



Preparation and pervaporation properties of silica–zirconia membranes

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ABSTRACT

It is well known that the hydrothermal stability of silica is improved by adding zirconia, and porous silica–zirconia membranes (with 50 mol% zirconia) were prepared by sol–gel techniques. A homogeneous silica–zirconia composite sol, prepared by the hydrolysis and condensation reactions of tetraethoxysilane (TEOS) and zirconium *n*-butoxide (ZrB) in an ethanol solvent, gave uniform and defect-free membranes. Since it was necessary for the hydrolysis and condensation reaction rates of ZrB to be reduced because these reactions are faster than those of TEOS, the chemical reactivity of ZrB was modified with the chelating agent acetylacetone (acac). Silica–zirconia membranes were used for dehydration of isopropyl alcohol/water mixtures at 348 K by pervaporation to evaluate the effect of preparation conditions such as temperature, $H^+/(Si + Zr)$, $H_2O/(Si + Zr)$ and acac/Zr molar ratios on membrane performance. The silica–zirconia membranes had the highest separation factor of 62.5 when they were prepared with $H^+/(Si + Zr)$, $H_2O/(Si + Zr)$ and acac/Zr molar ratios 0.05, 4 and 0.6, respectively, and three coating cycles. The membranes were characterized by Fourier transform infrared spectroscopy (FT-IR) and scanning electron microscope (SEM).

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1. Introduction

In general, distillation is used to separate multicomponent liquid mixtures. However, distillation requires large-scale equipment and a large amount of energy to separate mixtures with an azeotropic temperature, close boiling temperatures of the components and thermally sensitive components, because the process is based on differences of the boiling points of mixture components [1,2]. In recent years pervaporation, which is a membrane separation process, has attracted attention as a simple and energy-conservative separation method for azeotropic mixtures regardless of their vapor–liquid equilibrium characteristics. Pervaporation is based on the differences of solubility and/or diffusion rates of the permeants in the membrane [3]. Pervaporation generally has a higher energy efficiency than distillation, and leads to energy reductions of 40–60% [4]. In addition, it is possible to reduce equipment size because most of the volume for a pervaporation process is occupied by membrane modules.

Many studies on polymeric membranes and inorganic membranes for dehydration have been reported. Organic polymer membranes generally show high water-permeability for organic solvents such as ethanol in the pervaporation process. The drawbacks of these membranes are small flux owing to the low operating temperature that is used to ensure thermal stability, and their propensity to swell with an organic solvent [5–7]. Zeolite and silica membranes have

attracted attention as inorganic membranes. A zeolite membrane with high selectivity and flux has been commercialized, but it is unstable in acid media [8]. Silica as a membrane has characteristic features of controlled pore size, and functional groups on the silica surface can be modified relatively easily. However, silica shows poor hydrothermal stability and has limited chemical stability in alkaline media. Incorporation of metal oxides such as titania or zirconia in silica membranes has been investigated recently as a method for improving the hydrothermal stability of silica [9–13]. In particular, silica containing zirconia has a higher stability than other metal oxides in alkaline media [14].

A homogeneous silica–zirconia composite sol, which can be prepared by hydrolysis and condensation reactions of TEOS and ZrB in ethanol, is needed to obtain uniform and defect-free membranes. Moreover, homogenous incorporation of zirconia in a silica matrix is important for obtaining materials that exhibit chemical, thermal and mechanical stability [15]. However, because the reaction rates of ZrB are larger than those of TEOS it is difficult to obtain microscopically homogeneous structures by sol–gel techniques [5]. When the zirconia content of silica–zirconia mixed oxides is comparatively high (>40 wt%), the existence of some crystal structures of zirconia was confirmed, indicating that there were silica or silica-rich phases in the mixed oxide, and that the silica–zirconia mixture was inhomogeneous [15]. Asaeda et al. reported highly mixed silica–zirconia composite membranes prepared by rapid gelatification at 453 K, referred to as the hot-coating method, which showed high selectivity and high flux [5,16,17]. However, this preparation method might be unsuitable as an industrial production technique because it is necessary to make the membrane by rapid coating

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of silica–zirconia sol on a hot substrate at around 453 K using a wet cloth with the sol, where coating should be done while the substrate is hot [5]. Zhan and Zeng reported a synthesis method for well mixed silica–zirconia sol using acetylacetone (acac) to make the hydrolysis/condensation rate of the zirconia precursor slow [18]. However, preparation of silica–zirconia membranes for pervaporation using acac has not been reported.

In the present study, the chemical reactivity of ZrB was modified with the chelating agent acac to control the hydrolysis/condensation rate of ZrB. Porous silica–zirconia membranes with 50 mol% ZrO_2 were prepared by sol–gel techniques. The membranes were used for dehydration of isopropyl alcohol/water mixtures at 348 K by pervaporation, to evaluate the effects of preparation conditions such as temperature, and $H^+/(Si + Zr)$, $H_2O/(Si + Zr)$ and acac/Zr molar ratios on membrane performance. The membranes were characterized by Fourier transform infrared spectroscopy (FT-IR) and scanning electron microscope (SEM) to evaluate the effect of preparation conditions such as calcination temperature.

2. Experimental

2.1. Preparation of silica–zirconia membranes

Homogeneous silica–zirconia composite sols were prepared by hydrolysis and condensation reactions of TEOS (Wako) and ZrB (Alfa Aesar). The silica–zirconia sols were prepared at the relative molar ratio TEOS:ZrB:acac:HCl:H₂O:ethanol = 0.5:0.5:0.15–1.0:0.025–0.1:2.0–8.0:205 [16,18,19]. TEOS was dissolved in 100 ml of ethanol, and ZrB was dissolved in 100 ml of ethanol together with acac below 277 K. The TEOS and ZrB solutions were mixed at room temperature for 5 min, then aqueous hydrochloric acid (the catalyst for the hydrolysis and condensation reactions) was added dropwise at 1 ml min⁻¹. The mixture was stirred for 15 min at room temperature and refluxed for 24 h.

Silica–zirconia membranes were prepared on a porous alumina tube (diameter 10 mm, thickness 4 mm, mean pore size 0.15 μm, porosity 40%; Noritake, Japan) with a γ-alumina interlayer. The structure of the α-alumina support and preparation of the γ-alumina interlayer were as previously reported [20]. Briefly, γ-alumina interlayers were prepared by dipping the α-alumina tubes into 0.6 mol l⁻¹ boehmite (γ-AlOOH) sol with 1.4 wt.% polyvinyl alcohol. If silica sol was coated directly on the α-alumina support, the membrane had many cracks because the silica–zirconia particle size in the sol was too small compared with the pore size of the α-alumina support. Hence, the γ-alumina interlayer with 2–5 nm pore size was coated on the α-alumina surface to obtain crack-free membranes. The

outside of the α-alumina tubes was dip-coated with 0.6 mol l⁻¹ boehmite solution for 10 s, dried at room temperature for 3 h, then calcined at 873 K for 3 h with heating and cooling rate 1 K min⁻¹. After coating the α-alumina support with γ-alumina it was dipped into silica–zirconia sol and withdrawn after 10 s at a rate of 0.4 mm s⁻¹. The membranes were calcined in air at 373, 453, 573 or 673 K for 3.5 h with heating and cooling at 1 K min⁻¹. One or three coating–calcination cycles were used to determine the effect of the number of coating cycles. SEM (S-3500N, Hitachi) was used to examine the cross-sectional structure of the membrane. Samples were prepared by mechanically breaking the membranes, and coating them with a layer of gold by ion sputtering (E-1010, Hitachi). Powders of the silica–zirconia products were prepared for examination by FT-IR. After silica–zirconia sol was dried at 333 K for 15 h and at 393 K for 3 h, a silica–zirconia powder was obtained by the same procedure that was used for preparing the membrane. FT-IR spectra were obtained with a JEOL JIR-7000 spectrometer using the sample diluted 1:100 with potassium bromide (KBr). FT-IR spectra were collected after 30 scans with resolution 4 cm⁻¹.

2.2. Pervaporation

The pervaporation performance of the silica–zirconia membrane for IPA/water (10 wt.%; 27.0 mol%) mixture was determined at 348 K. Fig. 1 shows the pervaporation apparatus. A tubular membrane with closed end was placed in a 300 ml glass vessel, and the membrane was immersed in the IPA/water mixture. The vessel was filled with the IPA/water mixture that was then stirred. The pressure on the permeate side was maintained at about 100 Pa with a vacuum pump. Permeated vapor was collected in a liquid nitrogen cold trap. The weight of permeate was measured, and the water concentrations of feed and permeate mixtures were determined by Karl-Fischer titration (MKS-500, Kyoto Electronics Manufacturing). The pervaporation performance of the membrane was evaluated by the permeation flux F (mol m⁻² s⁻¹) and separation factor α (water relative to IPA), using expressions (1) and (2).

$$F = (P / 1000) / (At) \quad (1)$$

where P (mol), A (m²) and t (s) are molar quantity of permeate, membrane area and time, respectively.

$$\alpha = (y_w / y_o) / (x_w / x_o) \quad (2)$$

where x and y are the molar fractions of the components in the feed and the permeate, respectively. Subscripts W and O indicate water and IPA components, respectively.

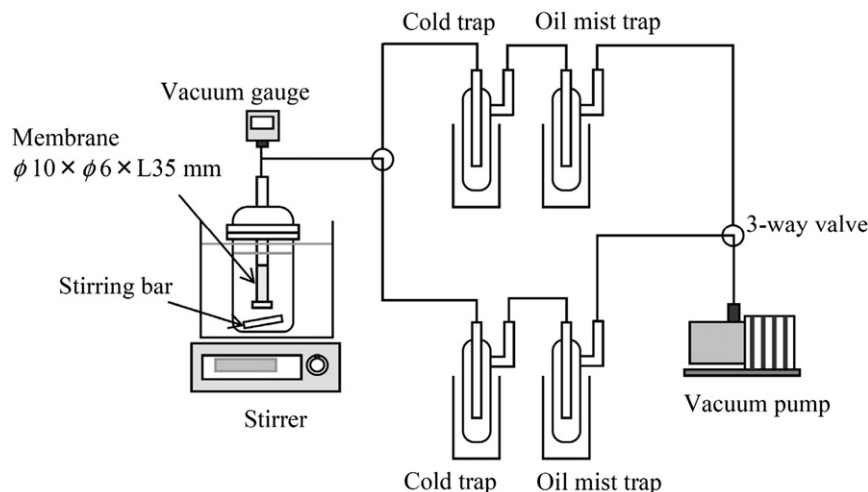


Fig. 1. Pervaporation apparatus.

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