



Characterization of thermally stable gamma alumina fibres biomimicking sisal



Mónica Benítez-Guerrero^{a,*}, Luis A. Pérez-Maqueda^b, Pedro E. Sánchez-Jiménez^b, José Pascual-Cosp^a

^a Departamento de Ingeniería Civil, Materiales y Fabricación, Universidad de Málaga, C. Dr. Ortiz Ramos s/n, 29071 Málaga, Spain

^b Instituto de Ciencia de Materiales de Sevilla, CSIC-Universidad de Sevilla, C. Américo Vespucio 49, 41092 Sevilla, Spain

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ABSTRACT

Mesoporous gamma alumina fibres of high surface area, stable up to 1000 °C, were synthesized by bio-replica technique using sisal fibres as templates. Alumina formation during pyrolysis and calcination of fibres infiltrated with aluminium chloride solution has been studied, paying special attention to the interaction between the precursor and sisal fibres, using several experimental techniques such as ATR-FTIR, coupled TG-FTIR and thermo-XRD analysis. The morphology and microstructure of the resulting alumina fibres were characterized using SEM and TEM. The crystallographic analysis of the alumina sample performed by electron and X-ray diffraction suggests that fibres are constituted by η and γ -Al₂O₃ crystallites, whose chemical structure was confirmed by ATR-FTIR and Al²⁷-MAS-NMR. The specific surface area and porosity of ceramic fibres were determined by N₂ and CO₂ adsorption–desorption measurements. Resulting alumina fibres retain high specific surface areas of 200 and 150 m²/g even after calcination at 1000 °C for 15 h in dry air and for 4 h in wet air, respectively.

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1. Introduction

High surface area mesoporous aluminas with narrow pore distribution have been the subject of extensive research employing different strategies [1]. However, the synthesis of aluminas with hierarchically ordered pore structure attracts more and more attention [2,3], due to the highly effective transport phenomena and the easy diffusion of reactants and products when pores of different sizes are interconnected. Generation of controllable hierarchical pores has been fundamentally carried out through agents acting as porosity generators like organic additives and surfactants [4,5], foams, emulsions or masks based on replica procedure [6], as well as by using others methods as hydrothermal treatment [7], and recently, nanocasting technique [8]. In any case, most of the employed processes generally involve the use of expensive porosity agents which must be finally removed by extraction or calcination.

A method of ceramic synthesis that has attracted significant attention in the scientific community is the variant of the infiltration-replica technique which uses natural masks or bio-templates [9–11]. Through bio-replica, it is possible to generate ceramic materials which faithfully reproduce the morphology and structure of the starting preforms in an easy way, with a porous architecture scaled from nano-, micro- to macro-sizes, with isotropic,

anisotropic, homogeneous or heterogeneous properties, which are either difficult or very costly to produce by conventional methods [12]. The interest on porous bio-replicas based on metal oxides such as Al₂O₃, TiO₂ and ZrO₂ has been increasing in the last decades for their interest in photocatalysis and photovoltaic, specially for manufacturing of gas sensors, filters, catalysts carriers, etc. [13,14]. Lignocellulosic masks stand out among the wide range of materials suitable to be used as templates [15,16], due to their ecological and economical origin, obtained from renewable and even residual resources, which make it interesting as valorization process [17,18].

The textural and crystallographic stability of aluminas are of great importance for processes involving high temperatures, such as regeneration of catalyst beds and membranes, being the collapse of alumina structure a limiting factor of the process efficiency. High temperatures and high residence times reduce the specific surface area of alumina due to the transformation to alpha phase, which is accompanied by coalescence and sintering phenomena. Thus, the attainment of thermally stable alumina keeping high specific surfaces areas is the goal of many researches. Ordered mesoporous aluminas exhibit S_{BET} values ranging between 200 and 500 m²/g after calcination at temperatures between 450 and 700 °C [1], and exceptionally 700–800 m²/g [19,20]. The surface area diminishes considerably at temperatures as high as 1000 °C. It was described the cationic surfactant synthesis of γ -Al₂O₃ with a resulting surface of 130 m²/g after a thermal treatment at 1000 °C for 2 h [21]. At the same calcination temperature, a

* Corresponding author. Tel.: +34 951952594.

E-mail address: monica_benitez_guerrero@yahoo.es (M. Benítez-Guerrero).

mixture of $(\gamma + \delta)\text{-Al}_2\text{O}_3$ with $90 \text{ m}^2/\text{g}$ was obtained by nanocasting [22]. Recently, it was reported the generation of gamma-alumina monoliths through gel-casting of mesoporous alumina powder and polymerization additives, reaching $110 \text{ m}^2/\text{g}$ after calcination at $1000 \text{ }^\circ\text{C}$ for 10 h [23].

Different works have dealt with the synthesis of porous alumina employing cellulose derived templates. The results obtained up to the moment consist of sintered alpha alumina cellular ceramics [24–26] and mesoporous aluminas which, as the ones obtained by conventional synthetic methods, do not maintain elevated specific surface area at high temperatures. Using filter paper as cellulose support, Shigapov et al. [27] synthesized alumina with $322 \text{ m}^2/\text{g}$ after calcination at $800 \text{ }^\circ\text{C}$ for 2 h, which decreases to $21 \text{ m}^2/\text{g}$ after treatment at $1050 \text{ }^\circ\text{C}$ for 12 h. Patel and Padhi [28] obtained at $1000 \text{ }^\circ\text{C}$ alumina fibres with $56 \text{ m}^2/\text{g}$ by infiltration of jute fibres. Fan et al. [29], through natural cotton fibres, attained $\gamma\text{-Al}_2\text{O}_3$ with surface areas of 127.6 and $125.1 \text{ m}^2/\text{g}$ after a calcinations period of 2 h at 800 and $1000 \text{ }^\circ\text{C}$, respectively.

In the present paper, it is described the synthesis of thermally stable alumina fibres of high specific surface area up to $1000 \text{ }^\circ\text{C}$, which reproduce the morphology of sisal fibres. In a first part, changes experimented by the lignocellulosic template after their infiltration with the inorganic precursor are presented, as well as thermal phenomena occurring during transformation to alumina during pyrolysis and calcinations stages. In a second part, the composition, morphology and structure of the resulting alumina ceramic fibres are characterized.

2. Experimental section

2.1. Synthesis

Natural sisal fibres used in this work, named NS, were provided by Cayetano García del Moral S.L. (Cabra de Santo Cristo, Jaén, Spain). The fibres, manually cut to 2–4 mm length, were subjected to an alkalization processes to conditioning the surface of the fibres before the infiltration stage. The alkali treatment was performed for 2 h at room temperature with a 4% NaOH solution (Panreac, 231686), followed by exhaustive washing with distilled water. Acetic acid drops were added in the penultimate washing step. Pretreated sisal fibres are designated as PS.

An aqueous solution of aluminium trichloride was prepared using $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ (Panreac, 141097), HCl (37% Panreac, 131020) and aluminium foil, with the following molar ratio 1.5:1:0.75. PS fibres were immersed in the precursor solution for 240 h, washed with absolute EtOH (Panreac, 141086) and allowed to dry at ambient temperature. Dry infiltrated sisal fibres, named IS, were thermally treated in tubular furnace (Thermolyne F59340CM). The process consisted of a pyrolysis/carbonization stage under nitrogen for 1 h, immediately followed by an oxidation stage under air for 15 h at $1000 \text{ }^\circ\text{C}$. An additional heating cycle was conducted at $1000 \text{ }^\circ\text{C}$ for 4 h using moistured air saturated at room temperature. In order to test its thermal stability, another sample was prepared under the same conditions but which is also subjected to an additional heating cycle at $1000 \text{ }^\circ\text{C}$ for 4 h using humid air, water saturated at room temperature. The resulting ceramic fibres are referred as AF and AFh, respectively.

2.2. Characterization methods

SEM analyses were performed on JSM-6400 and JSM-6490LV JEOL microscopes. The latter is coupled to an Oxford Instruments INCAx-Sight EDAX system, used to analyze infiltrated fibres.

ATR-FTIR spectra were collected, on a Bruker Vertex 77 spectrometer and a Specac Golden Gate ATR accessory, after 32 scans for the range $4000\text{--}500 \text{ cm}^{-1}$, with a resolution of 4 cm^{-1} .

XRD measurements were conducted in a Philips X'Pert PRO MPD, with a X'Celerator RTMS system, using $\text{Cu K}_{\alpha 1}$ ($\lambda = 1.5406 \text{ \AA}$) monochromatic radiation. The proportion of ordered regions of cellulose fibrils was determined for alkalinized and infiltrated fibres using the crystallinity index (CI), calculated by Segal equation [30]:

$$\%CI = (1 - (I_{am}/I_{max})) \cdot 100 \quad (1)$$

where I_{max} is the intensity of the main lattice reflection of cellulose, corresponding to the (002) plane located around 22° (2θ), and I_{am} is the intensity attributed to amorphous material, around 18° , for I_{β} type cellulose. Alumina crystallite size was estimated through the Scherrer equation applied to (440) and (113) planes for $\gamma\text{-Al}_2\text{O}_3$ and $\alpha\text{-Al}_2\text{O}_3$, respectively.

The crystallographic evolution of two portions of infiltrated fibres was followed dynamically by temperature programmed X-ray diffraction (TXRD), scanning each diffractogram every $50 \text{ }^\circ\text{C}$ for 40 min. A fraction of the sample was heated from room temperature to $400 \text{ }^\circ\text{C}$ under inert atmosphere with a rate of $5 \text{ }^\circ\text{C}/\text{min}$. Another fraction was pre-pyrolyzed at $500 \text{ }^\circ\text{C}$ and, after being finely ground, it was heated from 500 to $1150 \text{ }^\circ\text{C}$ at $10 \text{ }^\circ\text{C}/\text{min}$. The analysis was performed under nitrogen atmosphere between 500 and $900 \text{ }^\circ\text{C}$ and under oxidizing atmosphere between 950 and $1150 \text{ }^\circ\text{C}$.

TG/DSC analyses were carried out in a SDT 2960 TA Instrument, under nitrogen and air atmospheres with a rate of $10 \text{ }^\circ\text{C}/\text{min}$. The released gases were analyzed in a Bruker VECTOR 22 infrared spectrometer coupled to the outlet port of the SDT. The transfer line and the cell were kept at $300 \text{ }^\circ\text{C}$. Spectra were recorded in the range $4000\text{--}500 \text{ cm}^{-1}$ every 61 s, after 64 scans and with a resolution of 4 cm^{-1} .

XRF semi-quantitative analyses were performed using energy-dispersive X-ray instruments, Axios PW4400 from PANalytical and XGT-5000WR from Horiba.

TEM micrographs and SAED electron diffraction patterns were collected on a Philips CM-200 microscope. Previously, alumina sample was dispersed in EtOH, stirred in an ultrasonic bath and, finally, one drop was deposited on carbon-coated copper grid.

XPS analysis of ground alumina sample was performed in a PHI 5700 Physical Electronics spectrometer, employing non-monochromatic Mg K_{α} radiation (1253.6 eV). The photoemission peaks were calibrated respect to the signal C 1s for adventitious carbon (284.8 eV) prior to the fitting procedure.

Solid state ^{27}Al MAS-NMR analysis was conducted on a Bruker DRX-400 spectrometer, under a magnetic field of 9.6 T and a pulse of $1.1 \mu\text{s}$. The powdered sample was spun at a rate of 10 kHz and the chemical shifts were referenced to 1 M $\text{AlCl}_3 \cdot \text{H}_2\text{O}$ solution.

N_2 and CO_2 adsorption–desorption isotherms were measured with a Micromeritics ASAP 2020 instrument, at 77 K ($-196 \text{ }^\circ\text{C}$) and 273 K ($0 \text{ }^\circ\text{C}$), respectively. Samples were first degassed at $90 \text{ }^\circ\text{C}$ for 1 h and then at $150 \text{ }^\circ\text{C}$ for 8 h under vacuum. The total surface areas (S_{BET}) were determined using the BET equation [31]. The total pore volumes (V_{sp}) were calculated from the amount adsorbed at a P/P_0 value of 0.995. The average pore sizes (w_p) were determined approximating the pore geometry to a cylinder. The external surface areas ($S_{t_{ext}}$), micropore areas ($S_{t_{micro}}$) and micropore volumes ($V_{t_{micro}}$) were estimated from t -plot method [32]. Mesopore distributions were determined applying the BJH method to the adsorption branch of the isotherms [33]. The thickness t -equation employed is the one proposed by Harkins and Jura [34,35]. The surface areas and volumes of narrow-neck micropores, S_{DR} and V_{DR} , were estimated from the CO_2 adsorption data using the DR equation [36].

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