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Synthesis and characterization of α -Alumina membrane supports and the binding effect of Poly (Vinyl Alcohol)

ABSTRACT

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Ceramic Ultrafiltration membranes are considered as an alternative for the treatment of both stable water-in-oil and oil-in-water emulsions proved to be more effective in comparison with other conventional techniques. In this study, symmetric macro-porous ceramic membranes are prepared through dry pressing of α -alumina powder and the addition of various binders including Poly (vinyl alcohol). The disk is sintered after the organic material is burned away and the porosity can also be adjusted by the variation of sintering temperature. The results show that the fabrication of compact membrane supports can be done by increasing the sintering temperature which leads to grain size reduction. Moreover, application of different binders and additives result in various supports possessing different pore size and size distributions. Scanning electron Microscope (SEM) micrographs illustrate the surface and grain size distributions caused by various binders. These membranes can be used for microfiltration at elevated temperatures and extreme environmental conditions and also as porous supports for the fabrication of composite-asymmetric nanofiltration membranes.

Keywords: α -Alumina; Binder; Sintering temperature; Dry pressing; Nanofiltration.

INTRODUCTION

Membranes are classified into two general groups based on material properties, namely organic (polymeric) and inorganic also known as ceramic membranes. Ceramic membranes are versatile and can operate at a wide range of process conditions and various applications such as those involving elevated temperatures, high pressures and especially corrosive environments. These advantages make porous ceramic membranes particularly suitable for food, biotechnological and pharmaceutical applications in which repeated steam sterilization and cleaning with aggressive solutions is required [1-3].

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The treatment of wastewater produced from oil and gas fields is very difficult as a result of well to well variations and also stable oil-in-water emulsions involved [4]. Ceramic Ultrafiltration membranes are considered as an alternative for stable oil-in-water emulsion treatment which is proved to be more efficient in comparison with conventional techniques [5]. Several experimental and modeling studies are reported on the treatment of oily wastewater emulsions using low cost ceramic membranes [6]. Multistage treatment processing of oilfield produced water by different ceramic membranes is also investigated with insistence on the characterization of permeate flux using various ceramic microfiltration, Ultrafiltration and Nanofiltration membranes as potential techniques [4].

Ceramic membranes are usually composite in nature consisting of several layers from one or more ceramic materials. These membranes are made up of a macroporous support, one or two mesoporous intermediate layers and a microporous top layer. The bottom layer provides the mechanical strength, while the middle layers bridge the pore size variations in between the support and top layer where the actual separation takes place. The permeability and separation factor of a ceramic membrane are the two most important performance indices [4], typically governed by thickness, pore size and surface porosity [7-9]. On the other hand, the porosity of each layer depends strongly on the microstructure of the porous ceramic support [10]. The support material is also critical for effective performance of multilayered ceramic filters which affect the major properties expected from the support. The reliability of different ceramic materials including α -alumina, zirconia, and SiO_2 or a combination of these is being studied as alternatives for support structures [9].

One of the most important issues that should be considered extremely in the preparation of ceramic membranes is that the final product must be void of cracks. The permissible defect size depends on the function of the membrane layer (support for MF, UF and NF). As a result, defects in the support layer will be transferred if they have the same size or thickness compared to the next layer. The optimization of fabrication process and careful selection of raw materials can have a significant effect on defect formation [11, 12]. The quality of support under the separation layer is

critical for the quality of the membrane. Consequently, high quality supports should be smooth, possess constant and homogeneous surface characteristics (wettability) and preferably a relatively narrow pore size distribution. These supports should also have sufficient mechanical strength which is not degraded with time or under harsh processing conditions [12].

There are several techniques for manufacturing inorganic membrane disk supports among which the pressing method is very common. Usually, more than 100 MPa is applied to press powders into compact disks [7]. Upon powder compaction, membrane supports are sintered at elevated temperatures in order to make a rigid structure with high mechanical strength. Supported $\gamma\text{-Al}_2\text{O}_3$ nanofiltration (NF) membranes are prepared from colloidal dispersions of boehmite via sol-gel technique with more than 90% removal efficiency [13].

Also, special additives should be intermixed with the initial powder as the binder to stick the particles to prepare defect-free membranes [14]. The parameters affecting the membrane support porosity and pore size include the type of binder, powder and binder milling time, molding pressure and also the sintering temperature.

In this study, the fabrication of alumina supports by pressing process is studied. The α -alumina powder is mixed with organic binders initially and pressed afterwards in order to form disc membrane supports. These discs are sintered at high temperatures. Finally, the porosity and pore size distribution of the pressed alumina powder is evaluated. SEM micrographs illustrate the variations of pore and grain size and also size distributions as a result of various sintering temperatures, pressing pressures and binders.

EXPERIMENTAL

Ethanol was supplied by Merck, PVA by Sigma-Aldrich and α -alumina powder with an average size of 0.3 μm which is the initiating material for the preparation of ceramic membrane supports, is supplied by Presi. For preparing disk-like supports by the pressing process, two kinds of binders, namely ethanol and PVA (polyvinyl alcohol) were added to the α -alumina powder. The

microstructure and pore size distribution are characterized by SEM micrographs. The method proposed by Zheng *et al.* is used for porosity determination [15]. According to this technique, the support is aged in distilled water and then weighed. The wet membrane is placed in an air-circulating oven at 60°C for 24 h and then further dried in a vacuum oven at 80 °C for 24 h before being weighed at the dry state. The porosity is calculated by comparing the wet and dry sample weights using Eq. (1):

$$P(\%) = \frac{Q_0 - Q_1}{Ah} \times 1000 \quad (1)$$

Where P is the membrane porosity, Q_0 the wet sample weight (g), Q_1 the dry sample weight (g), A the membrane surface area (cm^2) and h is the membrane thickness (mm).

Ethanol

In this method, a mixed solution of α -alumina and ethanol is prepared at the first step. This mixture is prepared with 30vol% of α -alumina. Then, the prepared solution is placed in a shaker at 50 °C for 1 hour, in order to achieve a uniform α -alumina in ethanol. Afterwards, the mixture is placed in the oven and heated up to 110 °C for 24 hours to be dried completely and the resulting powder is milled before being pressed by two different pressures equal to 70 and 90 kN. The

resulting supports were sintered at 1100 and 1200 °C with a 5 °C/min heating rate for 1 hour.

PVA as the binder

At the first step, a solution of 10% PVA is prepared. Fully hydrolyzed PVA with MW=60000 Dalton is used for this purpose. Then, 8 wt. % of this solution is mixed with α -alumina powder. The mixture is milled completely for 3 hours before being pressed. The milled powder is pressed up to 70 and 90 kN and then the prepared discs are sintered at 1100 and 1200 °C with a 5 °C/min heating rate of for 1 hour.

RESULTS AND DISCUSSION

Permeability and separation factor are the two most important performance parameters regarding ceramic disc membranes. These parameters are dependent on the pore size, porosity and surface membrane characteristics. Figures 1(a-d) and 2(a-d) represent the SEM micrographs of disc membrane supports prepared by different sintering temperatures and molding pressures with ethanol and also PVA binder, respectively. According to these micrographs, the fabricated disc membrane supports have smooth and crack-free surfaces.

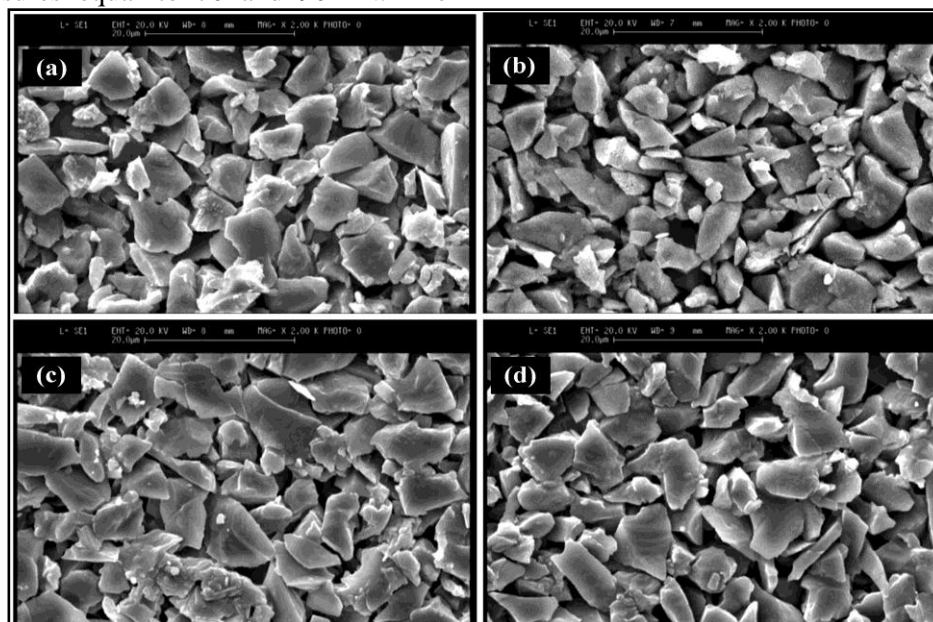


Fig.1. SEM micrographs for membrane supports, with ethanol binder, (a) 70 kN and 1100 °C (b) 90 kN and 1100 °C (c) 70 kN and 1200 °C (d) 90 kN and 1200 °C.

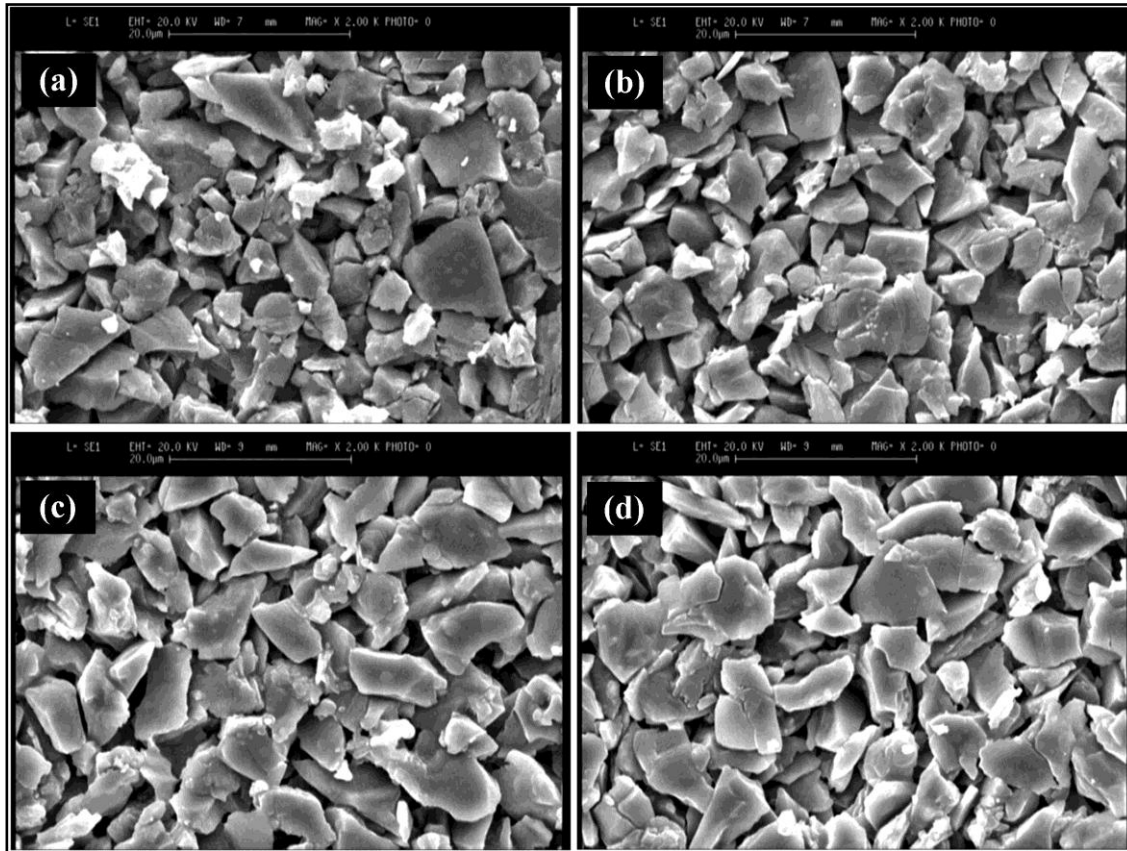


Fig. 2. SEM micrographs for membrane supports, with PVA binder, (a) 70 kN and 1100 °C (b) 90 kN and 1100 °C (c) 70 kN and 1200 °C (d) 90 kN and 1200 °C.

Figure 3 represents the SEM micrograph of the produced support highlighting the grain and pore size. Image analysis techniques are used to extract surface pore size distribution variations data from these SEM micrographs (Figure 4a and b). The upper and lower limits of pore sizes and a whole distribution can be extracted from image analysis based on the figures.

The effect of molding pressure

Figure 1a and b show the SEM Micrographs of disc membrane supports prepared with ethanol at 1100°C sintering temperature and 70 and 90 kN molding pressures. The results of porosity and pore size evaluation for these membrane supports are summarized in Table 1. The results show that the porosity and pore size are reduced by increasing the molding pressure. Actually, further molding pressures result in dense membranes with undesirable pore size distributions and increased bonding strength between particles.

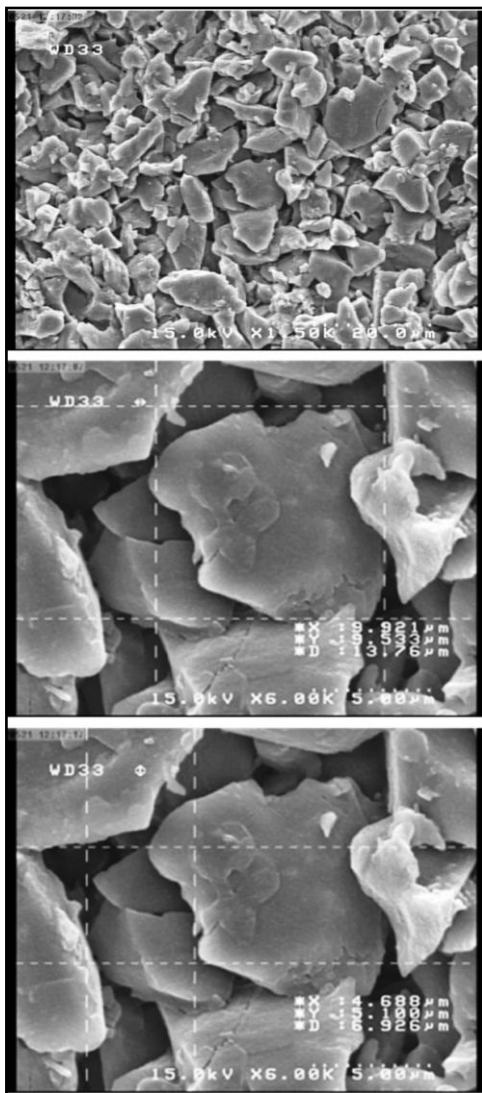
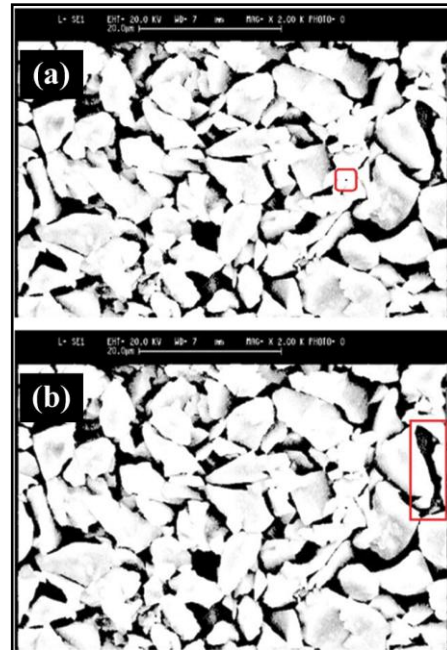
The SEM micrograph of disc membrane supports prepared with PVA binder are given in Figure 2a and 2b, and Table 2 shows the corresponding values for porosity and pore size.

Table 1. Characteristics of disc membrane supports with ethanol.

Molding pressure (kN)	Sintering temperature (°C)	Heating rate (°C/min)/hour	Porosity (%)	Pore size distribution (µm)
70	1100	5 / 1	46	3.5-13
90	1100	5 / 1	43	2-12
70	1200	5 / 1	38	2.5-8.5
90	1200	5 / 1	36	2-8

Table 2. Characteristics of disc membrane supports prepared with PVA.

Molding pressure (kN)	Sintering temperature (°C)	Heating rate (°C/min)/hour	Porosity (%)	Pore size distribution (µm)
70	1100	5 / 1	42	2.5-8
90	1100	5 / 1	40	1.5-7.5
70	1200	5 / 1	36	1.5-7
90	1200	5 / 1	34	1-6

**Fig. 3.** SEM micrograph highlighting the Grain and pore size for the membrane support.**Fig. 4.** a) The smallest pore is estimated to be 0.37µm. b) The largest pore is estimated to be 12.62µm.

The effect of sintering temperature

Figure 1a and 1c show the SEM micrographs of disc membrane supports prepared with ethanol at a 70 kN molding pressure and 1100 and 1200 °C sintering temperatures. Regarding the values of porosity and pore sizes in Table 1, it is obvious that porosity and pore size distribution are reduced by increasing the sintering temperature, but enhanced sintering temperatures result in larger grain sizes. The SEM micrographs of disc membrane supports are given in Figure 2a and c, in which PVA has been used as the binder and the corresponding values of porosity and pore size are summarized in Table 2. In fact, alumina particles stick together by increasing the sintering temperature, resulting in larger grains and also the reduction of porosity and pore size.

The binding effect of PVA and Ethanol

As can be seen from the SEM micrographs (Figures 1 and 2), the membrane surfaces are more uniform (in terms of grain size) in case of ethanol compared with PVA. Tables 1 and 2, show that the membranes prepared with PVA binder have narrower pore size distributions and reduced porosities. The surface uniformity caused by ethanol is due to powder preparation methods used

through the pressing process. When ethanol is used in the fabrication process, the alumina powder is dissolved in ethanol and the solution is mixed completely using shakers, which results in higher quality membrane surfaces. It must be added that the membranes prepared with PVA have a suitable surface also, which can be improved by further milling. Since PVA is a high quality binder having a proper softening feature, the membranes prepared with PVA binder have a denser structure with a smaller pore size, narrower pore size distribution and lower porosity in comparison with the membranes prepared with ethanol. The softening feature of these alcohols leads to crack-free surfaces for disc supports.

CONCLUSIONS

ZnO and ZrO₂ photo catalysts were synthesized by sol-gel auto combustion method. The average crystalline size was determined by the Debye-Scherrer formula by X-ray spectrum data and estimated about 51 nm to ZrO₂ and 44 nm for ZnO. The observations indicate high photo catalytic degradation strength of nano photo catalyst ZnO over Nitro phenol against ZrO₂. ZnO has a large initial rate of activities and its absorption efficacy of UV-C irradiation.

REFERENCES

- [1] Nath K., (2008), Membranes Separation Processes, PHI Learning Pvt. Ltd. New Delhi, pp. 20-22.
- [2] Li N., N., Fane A., G., Winston Ho W., S., Matsuura T., (2008), Advanced Membrane Technology and Applications, *John Wiley & Sons, Inc.*, pp. 899-903.
- [3] Baker R. W., (2004), Membrane Technology and Applications, John Wiley & Sons, Ltd. West Sussex, pp. 129-132.
- [4] Ebrahimi M., Kovacs Z., Schneider M., Mund P., Bolduan P., Czermak P., (2012), Multistage filtration process for efficient treatment of oil-field produced water using ceramic membranes. *Desal. Water Treat. J.* 42: 17-23.
- [5] Vatai G. N., Krstic D. M., Koris A. K., Gáspár I. L., Tekic M. N., (2009), Ultrafiltration of oil-in-water emulsion: Comparison of ceramic and polymeric membranes. *Desal. Water Treat. J.* 3: 162-168.
- [6] Nandia B. K., Uppaluria R., Purkaita M. K., (2010), Microfiltration of stable oil-in-water emulsions using kaolin based ceramic membrane and evaluation of fouling mechanism. *Desal. Water Treat. J.* 22: 133-145.
- [7] Li K., (2007), Ceramic membranes for Separation and Reaction, *John Wiley & Sons, Ltd.* West Sussex, pp. 1-28.
- [8] Veringa H. J., Terpstra R. A., Philipse A. P., (1990), Applications and design of porous ceramic structures, Elsevier Applied Science. London, pp. 312-330.
- [9] Patel F., Baig M. A., Laoui T., (2011), Processing of porous alumina substrate for multilayered ceramic filter. *Desal. Water Treat. J.* 35: 33-38.
- [10] Glass S. J., Green D. J., (1999), Permeability and infiltration of partially sintered ceramics. *J. Am. Ceram. Soc.* 82: 2745-2752.
- [11] Bonekamp B. C., (1996), Preparation of asymmetric ceramic membrane supports by dip coating, Elsevier Science B.V., Amsterdam, pp. 178-183.
- [12] Burggraaf A. J., Cot L., (1996), Fundamentals of Inorganic Membrane Science and Technology, Elsevier Science B.V., Amsterdam, pp. 269-270.
- [13] Sadeghian Z., Zamani F., Ashrafizadeh S. N., (2010), Removal of oily hydrocarbon contaminants from wastewater by γ -alumina nanofiltration membranes. *Desal. Water Treat. J.* 20: 80-85.
- [14] Hemra K., Aungkavattana P., Atong D., (2011), Micro-porous alumina membrane prepared by dip coating using latex binder, *Material Sci. fourm.* 695: 549-552.
- [15] Zheng Q. Z., Wang P., Yang Y. N., Cui D. J., (2006), The relationship between porosity and kinetics parameter of membrane formation in PSF Ultrafiltration membranes. *J. Membrane Sci.* 286: 7-11.

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