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Development and gas permeation properties of microporous amorphous TiO₂–ZrO₂–organic composite membranes using chelating ligands

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ABSTRACT

Sol-gel derived microporous amorphous TiO₂–ZrO₂–organic composite membranes were prepared by two different types of chelating ligands, diethanolamine (DEA) and isoeugenol (2-methoxy-4-propenylphenol, ISOH) as reaction inhibitors for hydrolysis and condensation of Ti- and Zr-alkoxide. The structural properties of the composite gels were characterized via a thermogravimetric study (TG), X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), and N₂ adsorption analysis; and the optimized calcination atmosphere and temperature conditions for a microporous membrane were examined. A crack-free thin (50 nm) TiO₂–ZrO₂–organic layer for gas separation was formed on a SiO₂–ZrO₂ intermediate layer (150 nm) supported on a macroporous α-Al₂O₃ substrate as an asymmetric membrane. Compared with DEA, more of the ISOH and its remnants effectively remained after calcination, which promoted higher permeance and selectivity as a microporous gas separation membrane by forming bimodal microporous structures that narrowed the original TiO₂–ZrO₂ pores. A TiO₂–ZrO₂ membrane with ISOH calcined at 350 °C under a N₂ atmosphere showed He and CO₂ permeances of 1.0 × 10^{−6} and 2.0 × 10^{−7} mol m^{−2} s^{−1} Pa^{−1}, respectively, at 200 °C. The CO₂/N₂ permeance ratio was 6.4 at 200 °C and 46 at 35 °C.

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1. Introduction

From the viewpoint of global warming countermeasures and improvements in manufacturing efficiency, energy-saving gas separation processes such as CO₂ separation in flue gas and organic gas purification under normal temperature and pressure conditions are important issues. Membrane separation is known for its utility in low-cost gas separation processes and is expected to be utilized in solving the above problems. Facilitated transport membranes [1,2] and polyamideamine (PAMAM) dendrimer membranes [3,4] are reported to have extremely high CO₂ selectivity, while their stability, permeability and conditions of use continue to be developed. Silica membranes are known to have mostly thermal and chemical stability and to show high permselectivity as inorganic gas separation membranes [5,6]. However, the problem with silica membranes is that their performance is reduced under hydrothermal conditions with water vapor [7]. In order to improve the stability of silica-based membranes against water, several methods have been reported: metal doping [8], introduction of organic groups [9,10], and direct

membrane preparation via chemical vapor deposition (CVD) under high temperatures [11]. On the contrary, the usage of other stable inorganic materials, such as zeolite [12–14], carbon [15–17], and either TiO₂ or ZrO₂ [18–22] for molecular separation membranes, seems to be another potential approach for the development of highly stable porous membranes. TiO₂ and ZrO₂ are known to be superior inorganic materials in chemical and physical stability [23–25], and are utilized for high performance filtration membranes with a cutoff of less than 500 Da [26]. If TiO₂ and ZrO₂ can be used as a material for microporous gas separation membranes, those membranes can be applied to several chemical industrial processes in a wide range of usage conditions and with long-term stability for precise separation operations. Both of the above materials, unfortunately, have a crystalline structure that is too dense for gas transportation and separation [27]. In addition, due to the high reactivity of Ti or Zr alkoxide, difficulties have been encountered in controlling the colloidal size of sols to a small enough degree for the preparation of sol-gel derived molecular sieving by TiO₂ or ZrO₂ membranes. Therefore, it is difficult to develop TiO₂- or ZrO₂-based porous gas separation membranes with effective pore sizes of around 0.26–0.5 nm for gas permeation.

The conjugation of TiO₂ and ZrO₂ has been examined in order to modify the crystalline structure, and a TiO₂–ZrO₂ composite

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material reportedly shows an amorphous structure [28]. In addition, a $\text{TiO}_2\text{-ZrO}_2$ composite material with a higher TiO_2 fraction allowed an easier fabrication of crack-free membranes with a smooth surface [28]. Other researchers have suppressed condensation by adding a chelating ligand that can coordinate with the metal atom in the hydrolysis reaction of a metal alkoxide during the preparation of stable sols [29]. Gestel et al. prepared TiO_2 membranes with a chelate, and conducted a pervaporation (PV) separation of 95/5 wt% for an IPA/water mixture at 70 °C to obtain a separation factor of $\alpha=570$ [30,31]. As an example of the application of a gas separation membrane, Spijksma et al. prepared a $\text{TiO}_2\text{-ZrO}_2$ membrane using Diethanolamine (DEA) as a chelating ligand. The H_2 permeance and $\text{H}_2/\text{C}_4\text{H}_{10}$ permeance ratio of the membrane at 200 °C were $3.0 \times 10^{-7} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$ and 54, respectively. The He permeance of another $\text{TiO}_2\text{-ZrO}_2\text{-DEA}$ membrane prepared by George van der Donk was $2.0 \times 10^{-8} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$, and its He/ N_2 permeance ratio was approximately 14 [29,32]. These $\text{TiO}_2\text{-ZrO}_2$ membranes showed moderate molecular sieving performance, while their gas permeance and selectivity were not as high as general SiO_2 membranes. Gestel et al.

studied the potential performance of porous inorganic membranes for H_2/CO_2 separation, and concluded that $\text{TiO}_2\text{-ZrO}_2$ membranes can be expected to have an improved permselectivity by optimizing the sol and membrane preparation conditions [33]. In the present work, for the development of sol-gel derived microporous $\text{TiO}_2\text{-ZrO}_2\text{-organic}$ hybrid membranes using a chelating ligand for gas separation, we studied the effect of the type and amount of a chelating ligand on a microporous structure and on the gas permeation properties.

Fig. 1 shows the chemical structures of two different chelating ligands, Diethanolamine (DEA) and Isoeugenol (ISOH), used in this work. Diethanolamine is known to inhibit the precipitation of oxides during the hydrolysis of an alkoxide [34]. Benfer et al. reported that ZrO_2 and TiO_2 nanofiltration membranes with a pore size from 1 to 2 nm could be successfully obtained using DEA as an organic additive [35]. Since DEA interacts with titanium alkoxide as a tridentate ligand [36], its chelate-forming ability with alkoxides was expected to stabilize the $\text{TiO}_2\text{-ZrO}_2$ sols and to produce clear solutions that would be suitable for the coating and preparation of thin layers for separation. Isoeugenol also possesses chelate-forming ability for the modification of the chemical reactivity of transition metal alkoxides such as Ti and Zr. In addition, Isoeugenol offers the possibility of polymerizing the organic chain due to its polymerizable double bond in order to create additional porosity in the oxide structure [37,38]. The bonds between the metals and ISOH are expected to remain connected by the $\text{TiO}_2\text{-ZrO}_2$ polymer network after hydrolysis and polycondensation.

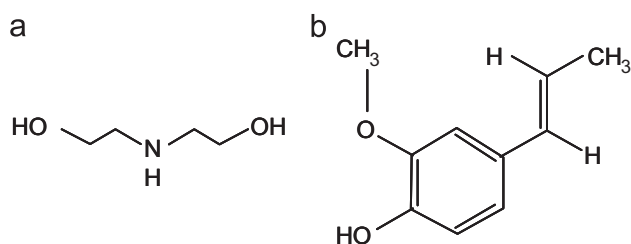


Fig. 1. Structural formula of (a) DEA and (b) ISOH.

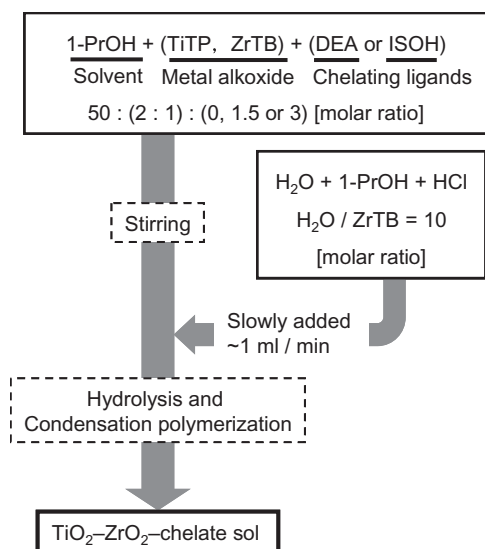


Fig. 2. Preparation procedure for $\text{TiO}_2\text{-ZrO}_2\text{-organic}$ sols.

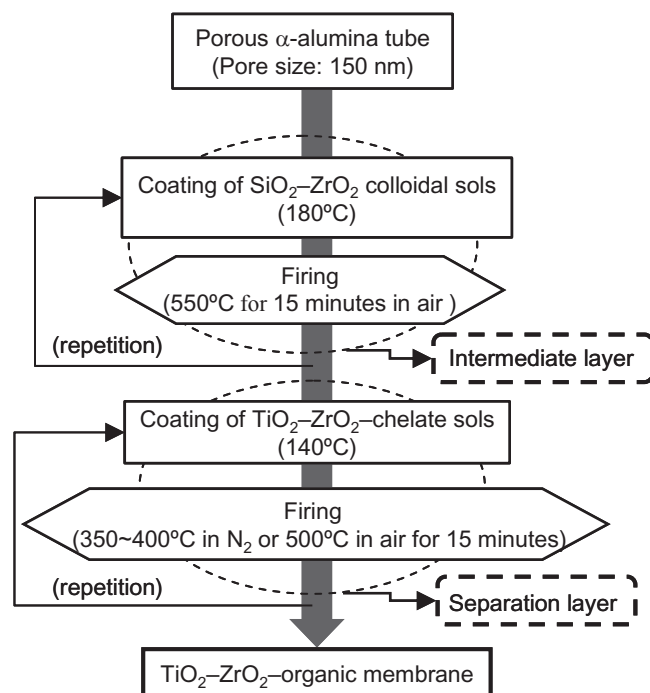


Fig. 3. Preparation procedure for $\text{TiO}_2\text{-ZrO}_2\text{-organic}$ membranes.

Table 1

Compositions of chemical reagents and solvents in the starting solutions for the preparation of $\text{TiO}_2\text{-ZrO}_2$ -based sols.

Sol type	Material	wt%	1-PrOH [g]	$\text{Ti}(\text{OC}_3\text{H}_7)_4$ [g]	$\text{Zr}(\text{OC}_4\text{H}_9)_4$ [g]	DEA or ISOH [g]	Alkoxide/chelate molar ratio [-]	H_2O [g]	HCl [g]
1	$\text{TiO}_2\text{-ZrO}_2\text{-DEA}$	9.0	103.1	5.8	4.8	3.2	1.0	1.8	0
2	$\text{TiO}_2\text{-ZrO}_2\text{-ISOH}$	4.0	55.4	1.3	1.1	1.1	1.0	0.4	0.6
3	$\text{TiO}_2\text{-ZrO}_2\text{-ISOH}$	4.0	56.0	1.3	1.1	0.6	2.0	0.4	0.6
4	$\text{TiO}_2\text{-ZrO}_2$	4.0	56.6	1.3	1.1	0	0.0	0.4	0.6
5	$\text{TiO}_2\text{-ISOH}$	4.0	54.1	2.4	0	1.3	1.0	1.5	0.6

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