

Preparation and characterization of multilayer mesoporous γ -alumina membrane obtained via sol-gel using new precursors

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In this paper, a mesoporous γ -alumina membrane coated on a macroporous α -alumina support via sol-gel method has been reported. A crack-free γ -alumina membrane was obtained by adding PVA to the alumina solution and optimum parameters of roughness, temperature and porosity were achieved. The support was dip-coated in different solutions using two new different solvents with different particle size distributions. Using these two solvents led to the uniform distribution of pore size in the final membrane. The alumina sols showed particle size distributions in the range of 20 to 55 nm which was measured by a DLS Zeta Sizer. X-ray diffraction technique, atomic force microscopy and scanning electron microscopy were used to characterize the membrane layer. XRD and DTA data for the γ -alumina membrane showed its thermal stability up to around 600 °C. The thickness of the mesoporous γ -alumina membrane was about 4 μ m with 16 nm of surface roughness and 5 nm pore size. The resultant crack-free mesoporous membrane shows that the membrane preparation procedure was optimum. In this work, it has been investigated the performance of γ -alumina membranes for single gas permeation and separation of binary gas mixtures.

Keywords: *mesoporous; macroporous; coating; alumina; sol-gel*

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1. Introduction

Industries are improving the separation technology to reduce their expenses. Adsorption and separation using membrane are two developed technologies which represent great asset in research and improvement. The first step in any separation procedure is membrane material selection. Inorganic membranes, particularly ceramic membranes, have several advantages, such as high mechanical strength, high longevity, thermal and chemical stability, easy access, reasonable cost, selectivity and reliability. These membranes are also suitable for high pressure environments. Therefore, they are good candidates for separation procedures [1]. The use of ceramic membranes in industry has increased, because most chemical and petrochemical processes occur at high temperature

in the presence of corrosive gas. Common ceramic membranes are made of silica, titania, zirconia and alumina [2–7].

Ceramic membranes consist of two main parts: a sublayer or support and a thin separation membrane layer. The final step in the multilayer preparation route involves synthesis of a thin separation top layer. Formation of such a layer with very small pores requires an appropriate sol consisting of very small nanometer-sized particles [8]. Nanostructure and mesoporous materials can be easily prepared using a colloidal sol-gel process. This process is based on metallic alkoxide and water suspension [9, 10]. Some organic stabilizers are used to accelerate or control the rate of hydrolysis in metal alkoxides as well as improve the adherence, transparency, and the quality of the corresponding films [11–15]. The membrane stability has not been investigated systematically by studying important parameters, such as the structural

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characteristics of the ceramic material (roughness, phase behavior, crystallinity, thermal stability, surface area).

In this research, α -alumina disks have been used as supports for a thin separation γ -alumina membrane. The sublayer preparation procedure was examined carefully and optimum parameters for roughness, temperature and porosity were achieved. The membrane included five thin layers, which were prepared using a combination of two new solvents. Also, the parameters which affect the alumina membrane with industrial quality were investigated. Different parameters, such as homogeneity of colloidal solution, additives, working temperature, roughness of the membrane surface, membrane thickness and porosity of the membrane, were optimized. The working temperature was increased and surface roughness and thermal stability were improved. The membrane had a uniform distribution of pore size. The final membrane can be used for the separation of binary gas mixtures.

2. Experimental

The sublayers were made of commercial alumina powders using a single-axis press and sintering process. The roughness properties of sublayers were investigated and their porosity was estimated by Archimedes principle. The membrane was made of multilayer consisting of macroporous α -alumina support and mesoporous γ -alumina thin separation layer. The particle size of the sols was measured using dynamic light scattering (DLS) analysis. The heat treatment cycle was investigated using thermo-gravimetric analysis (TGA). The phases of the alumina layer were studied using X-ray diffraction analysis (XRD). Surface properties and membrane pores size were investigated using atomic force microscopy (AFM) and field emission scanning microscopy (FESEM).

2.1. Sublayer preparation

In order to prepare α -alumina sublayer, alumina powder (Baikalox France, 99.99 % purity, 0.3 μm average size and 6 m^2/g specific surface area) was

used. The α -alumina disks with 4.5 cm diameter and 2 mm thickness were prepared using a single axis press at 90 MPa pressure. Sublayers should be thick enough to have good strength besides high permeability. For enough phase transformation to α -alumina, the alumina disks were sintered at different temperatures of 1300, 1400 and 1500 $^{\circ}\text{C}$.

2.2. Membrane layer preparation

Aluminium tri-sec butylate ($\text{C}_{12}\text{H}_{27}\text{AlO}_3$), ethanol, isopropanol, polyvinyl alcohol (PVA) [$\text{CH}_2\text{CH}(\text{OH})_n$], nitric acid and distilled water were used to prepare the alumina colloidal sol. All of resource materials were purchased from Merck Germany. Colloidal boehmite sol (aluminium hydroxide) was prepared by adding 5.1 mL of aluminium tri-sec butylate to the solvent and stirring for 30 min. Water was added drop by drop to the solution to complete the hydrolysis reaction. Nitric acid (1 M) was added to the solution after alcohol evaporating. Nitric acid changed the color of the solution from milky to semitransparent. The solution was refluxed for 18 hours. After 16 hours of refluxing, PVA solution (3.5 g/L) was added to the main sol. PVA controlled the drying stage. The sols were prepared with different PVA content. Colloidal alumina sols were prepared without any agglomerations.

2.3. Dip-coating

α -alumina disks were dip-coated with the alumina colloidal sol at different speeds and immersion times. A thin sol was used for dip-coating and the coating stage was repeated five times. The drying stage is very sensitive and should occur slowly to prevent cracking of coatings. The coatings were dried in a clean room with 80 % humidity at ambient temperature for one day. They were then dried at room humidity for one more day. These conditions were similar to previously reported [16].

2.4. Heat treatments

The coating was heated up to 200 $^{\circ}\text{C}$ and this procedure was repeated after each dip-coating process. After the fifth coating, the specimens were heated up to 600 $^{\circ}\text{C}$ until γ -alumina

transformation was completed. PVA was removed from the coating layer because of heating up to 600 °C. The heating rate was 1 °C/min. Fig. 1 shows schematically the drying cycle of an alumina membrane layer up to 200 °C.

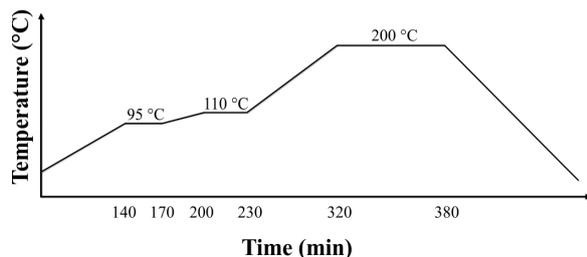


Fig. 1. Schematic graph of the drying cycle of an alumina membrane layer on the α -alumina support.

2.5. Evaluation methods

The roughness of the sublayers was measured using a roughness checker (Surtronic 25). The density and porosity were measured based on Archimedes principle (ASTM C20-92). The particle size of colloidal sols was specified using Zeta Sizer, Malvern Canada (ZEN3600 Zeta Sizer). 15 mg of alumina powder dried at 200 °C was heated up to 800 °C to identify DTA curve and perform the thermal analysis. The X-ray diffraction technique was utilized to determine the alumina phase transformation temperature using Bruker AXS D-8. The microstructure of the layer was examined using a FESEM-Hitachi S-4160. The surface topography of the membrane layer was investigated by the AFM technique using a CP Research System.

3. Results and discussion

3.1. Preparation of α -Al₂O₃ support

Appropriate support is needed to have a perfect membrane. The supports must have high thermal and mechanical stability, narrow size distribution and corrosion resistance. Conventional α -Al₂O₃ supports are usually used [17]. The macroporous α -alumina disks have been sintered at

different temperatures. Fig. 2 shows the SEM image of the surface of a symmetric α -Al₂O₃ support which was sintered at 1400 °C. The support surface is homogeneous without noticeable cracks. The image also shows that the average pore size of the support is about 200 nm. The porosity of the supports was measured using the Archimedes principle and is shown in Table 1.



Fig. 2. SEM image of the surface of an α -Al₂O₃ support.

Table 1. Porosity of the supports.

Sintering temperature (°C)	Porosity (%)
1300	43
1400	33
1500	17

The supports which were sintered at 1300 °C and 1400 °C have higher porosity compared to the supports which were sintered at 1500 °C. Although the mechanical and thermal stability is higher in the supports which were sintered at 1500 °C, but 17 % porosity is not sufficient for high permeability. Adequate sintering is needed for appropriate adherence between the support and membrane. Membrane properties could be affected by the interaction of support and separation layer, because this may lead to the appearance of defects and cracks upon calcination. Thermal expansion coefficients of the support and membrane should be of the same order. Pore size and distribution, porosity, roughness, topography of the surface and wetting ability must be considered for each support [3].

3.2. Roughness of the support

Supports of good quality enable us to obtain a perfect membrane. Roughness analysis was performed on the supports which were sintered at 1300, 1400 and 1500 °C. Table 2 compares the roughness of the supports.

Table 2. Roughness analysis of the supports.

Temperature (°C)	R _a (μ m)	R _p (μ m)	R _v (μ m)
1300	0.49	0.66	0.89
1400	0.26	0.47	0.58
1500	0.31	0.53	0.66

The quantity R_a is the average roughness, R_p is the maximum of the peak and R_v is the maximum of the valley. Roughness values of the specimens which were sintered at 1400 and 1500 °C are appropriate for coating. Low roughness of the support is needed to achieve a complete coating and perfect membrane. It was used the supports which were sintered at 1400 °C based on the porosity and roughness data.

3.3. Membrane characterization

Aluminium tri-sec butylate was hydrolyzed to prepare a colloidal sol. A fine and stabilized colloidal sol of boehmite (AlO(OH)) was prepared. Van Gestel et al. [18, 19] used an alumina colloidal sol for preparation of the intermediate layer of a membrane. In this research, two new different solvent types and additives were considered and compared to obtain a perfect colloidal sol. The colloidal sol of alumina was prepared using two different types of solvents. The sols using ethanol as a solvent, named Al-Et-F, and PVA as an additive, named Al-Et-F-PVA as well as the sols using isopropanol as a solvent, named Al-IP-F and PVA as an additive, named Al-IP-F-PVA. Table 3 shows the specification of the sols. The particle size of the sols was measured using Zeta Sizer (DLS). The particle size of the sol affected the porosity of the membrane. Smaller pores were obtained from sols with smaller particle size.

3.3.1. Effect of solvent type on particle size of colloidal sol

Fig. 3 illustrates the particle size distribution of Al-Et-F and Al-IP-F. As can be seen the particle size of Al-Et-F is smaller than that of Al-IP-F, therefore, ethanol is better solvent for preparing colloidal sols with smaller particle size.

Table 3. Specifications of the alumina colloidal sols.

Name of the sol	Average particle size (nm)	Particle size distribution (nm)
Al-Et-F	27	20 – 55
Al-Et-F-PVA	36	25 – 90
Al-IP-F	45	30 – 150
Al-IP-F-PVA	70	45 – 200

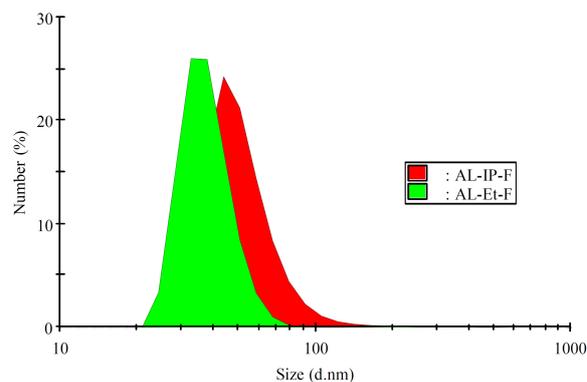


Fig. 3. Particle size distribution of alumina colloidal sols Al-Et-F and Al-IP-F.

Isopropanol has higher viscosity compared to ethanol, so the movement of particles is more difficult and particles stay together and agglomerate. Particle size in isopropanol is bigger than in ethanol.

3.3.2. Effect of PVA additive on particle size of colloidal sols

Particle size increases with the addition of PVA. The particles stay together because of interparticle connection by adding PVA. The sublayers were coated twice using Al-IP-F-PVA which had a larger particle size and better distribution. It suppressed the penetration of smaller particles to the sublayer

pores; therefore, the sublayers had adequate permeability. The sols with smaller particle size were prepared using ethanol as a solvent. The sublayers were coated three times with Al-Et-F-PVA colloidal sols.

3.3.3. Thermal analysis of alumina colloidal sol

Fig. 4 presents the TG and DTA curves of alumina gel. The TG curve of the sample shows that the weight of the specimen decreases nearly 8 % till 150 °C. This is because of H₂O vaporization and the associated endothermic peak in DTA curve proves this. At this stage there are exothermic peaks in each DTA curve of the samples which can be attributed to decomposition of PVA additive and combustion of the organic groups by releasing of CO₂ and H₂O. Thermal analysis was performed to assess the stability of the methyl groups. According to the analysis, it can be seen that it is appropriate to calcine the modified precursor at 600 °C in order to get the modified alumina particles. These results have been proved by other researchers [20, 21].

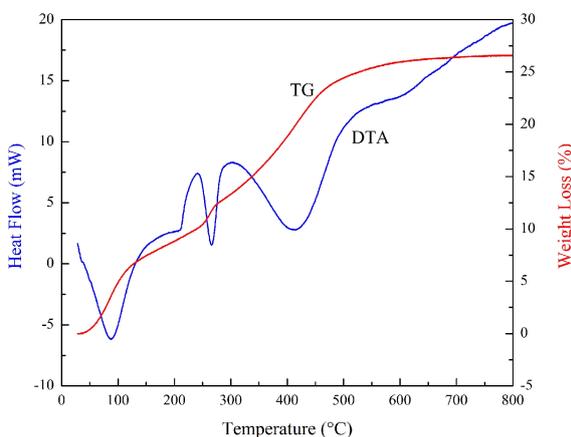


Fig. 4. TG and DTA curves of alumina gel.

3.3.4. The crystal structure of the alumina layer

The phase transformation temperature of the alumina coating was specified using XRD analysis. Fig. 5 presents the X-ray diffraction patterns of Al-Et-F-PVA specimens heat treated at 110, 400 and 600 °C. The phase detected at 110 °C was

boehmite (AlO (OH)). Increasing temperature up to 400 °C did not change the phase structure but the intensity of the peaks decreased.

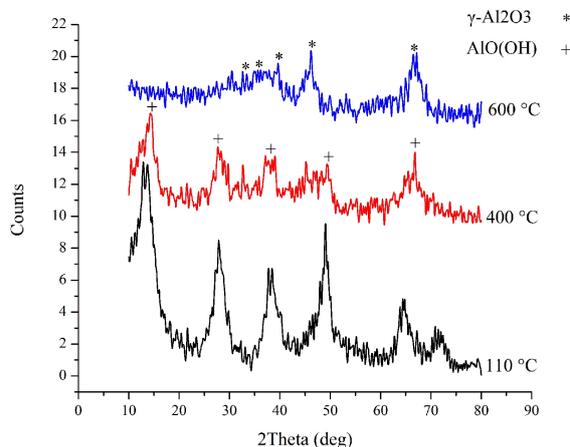


Fig. 5. X-ray diffraction patterns of the membrane heat treated at 110, 400 and 600 °C.

The membrane layer must be mesoporous and have enough mechanical and chemical stability. It is possible to achieve these properties simultaneously in the γ -alumina membrane. Transformation of boehmite to γ -alumina phase occurs at 600 °C. The specimens were calcined at 600 °C for three hours so the transformation was completed. Boehmite and γ -alumina exist together at 400 °C. However, at 600 °C only γ -alumina peaks were observed. Park *et al.* [22] and Radonjic *et al.* [23] came to the same conclusion.

3.3.5. Microstructure analysis of the membrane

As mentioned above, the average pore size of the support is about 200 nm. Alumina colloidal sol Al-Et-F-PVA with particle size of 25 to 90 nm has small particles compared to sublayer porosity. The particles of sol are able to penetrate into the sublayer and block the pores. Therefore, the alumina colloidal sol Al-IP-F-PVA with particle size of 40 to 200 nm was used for the first and second coatings. The sublayers were dip-coated with Al-Et-F-PVA for the next three coatings and the membrane with mesopores was achieved. Fig. 6 represents the images of microstructure of γ -alumina membrane heat treated at 600 °C

coupled with energy dispersive X-ray spectroscopy (EDX) diagram.

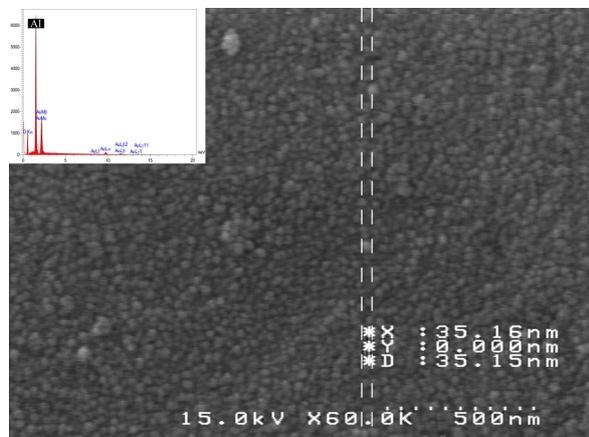


Fig. 6. SEM image of γ -alumina membrane heat treated at 600 °C with enclosed EDX diagram.

The membrane layer without any PVA additive does not have enough adherence to the sublayer, so cracks were formed on the surface of the membrane layer during the drying stage. Fig. 7 presents the effect of PVA additive in alumina colloidal sols.

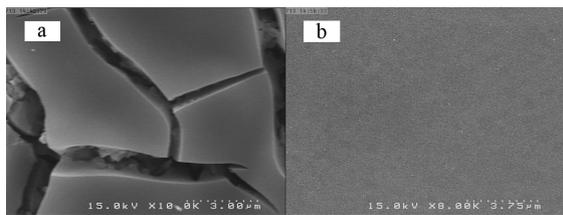


Fig. 7. SEM image of γ -alumina membrane surface: (a) without PVA (b) with PVA.

Addition of PVA decreases the surface tension and capillary pressure so the crack formation decreases. The capillary pressure can be calculated using the equation:

$$\Delta P_C = \frac{2\gamma_{LV} \cos \theta}{R_p} \quad (1)$$

where γ_{LV} is surface tension between liquid and gas and R_p is the radius of the pore. Fig. 8 presents the cross section of the membrane. The surface of the membrane is clean and perfect without any

large pores and the thickness of the membrane is about 4 μm . Membrane thicknesses reported in other articles are 2 to 5 μm [24]. Herein, different dip-coating speeds and several-time-coating were used to achieve a membrane with about 4 μm of thicknesses.

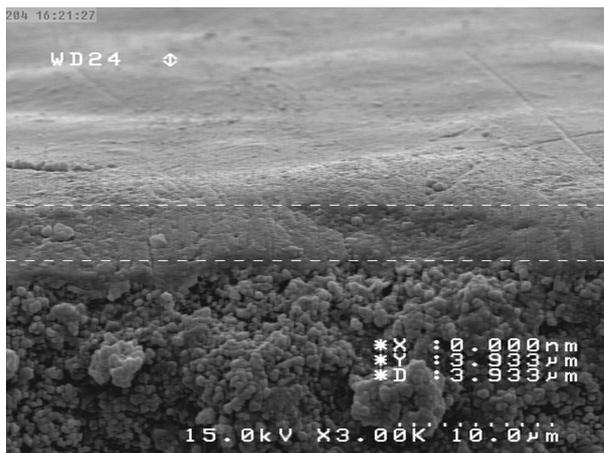


Fig. 8. SEM image of γ -alumina membrane coated on α -alumina sublayer.

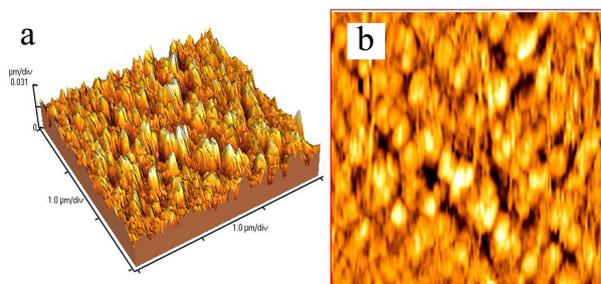


Fig. 9. (a) 3D and (b) 2D AFM images of the surface of a γ -alumina membrane.

3.3.6. Topographic analysis

Surface topography and the roughness, depth and size of the pores were observed using atomic force microscope. Fig. 9 presents the topography of a γ -alumina membrane. The average roughness of the membrane surface is about 16 nm. Pore size of the membrane, computed with AFM software, is about 5 nm. Van Gestel et al. [8] reported that γ -alumina membrane sintered at 600 °C had 3.8 nm mean pore size, 239 m^2/g surface area and 0.27 mL/g pore volume.

4. Conclusions

In this research, a perfect membrane of γ -alumina coated on an α -alumina sublayer was reported. Parameters that affect the industrial quality membrane were investigated. Alumina colloidal sols used in this process were stable and the obtained particle size was about 27 nm. The working temperature of the membrane was about 600 °C. In an environment with temperature higher than 600 °C the membranes cracked because of the transformation of γ -alumina phase. Colloidal sols with smaller particle size were obtained using ethanol as a solvent. Colloidal sols had the most significant effect on membrane coating. Membrane characteristics were determined by additive, primary materials and preparation conditions. A perfect and clean membrane was obtained using the PVA additive which controlled the drying stage of the sol. The membrane layer was prepared using two colloidal sols with different particle size distributions. The sublayer was dip-coated five times in thin stable sols. The membrane with 4 μm thickness, 16 nm average roughness (R_a) and 5 nm pore size was achieved. It is intended to use these γ -alumina membranes for the single gas permeation and separation of binary gas mixtures.

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