



Synthesis and structural evaluation of freeze-cast porous alumina



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ARTICLE INFO

Article history:

Received 4 June 2014

Received in revised form 7 August 2014

Accepted 10 August 2014

Available online 12 August 2014

Keywords:

Alumina

Freeze-casting

Scanning electron microscopy

X-ray microtomography

Microstructure

Gas permeability

ABSTRACT

In this work we fabricated alumina samples by the freeze-casting technique using tert-butanol as the solvent. The prepared materials were examined by scanning electron microscopy and X-ray microtomography. Next, they were coated with sol-gel silica films by dip-coating. Permeability tests were carried out in order to assess the permeation behavior of the materials processed in this study. We observed that the sintering time and alumina loading showed a remarkable effect on both the structural properties and flexural strength of the freeze-cast samples. Nitrogen adsorption tests revealed that the silica prepared in this study exhibited a microporous structure. It was observed that the presence of silica coatings on the alumina surface decreased the CO₂ permeance by about one order of magnitude. Because of the similar kinetic diameters of nitrogen and carbon dioxide, the CO₂/N₂ system showed a separation efficiency that was lower than that observed for the He/CO₂ and He/N₂ systems. We noticed that increasing the feed pressure improved the separation capacity of the obtained materials.

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1. Introduction

It is well established that the membrane separation process shows several advantages, including relative simplicity, ease of use, and low energy consumption. It can be used to separate both liquid and gas mixtures [1,2]. Although there are several methods commercially available for the separation and capture of gas mixtures, they are energy expensive and, in some cases, environmentally unfriendly [3]. For these reasons, the membrane technology has achieved in the last years a great commercial and strategic importance.

An inorganic membrane usually consists of a macroporous support with successive layers deposited on it. The support provides mechanical strength to prevent membrane unit failure under operating conditions. In addition, it also shows low resistance to the permeate flow. The intermediate layers bridge the gap between the large and small pores observed, respectively, in the support and top layers. It is important to mention that only the top layer shows separation capacity [4]. Both the intermediate and top layers are usually deposited on the substrate by dip-coating [5–8].

Porous supports obtained by conventional methods may show tortuous pore networks with many constrictions and dead-end pores.

This behavior could impair their mass transport capacity. The freeze-casting technique is an attractive forming process for preparing materials with tailored pore frameworks. In addition, it is an environmentally friendly, cost effective, and easy scale-up method. It consists of the preparation of a stable colloidal suspension of ceramic particles, pouring it into a mold, freezing the suspension, removing the dispersing medium, and sintering the obtained material. In this technique the slurry particles are rejected by the solidification front and trapped between the growing crystals [9]. Samples obtained by freeze-casting exhibit ordered pore networks which are accessible diffusion pathways for gas permeation. A range of ceramic materials has been prepared by this method in different configurations, including flat sheets and hollow tubes [10–14].

In this work we obtained alumina samples by the freeze-casting technique using tert-butanol as the solvent. The as-prepared samples were examined by scanning electron microscopy (SEM) and X-ray microtomography (μ -CT). Next, they were coated with sol-gel silica films by dip-coating. Permeability tests were carried out in order to assess the separation capacity of the materials fabricated in this study.

2. Materials and Methods

2.1. Freeze-Cast Samples

The freeze-cast samples were obtained as shown in Fig. 1. Initially a solution of citric acid (CA/Aldrich/ $\geq 99.5\%$) and anhydrous tert-butanol

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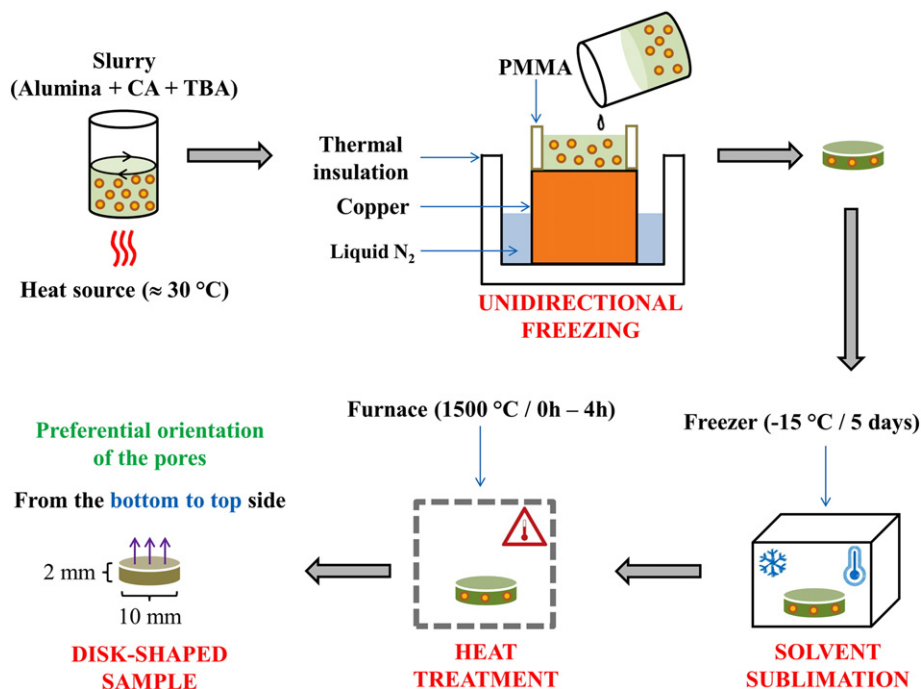


Fig. 1. Schematic of the steps used in this work for preparing the freeze-cast samples.

(TBA/Aldrich/ $\geq 99.5\%$) was prepared at 30 °C. CT3000SG alumina (Almatis) was added under strong stirring to the solution. According to the supplier, this material exhibits a mean particle size of about 1 μm and 99.8% purity. The as-prepared slurry was kept under sonication for 5 min. Slurries with alumina loadings ranging from 10 vol.% to 30 vol.% were prepared. The CA loading was kept at 0.5 wt.% of the alumina concentration. Next, the slurries were poured into molds designed as depicted in Fig. 1. These molds were composed of a copper plate of high thermal conductivity in the bottom side, whereas their walls were made of polymethylmethacrylate (PMMA). The top side of the mold was open so that the slurry surface was kept under atmospheric conditions. As a result, the solvent crystals obtained during the freezing step were stimulated to grow in the vertical orientation from the bottom side to the top one. Liquid nitrogen was used as a cooling agent in the freezing step. Liquid nitrogen was used because it leads to fast freezing rates, and consequently to a fine pore structure of the freeze-cast material [15,16]. The solvent removal step was performed by keeping samples in a freezer at -15 °C for at least 5 days. Next, these samples were heat treated in air at 1500 °C using a Thermolab furnace (Pt30%Rh/Pt6%Rh-thermocouple) and a heating rate of 2 °C/min. The sintering time ranged from 0 h to 4 h. It is worth mentioning that samples associated with a 0 h sintering were heated at 1500 °C and allowed to cool down to room temperature without holding them at the target temperature.

The freeze-cast samples were examined by SEM and $\mu\text{-CT}$. SEM was carried out with JEOL JSM-6360 LV and ASPEX EXPLORER microscopes. The samples used in the SEM examinations were not sputter coated before these tests. The SEM micrographs were obtained using a 10 kV accelerating voltage. Compositional analyses were performed using a NORAN EDS system available in the JEOL apparatus. $\mu\text{-CT}$ was carried out with a SkyScan 1172 high-resolution micro system. These tests were carried out using an X-ray voltage tube of 77 kV and a 0.5 mm thick aluminum filter. A CCD camera with 2000×1048 pixels was used to record the transmission of the X-ray beam across the samples. Three-frame averaging steps and a rotation step of 0.30° were used, covering a view of 180° . Smoothing and beam-hardening correction were applied to suppress noise and beam hardening artifacts. The morphological parameters addressed in this work were evaluated by

considering one hundred slices along the examined volume. The mean values were assessed by taking into account a 95% confidence level.

In order to observe the formation of solvent crystals during the freezing step, samples were examined using a two-stage solid-state Peltier device available in the $\mu\text{-CT}$ apparatus. The slurry of alumina, TBA, and CA was poured into a PMMA mold. Samples were examined while their bottom side was kept at about 0 °C. The three-point flexural strength of the sintered samples was assessed using a mechanical testing stage available in the $\mu\text{-CT}$ system. These tests were performed as described in ASTM C1674-11 [17]. Samples with dimensions of about $5 \text{ mm} \times 5 \text{ mm} \times 15 \text{ mm}$ were used in these tests. The flexural strength (σ) of the examined materials was evaluated using Eq. (1):

$$\sigma = \frac{3Fl}{2bh^2}, \quad (1)$$

where F represents the critical load at fracture, l the distance between the two supports pins, b the sample width, and h its height. It is worth mentioning that, in spite of the high porosity of the freeze-cast samples used in this study, they withstood the flexural tests (up to fracture) and did not crumble upon handling.

2.2. Sol-Gel Silica

The silica sol was obtained as follows. First, a solution of nitric acid (HNO_3 /Aldrich/65%), absolute ethanol (EtOH/Aldrich/ $\geq 99.5\%$), and deionized water was prepared at room temperature. Tetraethylorthosilicate (TEOS/Aldrich/98%) was slowly added under strong stirring to this solution. The molar ratio of TEOS:EtOH: H_2O : HNO_3 was kept at 1:3.8:6.4:0.085. The as-prepared solution was then heated at 90 °C for 3 h. A reflux cooler was used to prevent the solution evaporation. Aliquots of the obtained sol were used in the preparation of supported and unsupported membranes. Unsupported membranes were obtained by pouring the sol into a Petri dish and keeping it at 40 °C for 24 h. Supported membranes were fabricated by dipping freeze-cast samples in the sol. It is worth mentioning that the silica films were deposited on the bottom side of the freeze-cast samples. In this study we used dipping and withdrawing speeds of 5.7 cm/min. After

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