Synthesis of mesoporous alumina using polyvinyl alcohol template as porosity control additive

Zoltán Ecsedi*, Ioan Lazău and Cornelia Păcurariu

„Politehnica" University of Timişoara, Faculty of Industrial Chemistry and Environmental Engineering, P-ţa Victoriei, No.2, 300006 Timişoara, Romania

Received 28 August 2007; received in revised form 1 October 2007; accepted 24 October 2007

Abstract

The effects of polyvinyl alcohol (PVA) template and calcinations temperatures on the characteristics of the alumina films were investigated. The samples were prepared by sol-gel method using aluminium triisopropylate precursor. The variation of microstructure, pore size and pore volume, were determined by nitrogen adsorption/desorption analysis and the macropore size distribution was determined using mercury porosimetry. TEM and SEM were used to observe the texture of these samples and the particle morphology. Experimental observation after drying and annealing shows that it is possible to produce crack free nanoporous alumina films using polyvinyl alcohol template. The obtained alumina samples have macroporous microstructure (with the average pore diameter d_{av} = 34.9 μm, for sample prepared with 42.5 wt% of PVA addition and annealed at 1000°C) with high portion of mesopores (with the average pore diameter D_{av} = 14.0 nm for the same sample).

Keywords: Sol-gel process, alumina film, mesoporous alumina, polyvinyl alcohol template

I. Introduction

The sol-gel process is applied to prepare amorphous and poorly crystalline materials, as nanoporous ceramics with high surface areas and small pore sizes [1]. Synthesis of ceramic materials with high specific surface area and controlled porosity is of great interest for application such as catalysis, catalyst support and porous membrane technology for separation processes [2,3]. For use in separation processes, the mesoporous ceramic films are deposited onto a macroporous ceramic support, made by traditional ceramic technology, which confers the required mechanical resistance for micro and ultrafiltration processes, for high pressures industrial applications [4].

Different types of additives are used to improve the textural properties of the films prepared by sol-gel route and deposited on a ceramic support. However, their influence on the process has not been clearly elucidateed yet [1]. Among these the polyvinyl alcohol is by far the most studied. Using PVA, less critical but more controllable drying and calcination procedures are obtained [5]. Polyvinyl alcohol is a semicrystalline polymer having hydroxyl groups, which give rise to inter- and intramolecular hydrogen bonds formation [6]. Most PVA solutions including PVA/water solution are well known to form thermally reversible gels at low temperature. Additions of polyvinyl alcohol to the colloidal precursor solution prevent the defects formation in alumina films [2].

During the thermal treatment, cracking and crushing of the film are the most frequently phenomena. If PVA is used as template the densification process can be controlled, and nanoporous alumina films with controlled porosity can be prepared [4]. The thickness of the porous films shrank to be about 60% of the initial one after a heat treatment at high temperatures, up to 950ºC, accompanied by an abrupt decrease in porosity [7].

This paper summarizes the study about production and textural characterization of alumina membranes with nanoporous structure, deposited on glass support and as unsupported thin films. The alumina samples were prepared by the sol-gel method, based on hydrolysis and condensation reaction of the aluminium triisopropylate. The effects of polyvinyl alcohol template and calcinations temperatures on the characteristics of the prepared membranes were investigated.

* Corresponding author: tel: +40 256 404168,
fax: +40 256 403060, e-mail: *ecsedizoltan@gmail.com*

II. Experimental Procedure

Alumina gel was synthesized by sol-gel method, using aluminium triisopropylate (Al ($O^iC_3H_7$) $_3$ Merck), water, nitric acid (Riedel-de Haën) and PVA – polyvinyl alcohol (Moviol 10–98). The sol was prepared under continuous stirring using an experimental installation build with a glass flask having attached water cooled refrigerator, mixer and thermometer as follows: 1 mole aluminium triisopropylate (Al ($O^iC_3H_7$) $_3$) was diluted with 20 moles of isopropanol (Chimopar) and than hydrolyzed with 200 moles of water. As peptizetion agent, 1 mole of nitric acid was added dropwise to yield a stable sol. The temperature was kept constant at 80ºC, using a thermostated oil bath. The turbulent state of the reaction liquid was achieved using a blade mixer adjusted at 300 rpm. When the increase of the viscosity was observed due to the condensation processes, different amount of polyvinyl alcohol (42.5–60 % wt) was added as aqueous solution. After PVA addition, the system was opened for the evaporation of the alcohol and water until increasing of viscosity is observed. The as-prepared viscous sol was deposited as a thin film into Petri dishes, where gelation took place. The formed film has been dried 24 hours in normal conditions at room temperature, followed by 4 hours at 90ºC in a drying stove, than annealed at different temperature between 600–1000ºC. The used hydrolysis molar ratio, $r = H_2O : Al(O^iC_3H_7)_3$, pH and dilution agent ratio were determined in previous work [4]. In order to study the influence of PVA on the film porosity, samples were prepared with different PVA content in range of 1.85–3.75 g disolved in 50 ml distilled water and added to 250 ml sol containing 10 g aluminium triisopropylate.

The samples macroporosity was determined by mercury porosimetry (Pascal 240, Porotec) and the textural properties were determined using transmission electron microscopy (PHILIPS EM 201) and scanning electron microscopy (Hitachi S4700). The pore size distribution, pore volume, average pore size and surface area were determined by nitrogen adsorption/ desorption porosimetry (NOVA 2200, Quantachrome). The samples were previously degassed to below 6.7 kPa at room temperature and analyses were performed, using liquid nitrogen. The equilibration interval was 5 s. Surface areas were calculated from the isotherm data using the Brunauer–Emmet–Teller (BET) method.

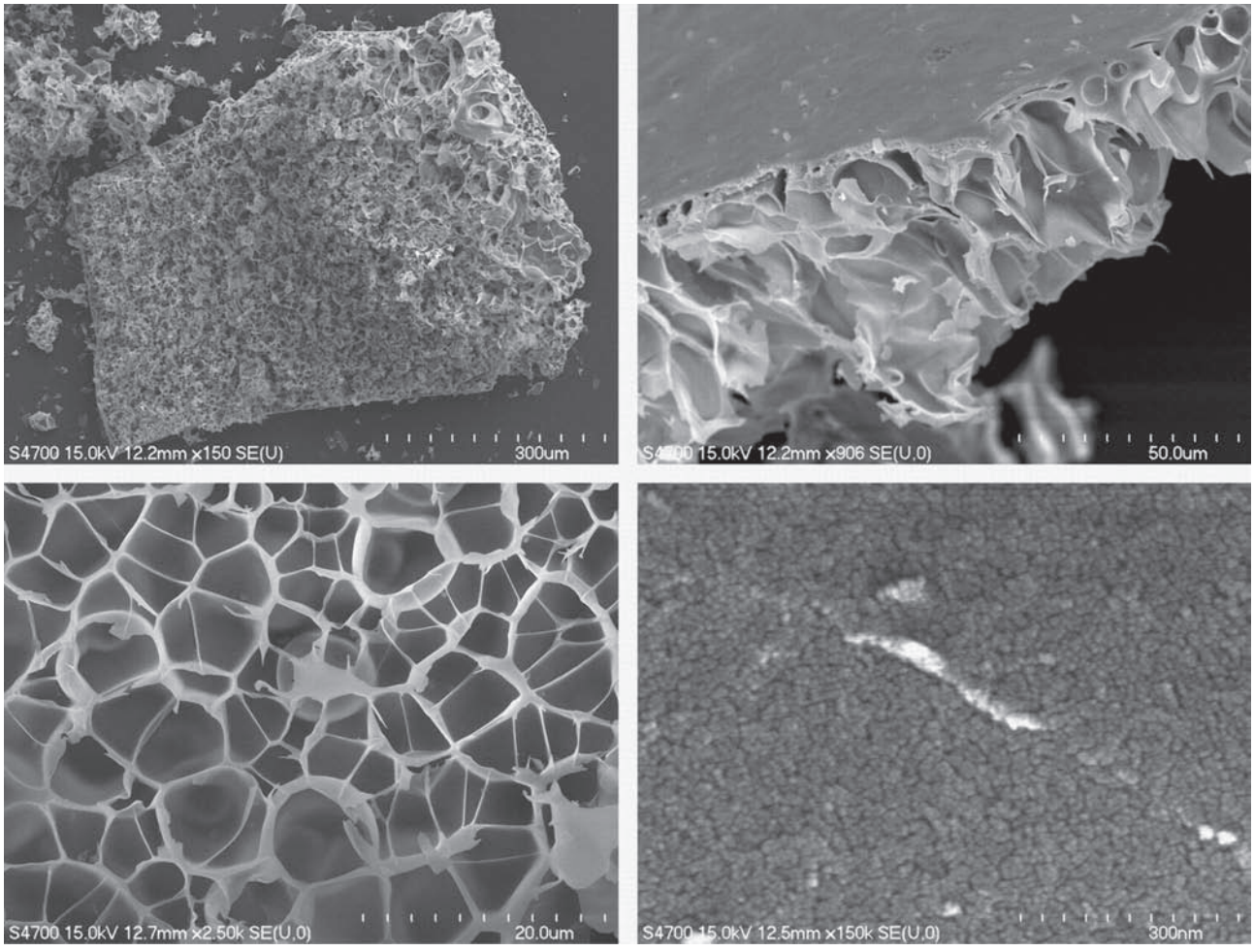
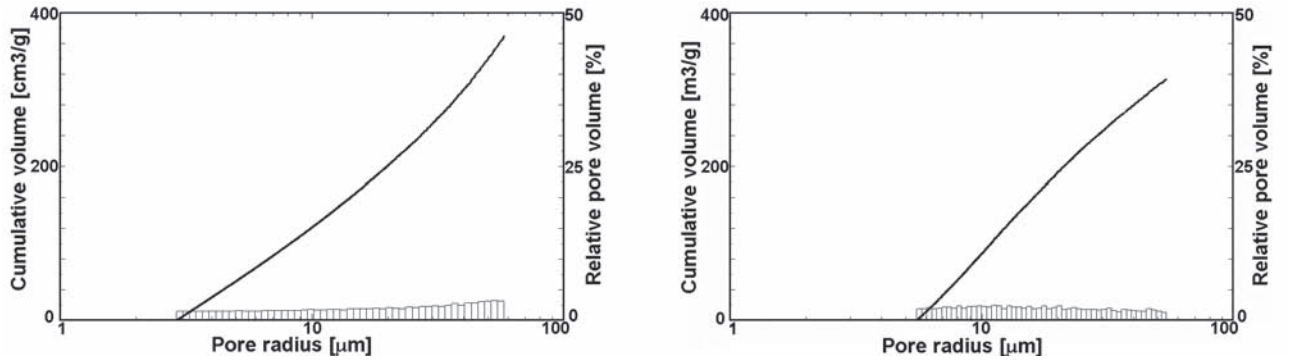


Figure 1. SEM images (at different magnifications) of the alumina film prepared with 60 wt% of PVA and annealed at 1000°C



a) b)

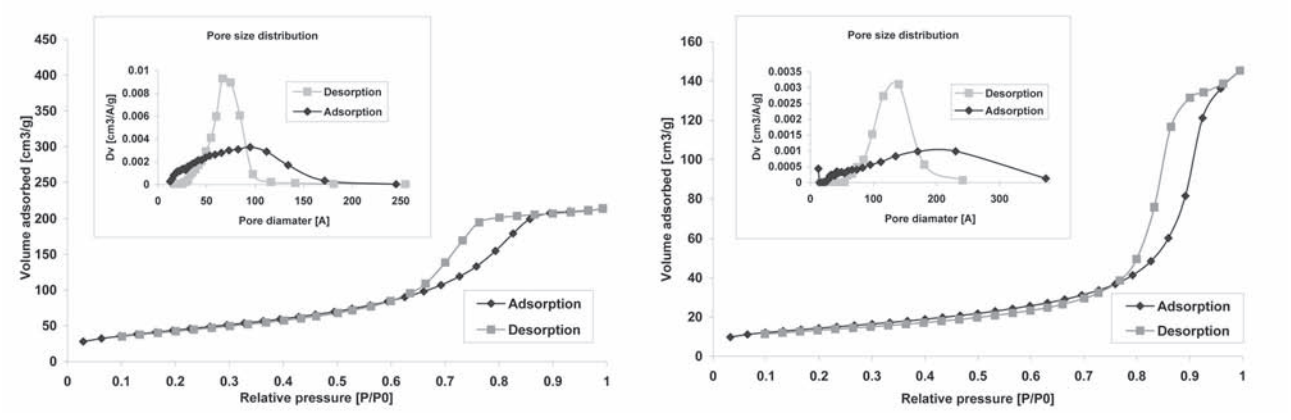
Figure 2. Pore size distribution of samples annealed at 1000°C: a) sample prepared with addition of 42.5 wt% PVA and b) sample prepared with addition of 60 wt% PVA.

Pore diameter distributions and cumulative pore volumes were determined with the Barret–Joyner–Halenda (BJH) method using the adsorption and desorption data. The total pore volume, *Vp*, was derived from the amount of vapor adsorbed at a relative pressure close to unit, by assuming that pores filled subsequently with condensed adsorbate in the normal liquid state.

III. Results and Discussion

The morphology of the alumina membrane prepared with 60 wt% of PVA and annealed at 1000ºC with thicknesses of about 20–40 μm is presented in Fig. 1. The SEM images of the sample show wormhole-like macrosized and relatively ordered pores, with diameters in range of 5–20 μm. The macroporous structure of the alumina membranes obtained using different amounts of PVA has been confirmed by mercury porosimetry. For the sample with 42.5 wt% of PVA addition, the pore size distribution chart (Fig. 2a) shows relatively wide range of pore sizes with the average pore diameter of 34.9 μm and 31.0 % of total macroporosity. For the sample with 60 wt% of PVA addition the pore size distribution chart (Fig. 2b) shows also relatively wide range of pore sizes with the average pore diameter of 31.3 μm and higher total macroporosity of about 56.7 %.

In order to evidence the presence and quantity of mesopores in the films, N_2 adsorption and desorption hysteresis curves were obtained. The samples present type IV isotherm (definition by IUPAC), which is characteristic for mesoporous materials (Figs. 3 and 4). The physisorption measurements reveal a high BET surface area and a narrow pore size distribution (inset Figs. 3 and 4). The experimental results show that the specific surface area is influenced by the annealing temperature while the mesopore size and the total pore volume are influenced both by the amount of PVA and the annealing temperature (Table 1). The average mesopore diameter and the total pore volume decreased with increasing amount of PVA. Increasing the sintering temperature the BET specific surface area and the total pore volume were decreasing rapidly due to the decay of the small pores during the sintering process. This lead to increase of the average mesopore diameter of the samples obtained at higher temperature. The pore diameter, cal-



a) b)

Figure 3. Nitrogen adsorption-desorption isotherms and pore size distribution (insets) of mesoporous alumina films prepared with 42.5 wt% of PVA addition and annealed at: a) 800°C for 1h and b) 1000°C for 1h.

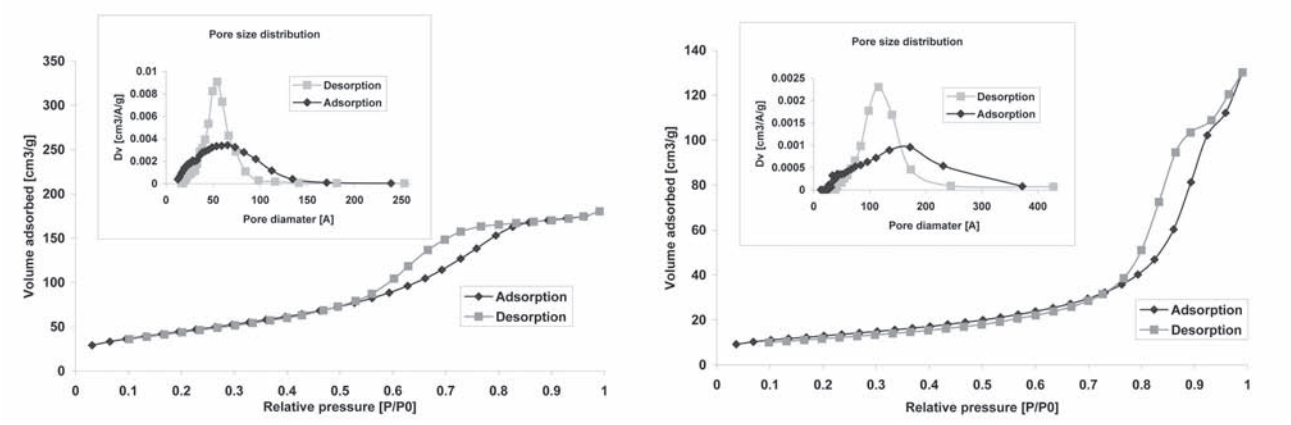


Figure 4. Nitrogen adsorption-desorption isotherms and pore size distribution (insets) of mesoporous alumina films prepared with 60 wt% of PVA addition and annealed at: a) 800°C for 1h and b) 1000°C for 1h.

Table 1. Characteristics of the alumina films

Sample	BET surface area [m^2/g]	Total pore volume [cm^3/g]
42.5 wt% of PVA (800°C)	164.5	0.33
42.5 wt% of PVA (1000°C)	51.3	0.22
60 wt% of PVA (800°C)	168.1	0.28
60 wt% of PVA (1000°C)	46.4	0.20

culated from the desorption branch of nitrogen adsorption-desorption isotherms, of sample sintered at 1000°C is larger than that of sample sintered at 800°C.

Transmission electron microscopy image of the mesoporous alumina membranes prepared using 42.5 wt% of PVA and annealed at 800°C (Fig. 5) confirms the presence of nanosized alumina particles with diameter in the range of 10–20 nm and shows no significant order in pore arrangement. The electron diffraction pattern (inset in Fig. 5) and XRD diffraction pattern (Fig. 6) of the same sample correspond to cubic γ-Al_2O_3 (a=7.939Å).

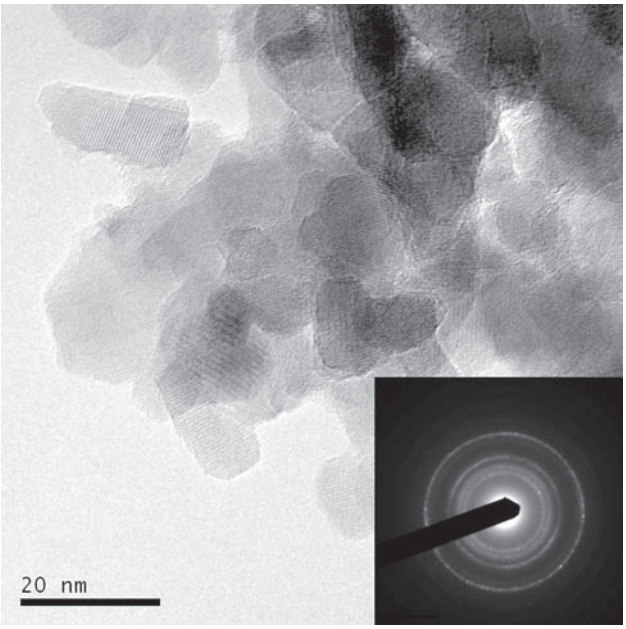


Figure 5. TEM image of the alumina film prepared with 42.5 wt% of PVA and annealed at 800°C and the electron diffraction pattern of a region (inset)

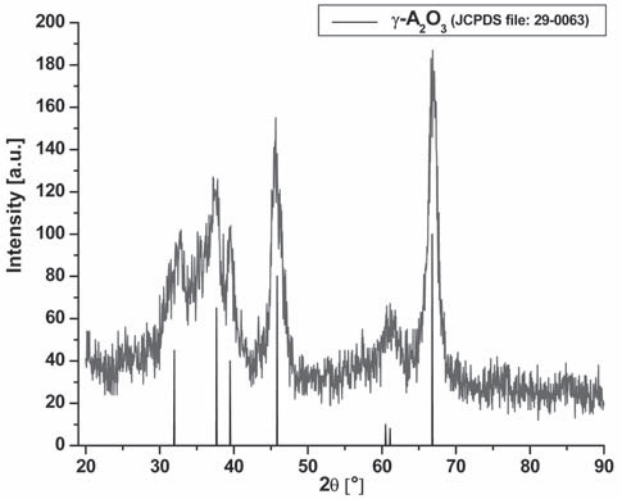


Figure 6. XRD pattern of the alumina film prepared with 42.5 wt% of PVA and annealed at 800°C

IV. Conclusions

The obtained results prove the possibility of producing mesoporous crack-free Al_2O_3 ceramic films by sol-gel synthesis using aluminum triisopropylate precursor. The obtained alumina membranes had macroporous texture, with the average macropore diameter in the range of 31.3–34.9 μm for temperatures in the range of 800–1000°C (confirmed by mercury porosimetry and SEM). The total macroporosity was in the range of 31–57 % and increased with the increase of the amount of PVA.

The mesoporosity of obtained membranes was confirmed by nitrogen adsorption/desorption isotherms. The average pore diameter and specific surface area were in the range of 5.3–22.8 nm and 46–168 m^2/g, respectively, for the samples annealed at temperature in the range of 800–1000°C.

The TEM images of the mesoporous alumina membranes showed that they consisted of alumina particles with the average diameter in the range of 10–20 nm.

The process of inducing nanometrical pore sizes in the crack-free alumina films requires a strict control of processing conditions. Textural characteristics and the nanometrical pore dimensions enable applicability of these membranes in ultrafiltration processes.

Acknowledgements: Some of these results were attained in the framework of National Excellency Research Program (CEEX-MATNANTECH), Contract No.51/2006.

References

1. C.J. Brinker, G.W. Scherer, *Sol-Gel Science*, Academic Press, Boston, 1990.
2. Y.-S. Lin, A.J. Burggraaf, "Preparation and characterization of high-temperature thermally stable alumina composite membrane", *J. Am. Ceram. Soc.,* **74** (1991) 219–224.
3. B. Xu, T. Xiao, Z. Yan, X. Sun, J. Sloan, S.L.Gonzales-Cortes, F.Alshahrani, M.L.Green, "Synthesis of mesoporous alumina with highly thermal stability using glucose template in aqueous solution system", *Microporous Mesoporous Mater.,* **91** (2006) 293–295.
4. Z. Ecsedi, A. Toth, L. Gagea, "Alumina films prepared by sol-gel method with applications in separation processes", pp. 248–255 in *Proceedings of the Romanian International Conference on Chemistry and Chemical Engineering*, Vol. 1, (S.08), Printech, Bucharest, 2005.
5. L. Shi, N.-B. Wong, "Preparation and characterization of alumina membranes and alumina-titania composite membranes", *J. Mater. Res.,* **14** [9] (1999) 3599–3603.
6. J.H. Choi, W.S. Lyoo, H.D. Ghim, S.-W. Ko, "High molecular weight syndiotacticity-rich poly (vinyl alcohol) gel in aging process", *Colloid. Polym. Sci.,* **278** (2000) 1198–1204.
7. A. Matsuda, Y. Matsuno, M. Tatsumisago, T. Minami, "Changes in porosity and amounts of adsorbed water in sol-gel derived porous silica films with heat treatment", *J. Sol-Gel Sci. Technol.*, **20** (2001) 129.