Available online at www.sciencedirect.com

SciVerse ScienceDirect

Ceramics International 38 (2012) 1943–1949

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Processing, structural characterization and performance of alumina supports used in ceramic membranes

Leonardo L.O. Silva [a], Daniela C.L. Vasconcelos [a], Eduardo H.M. Nunes [a], Lecino Caldeira [a], Vilma C. Costa [a], Ana P. Musse [b], Sueli A. Hatimondi [b], Jaílton F. Nascimento [b], Wilson Grava [b], Wander L. Vasconcelos [a,*]

[a] *Department of Metallurgical and Materials Engineering, Federal University of Minas Gerais, Avenida Presidente Antônio Carlos, 6627, Campus da UFMG, Belo Horizonte, MG, CEP: 31270-901, Escola de Engenharia, Bloco 2, Sala 2230, Brazil*

[b] *Petrobras/CENPES, Avenida Horácio Macedo 950, Cidade Universitária, Ilha do Fundão, Rio de Janeiro, RJ, CEP: 21941-915, Brazil*

Received 31 August 2011; received in revised form 27 September 2011; accepted 11 October 2011
Available online 21 October 2011

Abstract

Although there are various commercially available methods for the separation and capture of gas species such as CO_2 and H_2, they are energy expensive and in some cases environmentally unfriendly. The membrane separation process presents advantages such as its relative simplicity, ease of use, low energy consumption, and application in the separation of both liquid and gas mixtures. For these reasons, the membrane technology has achieved in the last years a great commercial and strategic importance. In this work we present a structural characterization of an alumina support, before and after the deposition of a titania film on its surface. The obtained asymmetric membranes are intended to be used in gas separation processes. The alumina supports and titania coatings were prepared by dry-pressing and sol–gel process, respectively. The processed samples were characterized by X-ray diffraction (XRD), nitrogen sorption, scanning electron microscopy (SEM), and X-ray microtomography (μ-CT). In order to evaluate the membranes performance, single-gas permeation experiments were performed at room temperature with nitrogen, helium, and carbon dioxide. We observed that although the alumina supports obtained in this work have not been submitted to any surface finishing procedure, the obtained membranes have potential application in gas separation processes. We observed that increasing the pressure feed leads to improving their separation capacity.

Keywords: Alumina; Titania; Support; Membrane; Sol–gel; X-ray microtomography

1. Introduction

Mulder [1] defined ‘‘membrane’’ as a selective barrier between two phases. Its primary function is to restrict totally or partially the transport of chemical species that compose these phases. According to Van de Water and Maschmeye [2], the membrane separation process presents advantages such as its relative simplicity, ease of use, low energy consumption, and application in the separation of both liquid and gas mixtures. In addition, it is possible to obtain membranes with tailored structures by using different materials including metals, polymers, glass, silica, alumina, and titania [3]. Although there are various commercially available methods for the separation and capture of gas species such as CO_2 and H_2, they are energy expensive and in some cases environmentally unfriendly [4]. For these reasons, the membrane technology has achieved in the last years a great commercial and strategic importance.

Inorganic oxide membranes have been developed over the last fifty years primarily for the separation of uranium isotopes during its enrichment. However, in the 1980s, the advantages of chemically inert ceramic membranes with well-defined pore structures encouraged researchers to investigate the gas separation properties and applications of inorganic membranes [5]. Inorganic membranes can be exposed to chemical surface modification processes, and also to cleaning procedures which organic membranes do not withstand. These processes allow

* Corresponding author. Tel.: +55 31 3409 1813.
E-mail addresses: eduardohmn@yahoo.com.br (E.H.M. Nunes), wlv@demet.ufmg.br (W.L. Vasconcelos).

0272-8842/$36.00
doi:10.1016/j.ceramint.2011.10.025

regenerating these materials, making them economically attractive.

An inorganic membrane generally consists of a macroporous support with successive thin layers deposited on it. The support must provide sufficient mechanical strength to prevent the membrane unit failure under the operating conditions. In addition, it also must have a low resistance to the permeate flow. According to Larbot [6], a ceramic support is commonly prepared by shaping a powder and sintering the obtained green body. The green bodies processing, where it is common the use of organic binders, is a critical step because it affects the properties and performance of the final material. These organic binders are eliminated during the heat treatment step. The intermediate layers bridge the gap between the large pores of the support and the small pores of the top layer. It is important to mention that only the top layer has separating capacities [7].

In this work we present a structural characterization of alumina support, before and after the deposition of a titania film on its surface. The obtained asymmetric membranes are intended to be used in gas separation processes. The alumina supports and titania coatings were prepared by dry-pressing and sol–gel process, respectively.

2. Experimental

First, a ceramic paste was prepared by mixing distilled water, polyvinyl alcohol (PVA – Aldrich), S3G alumina (Alcoa), and Alphabond hydratable alumina (Almatis). PVA is commonly used in the processing of ceramic materials as a binder. The Alphabond hydratable alumina also has binding properties, contributing to obtain ceramic supports with high mechanical strength. The relative amount of each component in the mixture was determined after their previous characterization. The particles morphology of the raw materials must be well controlled because it affects both the porosity and pore size of the support. The obtained ceramic paste had the following composition in weight: 70% S3G, 29% Alphabond, and 1% PVA. We added water enough to obtain a mixture of pasty consistency. The amount of water added is an important parameter because it gives the paste the necessary plasticity for shaping. Next, the obtained ceramic paste was shaped into a disc of 13 mm diameter and 1.5 mm thickness, using an uniaxial compression molder at a pressure of eight ton. The processed green bodies were heat treated in air at 800 °C, 1100 °C, 1300 °C, and 1500 °C for 1 h in a Lindberg/Blue oven. We used heating and cooling rates of 10 °C/min.

In this work a new methodology for the synthesis of sol–gel titania was used. Initially a solution of nitric acid (65% – Aldrich) and absolute isopropanol was prepared. Under strong stirring, the titanium isopropoxide (TIP – Aldrich) was slowly added in order to prevent the formation of precipitates. The polyethylene glycol was added to the sol after its previous dissolution in absolute isopropanol. The molar ratio TIP:isopropanol:HNO_3 was adjusted to 1:4:0.1. The supported membranes were obtained by dipping the supports in the titania sol and withdrawing them at a speed of 1.3 mm/min. Finally, the obtained samples were heat treated in air at 180 °C and 550 °C for 2 h.

The obtained supports were characterized by X-ray diffraction (XRD), nitrogen sorption, scanning electron microscopy (SEM), and X-ray microtomography (μ-CT). The XRD analyses were carried out in a Philips-PANalytical PW17-10 diffractometer, using Cu K_α radiation and operating at 40 kV and 30 mA. The diffractograms were recorded in the range of 20–90°, at a scan velocity of 0.06°/min. The nitrogen sorption experiments were performed in a Micromeritcs ASAP 2020, using samples preheated at 130 °C for until 48 h under vacuum. The SEM analyses were carried out with a FEI QUANTA 200F field emission scanning electron microscope (FESEM). The compositional analyses were carried out with an EDS system (EDAX – Pegasus Microanalyzer) available in the SEM equipment. The μ-CT tests were performed using a Skyscan 1172 high-resolution desktop X-ray microtomography system. A CCD camera with 2000 × 1048 pixels was used to record the transmission of the X-ray beam through the samples. Three-frame averaging and a rotation step of 0.30° were used, covering a view of 180°. Smoothing and beam-hardening correction steps were applied to suppress noise and beam hardening artifacts. The morphological parameters presented in this work were measured after considering one hundred slices along the analyzed volume for all studied samples. The mean values were obtained by considering a 95% confidence interval. All the morphological parameters addressed in this work have influence on mass transport phenomena in solids.

In order to evaluate the membranes performance, single-gas permeation experiments were performed at room temperature with nitrogen, helium, and carbon dioxide. The disc shaped membranes were placed in a modified Wicke–Kallenbach cell made of stainless steel. The gas flow through the membrane was measured with a soap film flow meter. The pressure difference across the membranes was measured with a MKS Baratron pressure transducer model 627B. Before each permeability experiment, the leak-free system was evacuated with an Edwards two stage vacuum pump model E2M2. A schematic representation of the gas permeation apparatus is shown in Fig. 1.

3. Results and discussion

XRD analyses revealed that increasing the heat treatment temperature leads to samples with higher crystallinity degree, where the α-phase is dominant. Fig. 2 shows a typical nitrogen adsorption/desorption isotherm of the obtained supports. According to IUPAC [8], it is a type II isotherm, typical of macroporous solids. We observed by means of the BET multipoint method that the obtained samples have specific surface areas of about 8 m^2/g.

Fig. 3 shows SEM micrographs of alumina supports obtained in this work. One observes the presence of coarse grains in these images. We believe that this is due largely to the high granulometry of the raw materials used in the green body processing step. Previous analyses revealed that both S3G

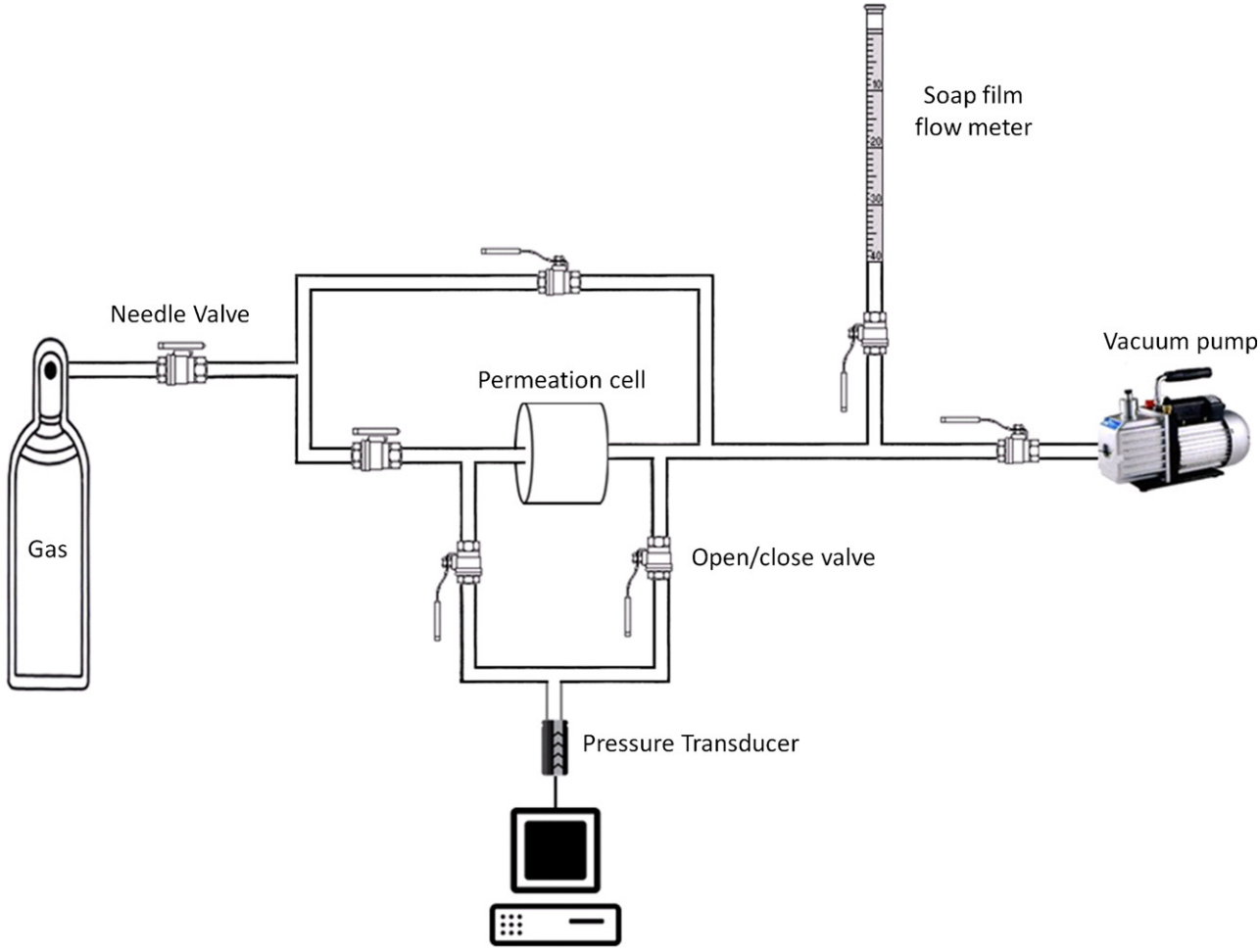

Fig. 1. Schematic representation of the gas permeation apparatus.

alumina and Alphabond hydratable alumina have mean particle sizes of about 7 μm. We also observed that the higher the heat treatment temperature, the more smooth are the shapes of the alumina particles.

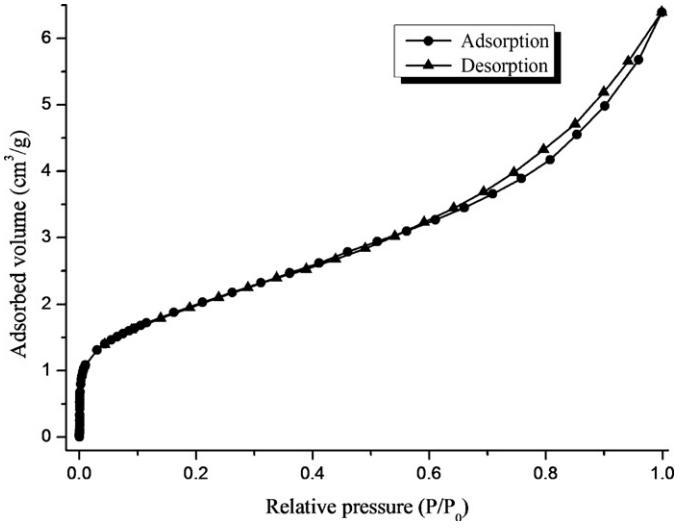

Fig. 2. Typical nitrogen adsorption/desorption isotherm of the obtained supports.

Fig. 4 shows a typical cross section obtained by μ-CT of alumina supports processed in this study. One observes a microstructure with non-homogeneous pore size distribution. In Table 1 we show the main morphological parameters measured. We observed that all samples have mean pore size (MPS) of about 23 μm. The object perimeter/area ratio (OPAR) is a parameter used to describe the complexity of a structure. According to Frisullo et al. [9], this parameter indicates the pore size distribution within the solid; the higher the value, the more finely distributed are the pores within the sample. We noticed that increasing the alumina heating temperature leads to structures with lower values of OPAR.

TP and TO are the total and open porosities, respectively. Open pores contribute to the permeability of both liquids and gases, whereas closed pores influence the mechanical strength of the material [10]. We observed that the higher the heat treatment temperature, the lower is the alumina porosity (see Fig. 5). Starting from the Fick's second law of diffusion, one can show that the ratio between the diffusion distances of an atom at two distinct temperatures is given by:

$$\frac{X_2}{X_1} = \sqrt{\frac{D_2}{D_1}} \quad (1)$$

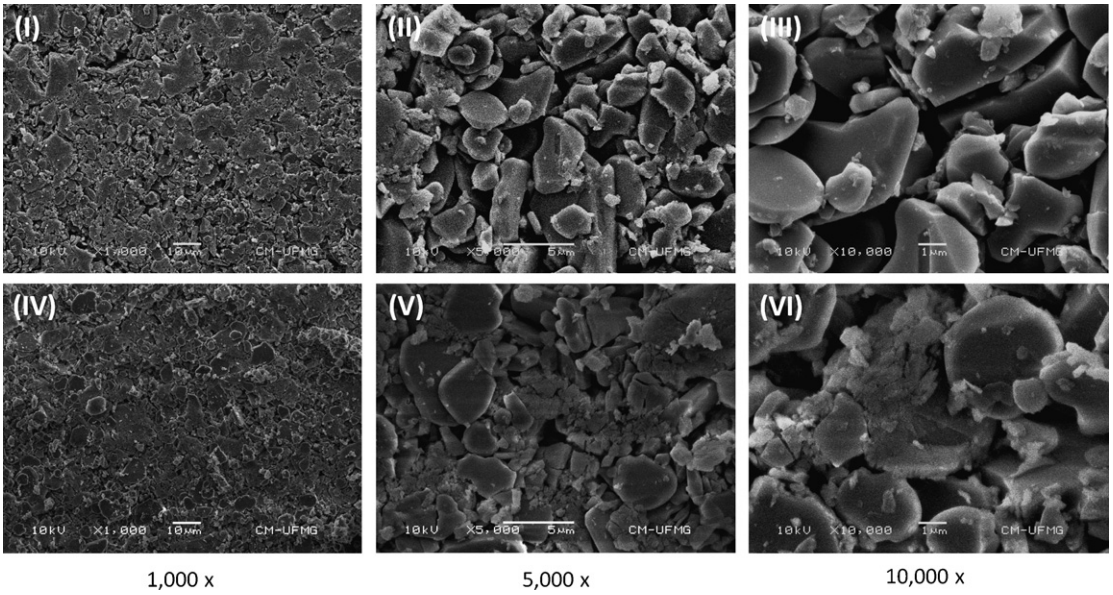

Fig. 3. SEM micrographs of alumina supports obtained in this work. (I–III) Green body; (IV–VI) support heat treated at 1300 °C.

where X and D are the diffusion distance and diffusion coefficient of the atom. Assuming T_1 = 800 °C and T_2 = 1500 °C, and taking into consideration the activation energy for diffusion of aluminum in alumina proposed by Kingery and Paladino [11] (477 kJ/mol):

$$X_2 \approx 38570 X_1 \quad (2)$$

Thus, it follows that increasing the alumina heat treatment temperature the densification degree also increases because the aluminum diffusion is favored at high temperatures. In an apparently contradictory way, the green body shows a porosity lower than that observed for the sintered samples. This is because pores of the green body are filled by the PVA used in its processing. During the heat treatment the PVA is removed, resulting in increasing the alumina porosity [12]. The high porosity shown by the sample heat treated at 800 °C could impair its mechanical stability, and also prevents its application in gas separation processes.

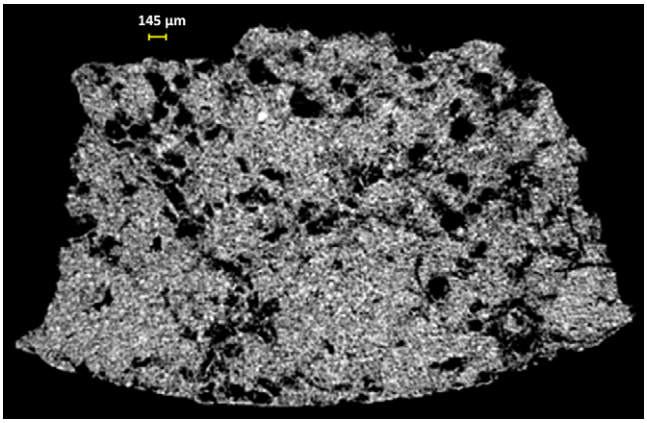

Fig. 4. Typical cross section obtained by µ-CT of the alumina supports produced in this study. The white and gray regions represent the solid phase.

The fragmentation index (FI) is an inverse index of connectivity and it is a measure of the relative convexity or concavity of the pores [13]. It was originally applied by Hahn et al. [14] to 2D images of trabecular bone. A low FI value signifies better-connected pore networks and has a negative index. On the other hand, a high FI indicates a more disconnected pore networks and has a positive index [9]. In general, the higher the heat treatment temperature, the higher is FI. This indicates that increasing the alumina heating temperature results in more disconnected pore networks. According to Burggraaf [15], systems with highly interconnected pore structures usually have tortuous pore networks with many constrictions and dead-end pores. This is not favorable for their transport properties and becomes more important the lower their porosity. On the other hand, systems with poorly interconnected pore structures show a low fluid permeability.

Based on the results presented until here, we have decided to carry out the single-gas permeation experiments in the alumina heat treated at 1300 °C, since it has presented a pore structure with proper characteristics to be used as support in gas separation processes. Fig. 6 shows the SEM micrographs of this support after its coating with the titania film. The presence of titania among the alumina particles is highlighted when this micrograph is compared with those shown in Fig. 3. This observation was also confirmed by EDS analyses.

Fig. 7 shows the CO_2 permeance as a function of the feed pressure for alumina support heat treated at 1300 °C, before and after the deposition of titania films on its surface. The dotted lines are used only as guide to the eyes. We observed that the influence of the titania coating is best viewed when the membrane heat treatment temperature is increased to 550 °C. Previous studies revealed that the rise of the titania heat treatment temperature leads to structures with lower pore connectivity [16]. The specific surface areas and pore volumes obtained by nitrogen sorption on titania self-supporting films are given in Table 2. From these data and the equation proposed

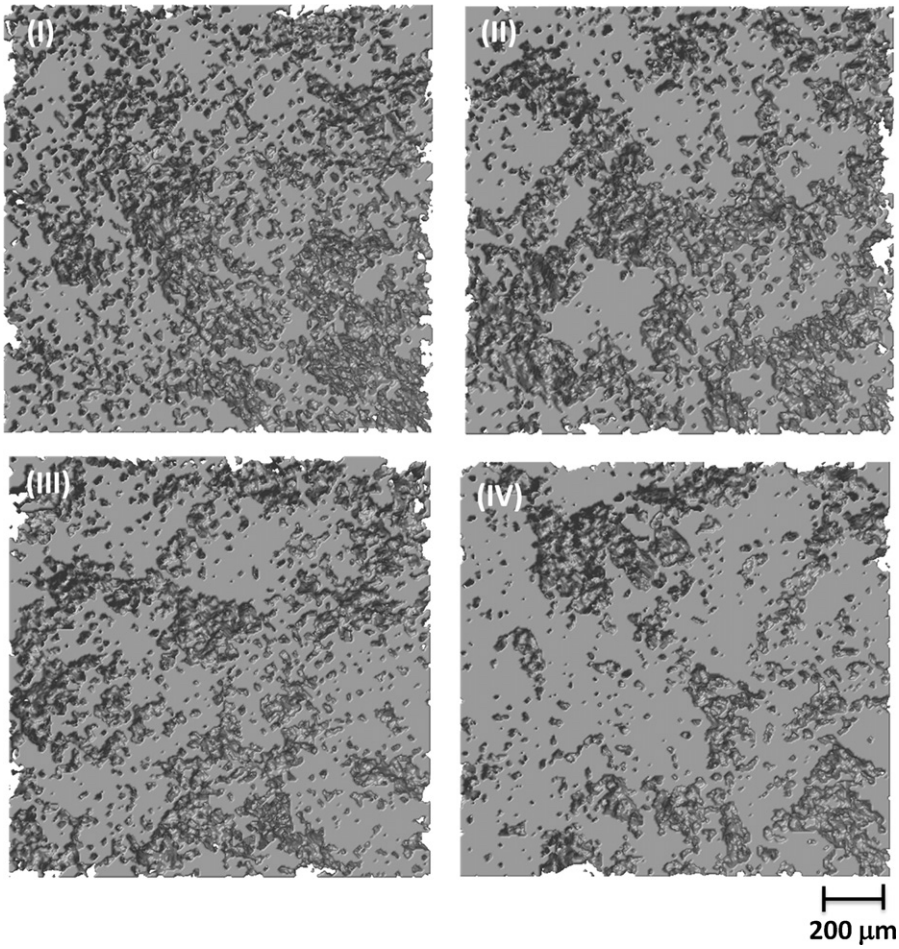

Fig. 5. Microstructural evolution of alumina during its heat treatment. 3D-models based on μ-CT results. (I) Sample heat treated at 800 °C; (II) heat treated at 1100 °C; (III) heat treated at 1300 °C; (IV) heat treated at 1500 °C.

by Vasconcelos et al. [17], we observed that the genus per unit volume of the titania films heat treated at 180 °C and 550 °C are 2.1×10^{19} cm^{-3} and 5.5×10^{15} cm^{-3}, respectively. As shown in Figs. 8 and 9, the supported membrane heat treated at 550 °C showed separation efficiency similar for the He/CO_2 and He/N_2 systems. Because of the similar kinetic diameter of nitrogen and carbon dioxide, the N_2/CO_2 system showed a separation efficiency lower than those observed for the He/CO_2 and He/N_2 systems; since helium is smaller and lighter than CO_2 and N_2, it diffuses much faster through the membrane framework [18].

Properties of gas flow in porous solids depend on the ratio of the number of molecule–molecule collisions to that of the molecule–wall collisions. When the number of intermolecular collisions is strongly dominant, the Poiseuille mechanism is present. It is well established that for systems in which this mass transport mechanism is dominant, the permeance (F_v) of a given gas is described by:

$$Fv \propto \frac{Pm}{\eta} \tag{3}$$

where P_m and η are the average pressure and dynamic viscosity of the gas. Based on this relation, we can conclude that at a given pressure:

$$F_v(\mathrm{He}) < F_v(\mathrm{N_2}) < F_v(\mathrm{CO_2}) \tag{4}$$

This was not observed in the analyzed membrane. This suggests that the Poiseuille mechanism is not dominant in the studied membrane, and indicates the absence of large amounts

Table 1
Main morphological parameters obtained by μ-CT for the samples analyzed.

Material	MPS (μm)	OPAR (μm^{-1})	TP (%)	OP (%)	FI (μm^{-1})
Green body	24.1 ± 0.1	0.05 ± 0.01	27.1 ± 0.4	10.6 ± 0.7	−0.024 ± 0.002
Alumina heat treated at 800 °C	22.5 ± 0.2	0.08 ± 0.01	43.4 ± 0.9	35.1 ± 1.4	−0.070 ± 0.002
Alumina heat treated at 1100 °C	22.8 ± 0.1	0.06 ± 0.01	33.7 ± 0.7	20.1 ± 1.4	−0.045 ± 0.001
Alumina heat treated at 1300 °C	20.7 ± 0.3	0.05 ± 0.01	30.2 ± 1.1	14.6 ± 1.5	−0.039 ± 0.002
Alumina heat treated at 1500 °C	21.7 ± 0.2	0.05 ± 0.01	26.4 ± 0.6	10.3 ± 0.9	−0.018 ± 0.002

MPS, mean pore size; OPAR, object perimeter/area ratio; TP, total porosity; OP, open porosity; FI, fragmentation index of pores.

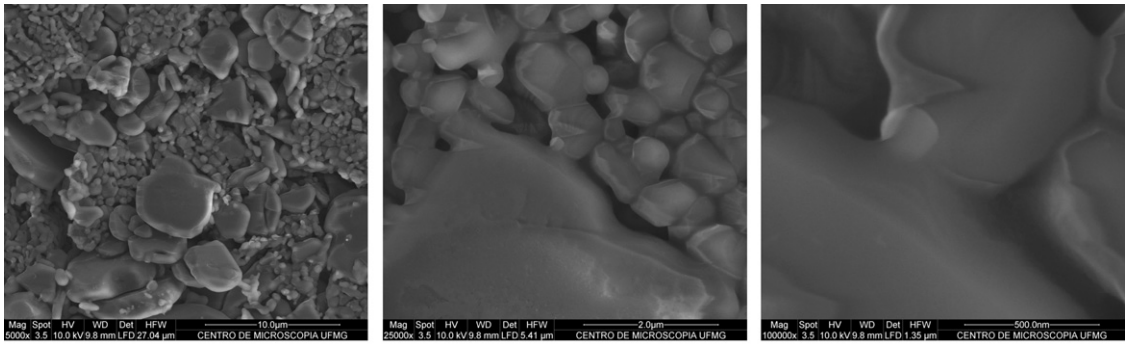

Fig. 6. SEM micrographs of alumina support heat treated at 1300 °C, after its coating with the titania film.

Table 2
Specific surface areas and pore volumes of titania self-supporting films.

Heat treatment temperature (°C)	Specific surface area (m^2/g)[a]	Pore volume (cm^3/g)[b]
180	187	0.08
550	7	0.01

[a] Evaluated by the BET multipoint method.
[b] Evaluated by the NLDFT method.

of defects in it. However, the linear increase of the permeance with the feed pressure reveals that the Poiseuille mechanism may be contributing to the gas flow through the membrane.

When the number of molecule–wall collisions is strongly dominant, the flow of a single gas through a capillary under the action of a pressure gradient can be described by the Knudsen equation:

$$F_{Kn} \propto \frac{1}{\sqrt{M}} \tag{5}$$

where F_{Kn} and M are the permeance and molecular weight of the gas. Thus, for membranes in which the Knudsen regime is dominant, the permeance plotted versus the feed pressure should give rise to a horizontal line because F_{Kn} is pressure independent. Moreover, it can be shown from Eq. (5) that:

$$\frac{F_{Kn}(\mathrm{He})}{F_{Kn}(\mathrm{CO_2})} \approx 3.3 \tag{6}$$

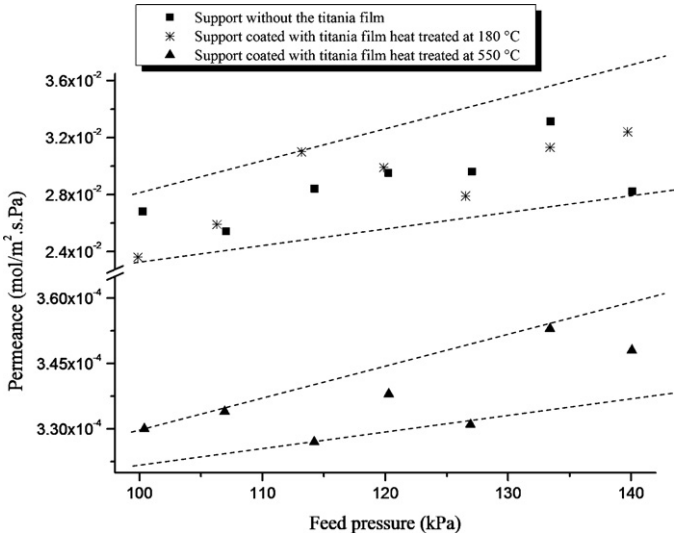

Fig. 7. CO_2 permeance as a function of the feed pressure for alumina support, before and after the deposition on its surface of titania films heat treated at 180 °C and 550 °C.

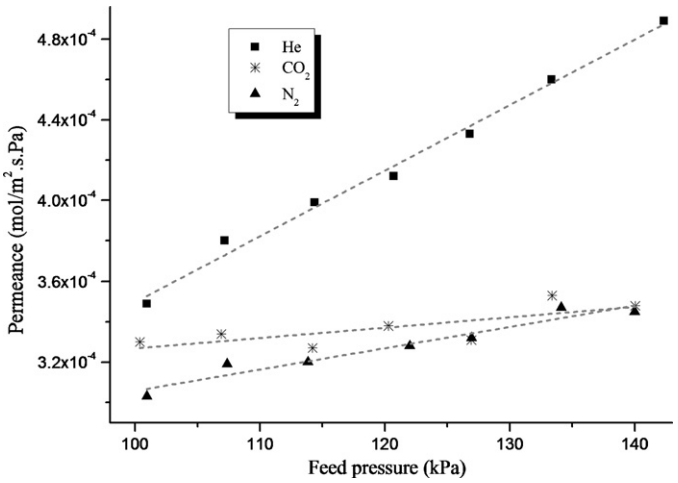

Fig. 8. Single gas permeances of He, N_2 and CO_2 through the membrane obtained after heat treatment at 550 °C.

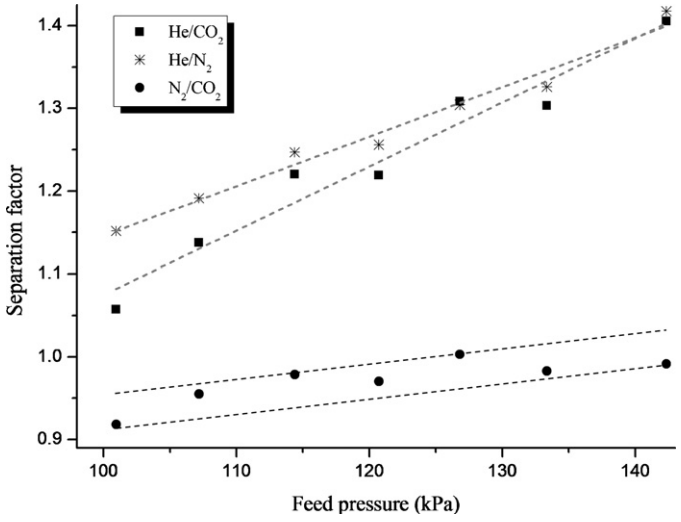

Fig. 9. Separation factors of He/CO_2, He/N_2, and N_2/CO_2 for the membrane obtained after heat treatment at 550 °C.

$$\frac{F_{Kn}(\mathrm{He})}{F_{Kn}(\mathrm{N_2})} \approx 2.6 \quad (7)$$

and

$$\frac{F_{Kn}(\mathrm{N_2})}{F_{Kn}(\mathrm{CO_2})} \approx 1.3 \quad (8)$$

We observed that the obtained membrane showed a separation factor lower than that expected for the Knudsen mechanism in the investigated pressure range. However, we must to consider that increasing the feed pressure leads to improving its separation capacity. It is an important result because the high thermal and mechanical stabilities of the alumina/titania system allow its use in high pressure applications.

4. Conclusions

XDR analyses revealed that increasing the heat treatment temperature leads to samples with higher crystallinity degree, where the α-phase is dominant. All obtained supports showed a type II nitrogen adsorption isotherm, typical of macroporous solids. We observed by means of the BET multipoint method that the obtained samples have specific surface areas of about 8 m^2/g. The SEM experiments showed the presence of coarse grains in their micrographs. We believe that this is due largely to the high granulometry of the raw materials used in the green body processing step. We also observed that the higher the heat treatment temperature, the more smooth are the alumina particles.

According to the μ-CT analyses, the alumina supports obtained in this work have mean pore size of about 23 μm. We also observed that the higher the heat treatment temperature, the lower is the alumina porosity. In an apparently contradictory way, the green body shows porosity lower than that observed for the sintered samples. This is because the pores of the green body are filled by the PVA used in its processing. During the heat treatment the PVA is removed, resulting in increasing the alumina porosity. In addition, the higher the alumina heating temperature, the more disconnected is its pore network.

We observed that although the alumina supports obtained in this work have not been submitted to any surface finishing procedure, the obtained membrane has potential application in gas separation processes. We observed that increasing the pressure feed leads to improving its separation capacity. This is an important result because the high thermal and mechanical stabilities of the alumina/titania system allow its use in high pressure applications.

Acknowledgements

The authors thank Andrea Bicalho and the UFMG Microscopy Center for their technical support in the XRD and SEM analyses, respectively. We also thank CNPq, Fapemig and Petrobras for the financial support of this research.

References

[1] M. Mulder, Basic Principles of Membrane Technology, fifth ed., Kluwer Academic Publishers, Dordrecht, 1996.
[2] L.G.A. Van de Water, T. Maschmeyer, Mesoporous membranes: a brief overview of recent developments, Top. Catal. 29 (2004) 67–77.
[3] E. Drioli, M. Romano, Progress and news perspectives on integrated membrane operations for sustainable industrial growth, Ind. Eng. Chem. Res. 40 (2001) 1277–1300.
[4] Y.T. Seo, S.P. Kang, H. Lee, C.S. Lee, W.M. Sung, Hydrate phase equilibria for gas mixtures containing carbon dioxide: a proof-of-concept to carbon dioxide recovery from multicomponent gas stream, Korean J. Chem. Eng. 17 (2000) 659–667.
[5] J.C.D. da Costa, G.Q. Lu, H.Y. Zhu, V. Rudolph, Novel composite membranes for gas separation: preparation and performance, J. Porous Mater. 6 (1999) 143–151.
[6] A. Larbot, Ceramic processing techniques of support systems for membrane synthesis, in: A.J. Burggraaf, L. Cot (Eds.), Fundamentals of Inorganic Membrane Science and Technology, Elsevier, New York, 1996, pp. 119–139.
[7] P.M. Biesheuvel, H. Verweij, Design of ceramic membrane supports: permeability tensile strength and stress, J. Membr. Sci. 156 (1999) 141–152.
[8] K.S.W. Sing, D.H. Everett, R.A.W. Haul, L. Moscou, R.A. Pierotti, J. Rouquérol, T. Siemieniewska, Reporting physisorption data for gas/solid systems with special reference to the determination of surface area and porosity, Pure Appl. Chem. 57 (1985) 603–619.
[9] P. Frisullo, A. Conte, M.A. Nobile, A novel approach to study biscuits and breadsticks using X-ray computed tomography, J. Food Sci. 75 (2010) E353–E358.
[10] P. Colombo, In praise of pores, Science 322 (2008) 381–383.
[11] A.E. Paladino, W.D. Kingery, Aluminum ion diffusion in aluminum oxide, J. Chem. Phys. 37 (1962) 957–962.
[12] J.W. Gilman, D.L. VanderHart, T. Kashiwagi, Thermal decomposition chemistry of poly(vinyl alcohol), Fire and Polymers II: Materials and Test For Harzard Prevention, vol. 11, American Chemical Society, 1995, pp. 161–185.
[13] K.S. Lim, M. Barigou, X-ray micro-computed tomography of cellular food products, Food Res. Int. 37 (2004) 1001–1012.
[14] M. Hahn, M. Vogel, M. Pompesius-Kempa, G. Delling, Trabecular bone pattern factor – a new parameter for simple quantification of bone microarchitecture, Bone 13 (1992) 327–330.
[15] A.J. Burggraaf, Important characteristics of inorganic membranes, in: A.J. Burggraaf, L. Cot (Eds.), Fundamentals of Inorganic Membrane Science and Technology, Elsevier, New York, 1996, pp. 331–434.
[16] L. Caldeira, D.C.L. Vasconcelos, E.H.M. Nunes, V.C. Costa, A.P. Musse, S.A. Hatimondi, J.F. Nascimento, W. Grava, W.L. Vasconcelos, Processing and characterization of sol–gel titania membranes, unpublished results.
[17] W.L. Vasconcelos, R.T. DeHoff, L.L. Hench, Structural evolution during sintering of optical sol–gel silica, J. Non-Cryst. Solids 121 (1990) 124–127.
[18] K. Kusakabe, T. Kuroda, S. Morooka, Separation of carbon dioxide from nitrogen using ion-exchanged faujasite-type zeolite membranes formed on porous support tubes, J. Membr. Sci. 148 (1998) 13–23.