Chinese Journal of Chemical Engineering 23 (2015) 31–41

Contents lists available at ScienceDirect

Chinese Journal of Chemical Engineering

journal homepage: www.elsevier.com/locate/CJCHE

Separation Science and Engineering

Effect of sol size on nanofiltration performance of a sol–gel derived microporous zirconia membrane☆

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ARTICLE INFO

Article history:
Received 18 March 2013
Received in revised form 3 December 2013
Accepted 30 December 2013
Available online 2 October 2014

Keywords:
Microporous ceramic membranes
Zirconia
Nanofiltration
Sol size
Sol–gel

ABSTRACT

This paper reports the effect of sol size on nanofiltration performances of sol–gel derived microporous zirconia membranes. Microstructure, pure water flux, molecular weight cut-off (MWCO) and salt retention of zirconia membranes derived from zirconia sols with different sizes were characterized. Thermal evolution, phase composition, microstructure and chemical stability of unsupported zirconia membranes (powder) were determined by thermogravimetric and differential thermal analysis, X-ray diffraction, nitrogen adsorption–desorption and static solubility measurements. Results show that nanofiltration performance of zirconia membranes is highly dependent on sol size. The sol with an average size of 3.8 nm, which is smaller than the pore size of the γ-Al_2O_3 support (pore size: 5–6 nm), forms a discontinuous zirconia separation layer because of excessive penetration of sol into the support. This zirconia membrane displays a MWCO value towards polyethylene glycol higher than 4000 Da. A smooth and defect-free zirconia membrane with a MWCO value of 1195 Da (pore size: 1.75 nm) and relative high retention rates towards $MgCl_2$ (76%) and $CaCl_2$ (64%) was successfully fabricated by dip-coating the sol with an appropriate size of 8.6 nm. Zirconia sol with an average size of 12 nm exhibits colloidal nature and forms a zirconia membrane with a MWCO value of 2332 Da (pore size: 2.47 nm). This promising microporous zirconia membrane presents sufficiently high chemical stability in a wide pH range of 1–12.

1. Introduction

Ceramic membranes have drawn a great deal of attention in the recent two decades because of their high chemical, thermal and mechanical stability in comparison with polymeric membranes. Ceramic membranes can be generally categorized into macroporous, mesoporous and microporous membranes based on the pore size [1]. In terms of the fabrication of macro- and mesoporous ceramic membranes, suspensions or colloidal sols are normally deposited onto the porous support, with subsequent sintering or calcination process. The pore structure is formed through particle packing and the relationship between the particle size of the starting material and the resulting pore size of the membrane can be quantitatively calculated [2]. Microporous ceramic membranes, including γ-Al_2O_3 [3], SiO_2 [4], TiO_2 [5], ZrO_2 [6] and HfO_2 [7], are hot topics in membrane research field in recent years, owing to their great potential applications in nanofiltration (NF), pervaporation (PV) and gas separation. Among them, TiO_2 and ZrO_2 are the most promising materials due to their high stability in harsh environments, especially long-term stability in a large pH range [1].

Polymeric sol–gel process is considered to be the most appropriate route for the fabrication of microporous ceramic membranes [1]. It is based on the chemistry of metal organic precursors in organic solvents. The first stage in the polymeric sol–gel process consists in the synthesis of a sol using molecular precursors (metal organics). Then the condensation reactions occur at the sol stage with the formation of polymeric clusters which interpenetrate with each other at the final stage to form the gel [8]. However, the extremely high hydrolysis and condensation rate of alkoxide precursors is one of the main hurdles for the synthesis of titania and/or zirconia polymeric sols and, further, quantitatively controls the sol size [9,10].

Table 1 summarizes the effect of sol size on the performance of microporous ceramic membranes. Polymeric hybrid SiO_2 sol presents an average size of 1.4 nm, which is much smaller than the pore size of the support, resulting in a discontinuous separation layer with a thickness less than 30 nm. The hybrid silica membrane fabricated by such sol exhibits a much lower separation factor of 8 for a mixture of *n*-butanol and water (95/5 , mass ratio) during PV processes [11]. On the other hand, a hybrid SiO_2 membrane fabricated with a polymeric

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☆ Supported by the National Natural Science Foundation of China (20906047, 21276123), the National High Technology Research and Development Program of China (2012AA03A606), State Key Laboratory of Materials-Oriented Chemical Engineering (ZK201002), the Natural Science Research Plan of Jiangsu Universities (11KJB530006), the “Summit of the Six Top Talents” Program of Jiangsu Province, and a Project Funded by the Priority Academic Program development of Jiangsu Higher Education Institutions (PAPD).

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http://dx.doi.org/10.1016/j.cjche.2014.09.045
1004-9541/

Table 1
The effect of sol size on performance of microporous ceramic membranes

Membrane material	Average sol size /nm	Support	Membrane thickness/nm (micrograph)	PV or NF performance	Reference
Hybrid SiO_2	1.4	Tubular γ-Al_2O_3 (pore size: 5–6 nm)	30 (not clear)	$\alpha = 8$	[11]
	8		120 (continuous and defect-free)	$\alpha = 300$	
	13		>1000 (visible cracks)	–	
Hybrid SiO_2	3.3	Tubular γ-Al_2O_3 (pore size: 4 nm)	150 (continuous and defect-free)	$\alpha = 361$	[12]
	5.7		250 (continuous and defect-free)	$\alpha = 2695$	
ZrO_2	2	Tubular γ-Al_2O_3 (pore size: 4 nm)	<10 (not clear)	–	[13]
	3		110 (many defects)	–	
	10		~150 (continuous and defect-free)	$\alpha = 171361$	
ZrO_2	About 6	Tubular γ-Al_2O_3 (pore size: 4 nm)	~200 (clear)	No water permeation	[14]
	5–10		50 (clear)	MWCO < 300, pure water permeability: 0.256 $L\cdot m^{-2}\cdot h^{-1}\cdot MPa^{-1}$	[15]
TiO_2	3	Tubular γ-Al_2O_3 (pore size: 4 nm)	20–30	–	[13]
	10		150 (smooth and defect-free)	$\alpha = 171\ 361$	
SiO_2–ZrO_2 (mole ratio = 9:1)	11	Tubular SiO_2–ZrO_2 (pore size: 3 nm)	–	MWCO = 200	[16]
	13		–	MWCO = 500	
	16		–	MWCO = 1000	
ZrO_2	3.8	Disk γ-Al_2O_3 (pore size: 5–6 nm)	(Discontinuous)	MWCO > 4000	This work
	8.6		(Smooth, continuous and defect-free)	MWCO = 1195	
	12		(Continuous and defect-free)	MWCO = 2332	

α: separation factor towards a mixture of *n*-butanol and water (95/5, mass ratio) operated at 95 °C (PV performance).

sol size of 13 nm, which is larger than the pore size of the support, exhibits visible cracks [11]. This phenomenon can be attributed to the fact that the membrane thickness is larger than the critical value. A microporous SiO_2-based membrane, fabricated by dip-coating a hybrid SiO_2 sol with an average size of 8 nm, gives a separation factor (α) of 300 for a mixture of *n*-butanol and water (95/5, mass ratio) during PV process [11]. It is also reported that a hybrid SiO_2 sol with an average size of 5–6 nm is suitable for fabrication of SiO_2-based membranes [12,17–19]. Although the relationship between silica-based sol size and PV performance of microporous SiO_2 membranes is clear, few silica-based NF membranes are reported due to its chemical instability in extreme pH environments. In comparison with SiO_2-based materials, TiO_2 and ZrO_2 materials exhibit much higher chemical stability and, hence, much research work is focused on the development of TiO_2 and ZrO_2 NF membranes [1]. These NF membranes hold great promise for the separation and purification of catalyst [20], dyes [21], and heavy mental ions [22,23] *via* the charging mechanism and sieving effect. However, the investigation on the relationship between titania and/or zirconia sol size and NF performance of those membranes is scarce. More importantly, appropriate sol size for fabrication of TiO_2 and/or ZrO_2 nanofiltration membrane is still ambiguous. As can be seen in Table 1, a zirconia membrane derived from a zirconia sol with an average size of 2–3 nm shows a discontinuous separation layer with many defects [13]. A dense zirconia membrane fabricated by using the sol with a size of about 6 nm cannot permeate water even under a trans-membrane pressure as high as 1.0 MPa [14]. It is also reported that a zirconia nanofiltration membrane, fabricated by dip-coating zirconia sol with particle size in the range of 5–10 nm, presents a MWCO < 300 and a pure water flux of 0.256 $L\cdot m^{-2}\cdot h^{-1}\cdot MPa^{-1}$ [15]. Therefore, more information on the effect of sol size on nanofiltration performance of zirconia membranes is urgently needed. Such investigation will guide the fabrication of zirconia nanofiltration membranes.

In previous work [24], we synthesized stable zirconia polymeric sols with the average sizes in the range of 1–12 nm and investigated the effects of the processing parameters (*e.g.* hydrolysis time, hydrolysis temperature, hydrolysis ratio and doping of chelating agent) on the state and average size of ZrO_2 sols. The aim of this work is to systematically investigate the effect of sol size on NF performance of microporous zirconia membranes. High quality supported mesoporous γ-Al_2O_3 layer with controlled pore size (5–6 nm) is used as the support for dip-coating. Microstructure, pure water flux, molecular weight cut-off (MWCO) and salt retention of zirconia membranes from zirconia sols with different sizes are characterized. The properties of unsupported zirconia membranes (powder) are also determined by XRD, TG/DTA, nitrogen adsorption–desorption and static solubility measurements.

2. Experimental

2.1. Synthesis of ZrO_2 sols and fabrication of ZrO_2 membranes

Zirconia sols were synthesized through polymeric sol–gel route by using zirconium *n*-propoxide (70% in propanol, ABCR GmbH & Co., denoted as ZnP) as a precursor and diethanolamine (DEA, Shanghai Lingfeng Chemical Reagent Co.) as a chelating agent. Recipes for the synthesis of ZrO_2 sols are displayed in Table 2. The general procedure for the preparation of a ZrO_2 sol is as follows. 4.5 ml ZnP was added into 20 ml 1-propanol (Shanghai Lingfeng Chemical Reagent Co.), and then a certain quantity of DEA was drop-wise introduced into the ZnP solution under vigorous stirring. Both operations were carried out in a nitrogen glove box. The mixture was immediately placed into an ice bath to prevent premature hydrolysis. Deionized water was drop-wise added into the solution under vigorous stirring and subsequently maintained at a fixed temperature for a certain period of time. The obtained ZrO_2 sols (referred to as DZ sols) were cooled down to room temperature and diluted 6 times with 1-propanol before dip-coating. Dip-coating is the most commonly used method for the formation of a membrane layer on porous supports. With a disk support withdrawn from a sol in a well-defined manner, a wet layer covering the substrate can be obtained either through capillary filtration or film-coating mechanism. In this study, supported ZrO_2 membranes were fabricated