

Sol-gel synthesis of alumina-titania ceramic membrane: Preparation and characterization

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Abstract

Alumina-titania ceramic membrane with mesopore and narrow pore size distribution was prepared by the sol-gel process. Observations were based on membrane weight loss, morphology, pore size distribution and BET surface area. Thermogravimetric analysis (TGA), Scanning Electron Microscopy (SEM) and N₂ adsorption-desorption analysis were employed for the membrane characterization. TGA curve shows that the suitable temperature for calcination of alumina-titania membrane is at 600°C. The SEM morphology displays a smooth and free-crack layer of alumina-titania membrane after calcination at temperature of 600°C. Furthermore, the membrane was also successfully coated with a good adhesion to complement with support. The thickness of the membrane layer was estimated at 4 μm. N₂ adsorption-desorption confirms the existence of a mesoporous structure for membrane as BET surface area and average pore size of the membrane layer were 292 m²g⁻¹ and 1.8 nm respectively.

Keywords: Alumina-titania, ceramic membrane, sol-gel process, dip coating.

Introduction

Membrane processes have become an accepted unit operation for a variety of separations in industries. The development of ceramic membranes is mainly driven by the need to produce membranes with greater chemical and thermal tolerance. Because, inorganic materials have advantages over polymeric materials for their thermal stability, good chemical resistance to solvents, high mechanical strength and long lifetime (Bhave, 1991, Hsieh, 1996, Burggraaf & Cot, 1996, Tsuru, 2001). Commonly used materials for ceramic membranes are Al₂O₃, TiO₂, ZrO₂, SiO₂ etc. or a combination of these materials.

Membranes can be classified into 2 main groups, porous and non-porous membranes. Separation mechanism in porous membranes is by molecular sieving. On the other hand, solution-diffusion is responsible for the separation in non-porous membranes where permeating molecules dissolve into a membrane, diffuse, and desorb from the membrane (Tsuru, 2008). The definition of porous membranes is more in agreement with the definitions adopted by the International Union of Pure and Applied Chemistry (IUPAC), the pore size classification given is referred to pore diameter (Rouquerol *et al.*, 1994): (i) Macropores > 50 nm. (ii) Mesopores 2 nm < pore size < 50 nm. (iii) Micropores < 2 nm. Transport occurs through porous membranes rather than the dense matrix and ideal gas separation membranes possess a high flux and a high selectivity (Mulder, 1996).

Sol-gel process has many advantages and it is the most practical process in preparation of porous ceramic membrane. The advantages include the preparation of materials with superior homogeneity and purity, higher BET surface areas, well-defined pore size distribution and

a better control over the micro-structural properties of the metallic particles (Klein & Gallagher, 1988, Larbot *et al.*, 1989, Brinker *et al.*, 1994, Burggraaf & Cot, 1996, Yang & Xiong, 1999). The sol-gel process was first applied for development of ceramic ultrafiltration membranes by Leenaars *et al.* (1984, 1985). The alumina and titania membranes by Anderson *et al.* (1988), Moosemiller *et al.* (1989), Zaspalis *et al.* (1992), Kumar (1993), Chang *et al.* (1994), Schaep *et al.* (1999) and Chuah *et al.* (2000) have been studied separately but alumina-titania membranes have been studied very little (Van Gestel *et al.*, 2002). The combined Al₂O₃-TiO₂ membrane were developed in order to obtain the specific properties of both materials, namely the possibility of obtaining membrane layers with a high thickness, without defects and a good thermal, mechanical and chemical stability (Van Gestel *et al.*, 2002).

This work is mainly dealt with the preparation and characterization of combined alumina-titania ceramic membrane by sol-gel process. The thermal treatment, morphology and BET surface area of the membrane were characterized with TGA, SEM and N₂ adsorption-desorption analysis, respectively.

Experimental method

Material

Isopropoxide aluminium (Al(OC₃H₇)₃, Aldrich) and titanium-tetra-isopropoxide (Ti(OC₃H₇)₄, Merck) as organic reactant, nitric acid (HNO₃, Merck) as peptization agent, polyvinyl alcohol (PVA, Erkol) as binder agent and isopropanol (Merck) as dispersing solvent were used to prepare alumina, titania and alumina-titania membranes.

Preparation of alumina, titania & alumina-titania sol

The alumina, titania and alumina-titania sol were prepared by sol gel process. For preparation of colloidal sol of boehmite (γ-AlOOH), isopropoxide aluminium (5.1

g) was added to distilled water (50 ml). The solution at about 90°C while refluxing was hydrolyzed for 2 h. Then HNO₃ (1.75 ml) was added for peptization and the process refluxing was continued for 18 h. A solution of polyvinyl alcohol with an average molecular weight of 72000 (3.5 g/100 ml H₂O) was added to this sol before membrane formation as drying chemical controlling additive (DCCA). For preparation of sol of titania, titanium-tetra-isopropoxide was added to a solution of water in isopropanol (4.5 mol dm⁻³) while stirring at high speed. Hydrolysis was carried out at room temperature. The resultant white precipitate of titanium hydroxide was filtered and then washed with water to remove impurities. Subsequently, precipitate was disturbed in H₂O and refluxed at 80°C for 2 h and then HNO₃ was added for peptization and continued refluxing for 18 h. Ultrasonic treatment with a power of 60 W was applied for 30 min to disperse accumulate particle to obtain the sol as a stable semi-opaque solution. For preparation of ultimate stable sol, two sols that prepared in previous stages were mixed with 3:1 volume ratio of boehmite sol to titania sol. Experimental conditions for the preparation of stable sol are given in Table 1.

Table 1. Experimental conditions for the preparation of stable sols.

Stable sols	[H ₂ O]/[M] (mol)M=Al,Ti	[HNO ₃]/[M] (mol)	pH	Temperature (°C)
γ-AlOOH	100	0.07	4.1	90
TiO ₂	25	0.5	2	80
Combined sol	--	--	2.6	--

Formation of alumina-titania membrane layer for support

The support of membrane was disk-shaped support of α-alumina with 30 mm in diameter and 2 mm in thickness. The membrane layer was formed of combined sol by dip-coating process. The dipping time was 5 s. Non-supported gel layer was formed by pouring some of combined sol in Petri dish and were dried at 25°C for 24 h. Finally, the membrane with and without support was calcinated for 1 h at 600°C with heating and cooling rates of 15°C/h. Dip coating, drying and calcinations steps were repeated 2 times for crack and defect reparation and the increase in membrane thickness.

Apparatus

Thermogravimetric analysis (TGA) was carried out using a TG-50 Shimadzu Japan Co thermal analysis system. The programmed heating rate was 10°C/min. The thickness and surface morphology of the membrane was observed using XL30 scanning electron microscope (SEM) from Philips company operating at 20 kV. Nitrogen isotherm measurements were performed on a Quantachrome Autosorb I surface area analyzer.

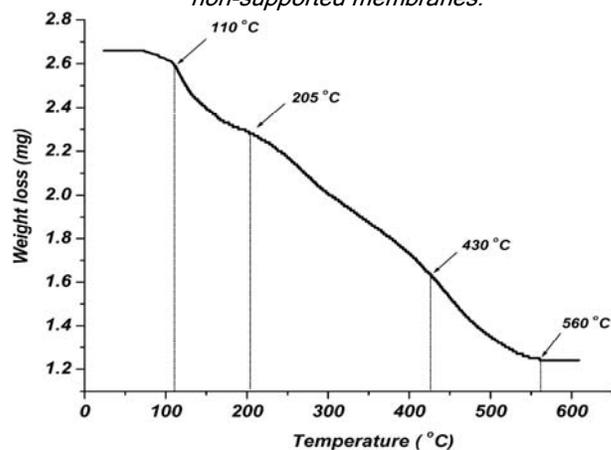
Results and discussion

Thermal analysis

To determine the adequate temperature range for thermal treatment of alumina-titania non-supported

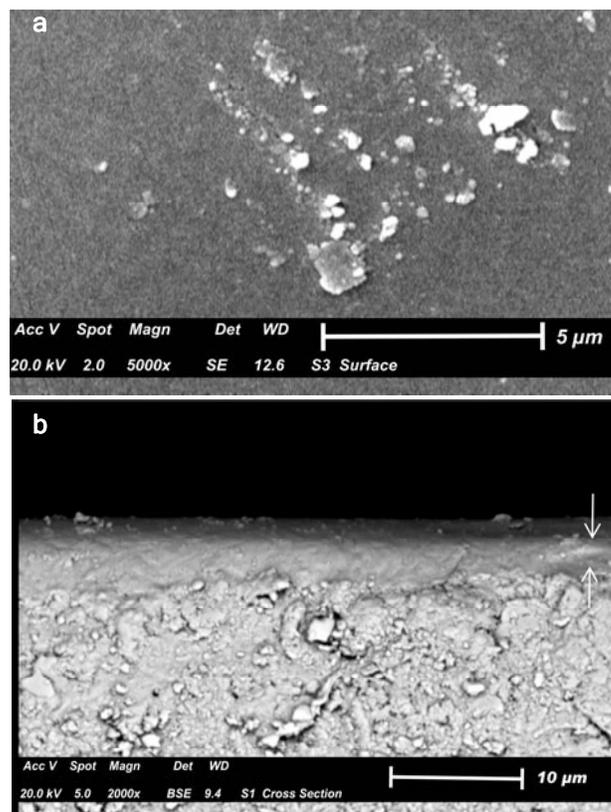
membranes, thermogravimetric analysis of the dried gel was carried out in air atmosphere. It can be seen as a typical TGA curve shown in Fig. 1. The weight loss proceeds in 3 step: A smooth loss in the range from 110-205°C which may be related to removing the solvent

Fig. 1. TGA curve for alumina-titania non-supported membranes.



residues and water condensate in porous gel network. The subsequent near linear decrease in the weight around 205-430°C seems to the elimination of organic materials and nitric acid. Above 430 °C, the weight loss becomes smooth again and is stopped at about 560°C. Probably,

Fig. 2. SEM images of supported alumina-titania ceramic membrane. (a) surface & (b) Cross-section.



this loss is related to the removal of residual structural water and stabilizing acid anions. Therefore, the calcination temperature is selected as 600°C.

Scanning electron microscopy

The SEM images were applied for the determination of surface morphology and thickness of the supported membrane layer. Fig. 2a & 2b show surface and cross-section of membrane layer on the support. Fig. 2a shows that the membrane surface was morphologically homogeneous, smooth and free of cracks. Using of PVA as drying chemical controlling additive (DCCA) is more effective in preventing crack formation (Yeung *et al.*, 1997; Guimarães *et al.*, 2006). The white dots that were observed in the Fig. 2a represents titanium particles which were not well dispersed (Bernal & Lopez, 2000). The cross sectional image of supported membrane demonstrates that the upper membrane layer was successfully coated and fused with the alumina support. The thickness of the membrane layer is approximately 4 μm (Fig. 2b).

N_2 adsorption-desorption analysis

Pore size distribution and surface area of alumina-titania ceramic membrane were measured by Quantachrome Autosorb I analysis. Characterizations were carried out on unsupported membranes by assuming that their properties are similar to those of supported membrane layers (Stevenson *et al.*, 1987). Fig. 3a & 3b show adsorption-desorption isotherm of membrane and pore size distribution, respectively. Fig. 3a displays adsorption-desorption isotherm obtained for sample generated by physisorption technique in the partial pressure, p/p_0 range of 0.0489-0.9994. The numerous profile correspond to a IV-type adsorption isotherm curve, on which a hysteresis loop can be observed, suggesting the presence of a porous structure and more precisely a mesoporous structure (Gregg & Sing, 1982). The horizontal branch near the saturation pressure ($p/p_0=0.9$) indicates the all mesoporous are filled with liquid adsorbate.

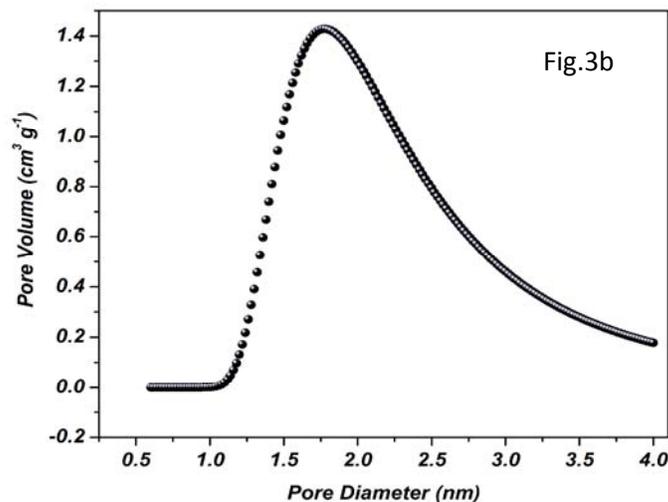
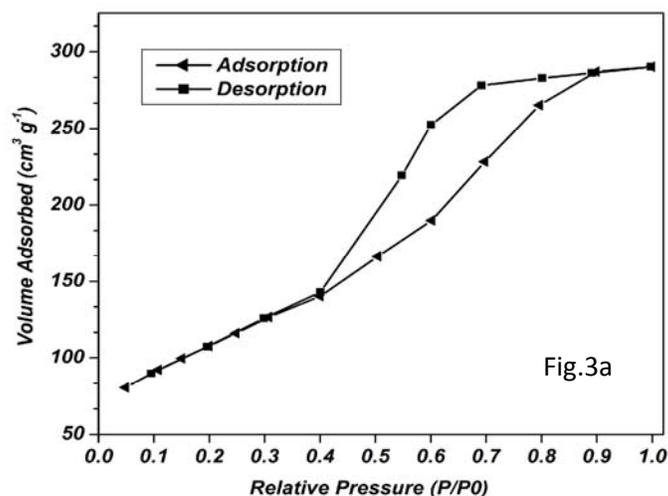
The surface area was determined according to the Brunauer-Emmet-Teller (BET) method. The pore size distribution was obtained by following the Barrett-Joyner-Halenda (BJH) approach (Barrett *et al.*, 1951). BET surface area of the membrane has been obtained 292 m^2g^{-1} . As seen from the Fig. 3b, the pore size distribution of the membrane showed narrow pore size distribution. This indicated that the membrane sample had relatively uniform pore size (Dumeignil *et al.*, 2006). Moreover, average pore diameter is 1.8 nm. This pore size distribution confirms the existence of a mesoporous structure as was previously supposed from isotherm profile.

Conclusion

Alumina-titania ceramic membrane was prepared by the sol-gel process. From thermogravimetric analysis of the dried gel, calcination temperature is selected 600°C.

The SEM images displayed that the membrane surface was homogeneous, smooth and free of cracks as the thickness of membrane layer was 4 μm . N_2 adsorption-desorption analysis showed alumina-titania ceramic membrane with mesopore and narrow pore size distribution. In addition, BET Surface area and average pore size distribution for the membrane were 292 m^2g^{-1} , 1.8 nm, respectively.

Fig. 3a. Adsorption-desorption isotherm; Fig. 3b. Pore size distribution of alumina-titania membrane.



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