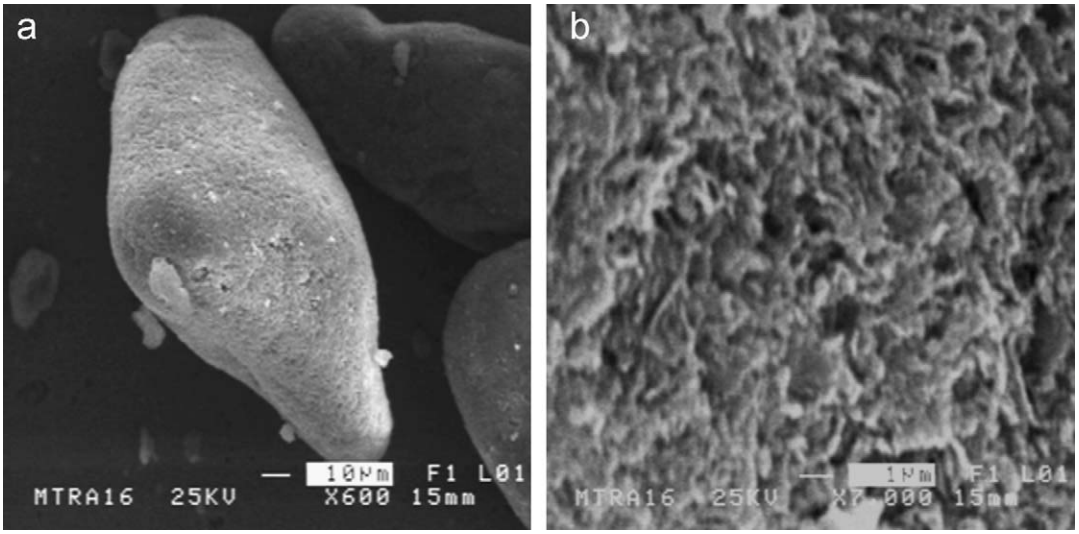

Fig. 7. SEM photographs at different magnifications of the sample obtained from the polymer containing precursor decomposed by heating in nitrogen.

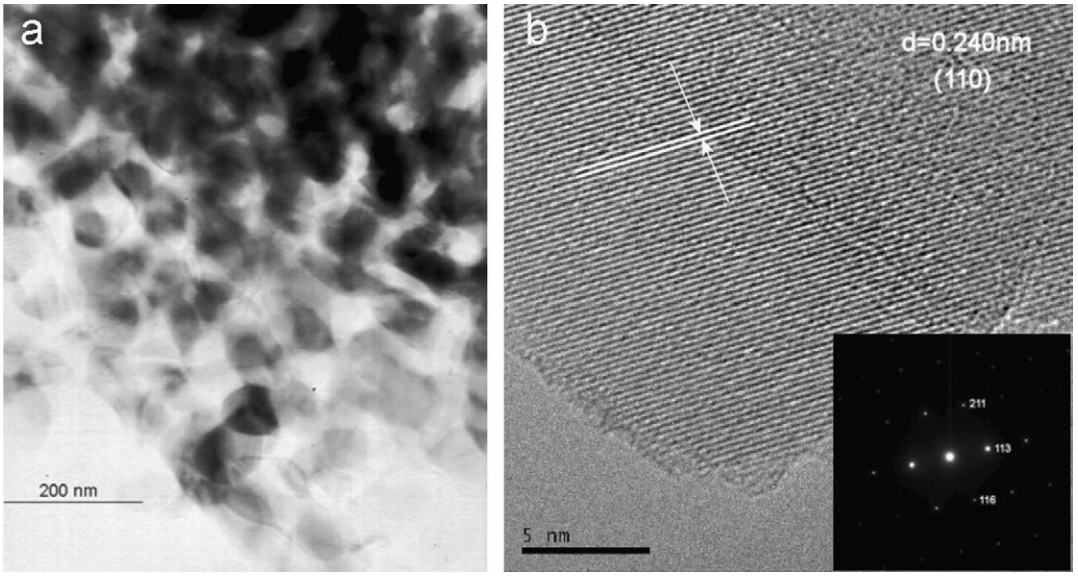

Fig. 8. TEM (a) and HRTEM (b) micrographs for the alumina sample obtained from the polymer containing precursor decomposed by heating in nitrogen. The corresponding selected area electron diffraction (SAED) is also included (inset).

place up to the maximum pressure for smaller pores, therefore no meso-porosity (250–40 Å) is observed. Taking into consideration that the sample density is 1.1042 g cm^3, that corresponds to a specific volume of 0.9056 cm^3 g, the resulting macropore volume of 0.545 cm^3 g means a void volume percentage of 60.18%.

The SEM micrographs of the sample prepared by heating the alumina precursor in nitrogen (Fig. 7a and b) showed high particle density agglomerates with porous morphology. Agglomerate surface can be appreciated in detail in Fig. 7a, which is an enlargement of Fig. 7b. The agglomerates show a bimodal particle size distribution with modal sizes at 1.2 μm and 22.5 μm, being the number percentage of the smaller and larger particles 15% and 22.5%, respectively. The TEM micrographs for this sample (Fig. 8a) showed that the material is constituted by about 95 nm alumina crystals.

Fig. 8b includes, the HRTEM micrograph of alumina crystal, with interlayer spacing of 0.24 nm, taken along the (1 1 0) plane and the corresponding selected area electron diffraction (SAED) show well ordered α-alumina phase.

4. Conclusions

A new preparation method of a highly crystalline α-alumina with large micropores and macropores volumes from urban waste material is described.

The method implies using a linear polymer in the preparation of the alumina precursor. The thermal decomposition of the alumina precursor above 1200 °C under different atmospheres allows the preparation of a highly crystalline α-alumina with large micropores and macropores volumes.

Acknowledgments

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