

Enhanced Ethanol Dehydration with Hydrostable Inorganic Pervaporation Membranes

M. C. DUKE

ARC Centre for Functional Nanomaterials, School of Engineering, The University of Queensland, Brisbane Qld 4072, Australia

B. LIM

*ARC Centre for Functional Nanomaterials, School of Engineering, The University of Queensland, Brisbane Qld 4072, Australia
School of Life Sciences and Chemical Technology, Ngee Ann Polytechnic, Singapore 599489*

J. C. DINIZ DA COSTA

ARC Centre for Functional Nanomaterials, School of Engineering, The University of Queensland, Brisbane Qld 4072, Australia

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ABSTRACT

Membranes which allow water diffusion in favour of other substances can offer increased efficiency in processes to dehydrate ethanol. Silica membranes can perform this selective diffusion, but have mostly been reported for their gas high gas separating ability. This work investigates the effectiveness of carbonised template molecular sieve (CTMSS) membrane to dehydrate ethanol/water mixtures. The silica derived top layer of the membrane was measured at 20nm thickness by XPS sputtering technique. However, the silica enters the porous structure of γ -alumina layer in excess of 90nm. After 200 minutes of operation, $H_2O/EtOH$ selectivity increased to 5.6 from around 1 due to gradual pore filling by adsorbed water and ethanol which contributed to inhibiting ethanol transport. The smaller water molecules were thus favoured in transporting to the permeate side. Total mass flux using a 10% ethanol feed remained constant at around $1.5 \text{ kg}\cdot\text{m}^{-2}\cdot\text{hr}^{-1}$. Selectivity of up to 9.5 was achieved when azeotropic feed solutions of 95% were used, displaying

the potential for this technology for a wide range of ethanol dehydration applications. Pressurising the feed up to 400 kPa doubled the permeate flux, but enhanced the transport of ethanol over water.

Key words: carbonised templates, molecular sieve membranes, water and ethanol separation.

INTRODUCTION

Economies across the world are demanding more energy to fuel sectors such as transport and industry. In tandem, our awareness of the negative climatic impacts of fuelling energy demands with fossil fuels also grows. There are major incentives for research towards cleaner means to store and utilise fuels, especially those for which are potentially renewable such as ethanol. This simple, water soluble hydrocarbon, is most popularly sourced from catalytic hydration with ethylene for industrial purposes, while for food use, is sourced from fermentation of glucose and fructose. Ethanol purification is by fractional distillation. However, thermodynamic limitations of distillation mean ethanol reaches its azeotrope at 96%. Benzene can be added to form a tertiary azeotrope to remove water, but besides the use of the tertiary product, small amounts of benzene remain in the ethanol. A popular alternative is using molecular sieve zeolite adsorbates whereby the small water molecule (kinetic diameter, d_k , 0.28 nm) is taken into the pores of the zeolite while ethanol (d_k 0.44nm) is not.¹ But as with any adsorptive process, batch systems and adsorbate regeneration/replacement leads to reduced efficiencies.

With the use of membrane films that selectively diffuse water over ethanol, a continuous process can be established which dehydrates ethanol beyond its azeotropic limits. Such a membrane could lead to increased efficiency compared to traditional distillation in that water is selectively taken to the vapour phase, leading to reduced separation stages and lower energy requirements. Microporous inorganic (silica) membranes show promise in this area as they have in the past shown excellent selectivity to gases with reasonable fluxes.^{2,3,4} In these membranes, the silica film allows smaller molecules to diffuse through the membrane over larger ones simply by size exclusion by the rigid inorganic silica matrix. Recent membranes developed by Yoshino's group⁵ displayed a H_2 (d_k 0.289 nm) permeance of 2×10^{-7} mol.m⁻².s⁻¹.Pa⁻¹ and H_2/N_2 (d_k 0.364 nm) permselectivity of 20 at 150°C.⁵

The favourable stability in solvents compared to their organic counterparts, has started researchers to trial their microporous silica membranes for dewatering of ethanol.^{6,7,8} For example Van Veen and co-workers⁹ achieved a selectivity of up to 350 for removing water from a 95% ethanol solution. Amorphous hydrophilic silica is however soluble in water¹⁰ and eventual irreversible membrane deterioration will result. Past work addressing this issue has reported effective use of silica-zirconia hybrids for *iso*-propyl alcohol and tetrahydrofuran.¹¹ However, these materials are more suitable to inhibiting the larger sized organics and not ethanol.

This work addresses the application of CTMSS membranes for

ethanol dehydration in a pervaporation setup. In addition, CTMSS membranes are characterised by SEM and XPS techniques to investigate the thickness of silica derived layers, which are responsible for the water and ethanol separation.

EXPERIMENTAL

The CTMSS membrane was formed on the surface of an α -alumina substrate (pore size 0.5-1 μ m, 30% porosity) from Rojan Ceramics, Australia, a flat platelet with 1.4 cm² active permeation surface area. Subsequent coatings of intermediate and top selective film layers were carried out, both comprising of silica sourced from tetraethyl ortho silicate (TEOS – Aldrich). Calcination was performed in vacuum to preserve organic pyrolysis products, leading to the formation of CTMSS. The intermediate layer included a methyl template sourced from methyl triethoxy silane (MTES –Aldrich) to control pore size around 0.5nm. Details of the sol-gel synthesis procedure, dipping and calcination methods are found elsewhere.¹² The schedule for coating the three membranes used in this study is shown in Table 1.

Table 1: Layer schedule for CTMSS membranes in this ethanol pervaporation study.

Layer Function	Number of Layers	Material
Primary	2	α -alumina
Intermediate	2	10/90 ratio corresponds to molar proportion of MTES/TEOS
Top 1	2	SS as single step sol gel
Top 2	2	TS as two stop sol gel
Template	All layers except the primary layer	C6 as hexyl triethyl ammonium bromide surfactant template

SEM samples were prepared by fracturing a membrane cross section then coated with platinum. SEM of the fracture surface was performed using a JEOL JSM-890 SEM at an accelerating voltage of 20 kV. Membrane films can be characterized by XPS for surface composition by detecting binding energies of various elements including oxygen, aluminium, silica and carbon. XPS data was acquired using a Kratos Axis ULTRA X-ray Photoelectron Spectrometer incorporating a 165 mm hemispherical electron energy analyser. The incident radiation was Monochromatic Al X-rays (1486.6 eV) at 150 W (15 kV, 10 mA). Survey (wide) scans were taken at an analyser pass energy of 160 eV and multiplex (narrow) high resolution scans at 20 eV. Base pressure in the analysis chamber was 1.0×10^{-9} torr and during sample analysis 1.0×10^{-8} torr. Depth profiling was performed using a differentially-pumped Kratos Minibeam III ion gun. 4 keV Argon ions were used at an ion source extractor current of 630 nA, rastered over an area of $\sim 3 \text{ mm} \times 3 \text{ mm}$ and stabilized by a Pfeiffer RVG 050C controller in conjunction with the Pfeiffer

UDV 140 leak valve. Sputter rates were calculated from the calibrated sputter rate for dense Ta₂O₅ in the range of 11.4 Å.min⁻¹.

Pervaporation was conducted at 25°C using a continuous mode setup with ethanol fed to the membrane side by means of a burette. Flow over the membrane was kept constant at 2 mL.min⁻¹ to reduce concentration polarisation effects. For high pressure feed testing, the ethanol reservoir was pressurised using argon gas. Permeate was driven through the membrane by applying vacuum (<10 mbar) to the permeate side, with the vapour passing through a trap immersed in liquid N₂. Figure 1 displays this pervaporation setup. The captured permeate was measured for ethanol and water concentration by a Shimadzu GC-17A gas chromatograph with a H-PLOT-U column, split ratio 1/75 and He carrier gas to take the sample to the TCD detector.

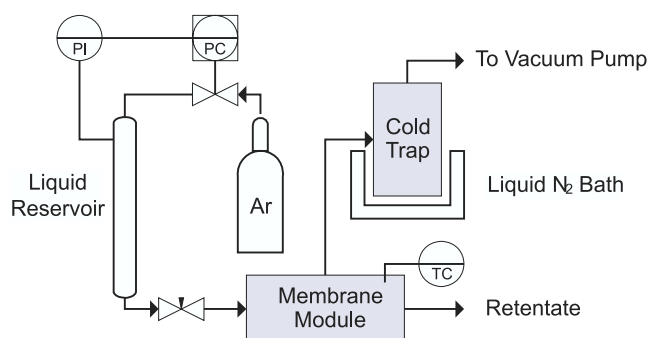


Figure 1: Pervaporation rig schematic

Process selectivity of H₂O to ethanol (EtOH), $\alpha_{H_2O/EtOH}$ was calculated using the commonly used equation for binary component pervaporation systems:^{8,9,13,14,15}

$$\alpha_{H_2O/EtOH} = \frac{y_{H_2O} x_{EtOH}}{x_{H_2O} y_{EtOH}}$$

Where y denotes permeate side molar fraction and x denotes the feed molar fraction. $\alpha_{H_2O/EtOH}$ together with mass flux in kg.m⁻².hr⁻¹ are used to measure the effectiveness of each membrane for dehydration of ethanol solutions.

RESULTS AND DISCUSSION

The representative XPS spectrum for the CTMSS membrane surface is presented in Figure 2. 90 minutes of etching corresponded to a depth of 103 nm. The response at 530 eV showed O_{1s} amount was unchanged between the initial and final surface approximately 100 nm deep. At 232 eV, C_{1p} response was only present at the initial surface, either because of surface organic contamination or from the carbonised surfactant. Si_{2p} response at 100 eV declined from the initial surface indicating the presence of the silica film. A response from

Al_{2p} at 72 eV was not visible on the initial surface, but appeared on the final spectrum due to the γ -alumina primary layers and α -alumina substrate.

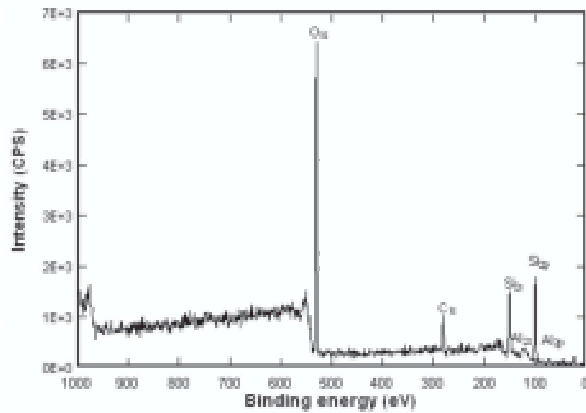


Figure 2: XPS spectrum of CTMSS membrane.

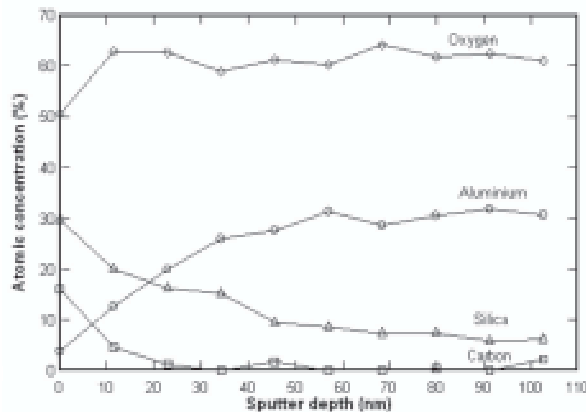


Figure 3: XPS Depth Profile Plot of top layers of CTMSS membranes.

Depth profile plots showing the atomic composition of each element corrected for response sensitivity along with sputter depth for the CTMSS membrane, is presented in Figure 3. At ~20 nm, Al composition overtook Si. The alumina layer was most dominating after 30 nm for both membranes. At a 20 nm thickness, the silica film enters the pores of the γ -alumina layer, with a signal still present up to 90 nm. This 20 nm effective silica film thickness is consistent with thickness observed in the literature for membranes made via the sol-gel method.^{2,3,16}

The SEM micrograph in Figure 4 shows a CTMSS profile. A film is clearly present above the substrate (α -alumina) with a 1.5-2.0 μm thickness. The major content of this film is γ -alumina from Locron.

The γ -alumina layer thickness was similar to silica membranes made by de Vos and Verweij.³

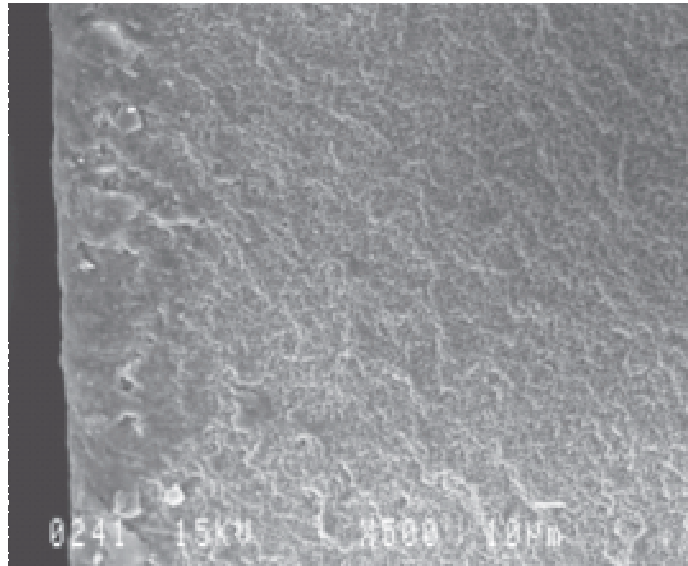


Figure 4: SEM of a CTMSS membrane.

The initial pervaporation results for the CTMSS membrane are shown in Figure . Flux varied between 1 and 2 $\text{kg}\cdot\text{m}^{-2}\cdot\text{hr}^{-1}$, but no trend was observed and is likely to be stable around 1.5. Process selectivity was less than unity during the initial stages of the experiment, but after 250 minutes, selectivity jumped to 5.6. Increases in selectivity with time were also observed during organic pervaporation in past work.⁹ The increase in selectivity is due to blocking of pores with water molecules, both physisorbed (hydrogen bonding) and chemisorbed (as hydroxyl groups) to the surface.¹⁷ Ethanol may have also been adsorbed into the structure.

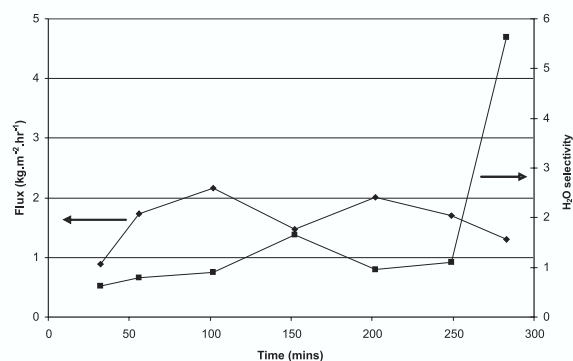


Figure 5: Total flux and H₂O selectivity of CTMSS membrane at 25°C.

The effect to flux and selectivity under different feed concentrations of ethanol is shown in Figure . Flux was less affected

by ethanol as no trend was observed outside experimental error ($\pm 0.5 \text{ kg}\cdot\text{m}^{-2}\cdot\text{hr}^{-1}$). On the other hand, water selectivity showed an initial decline at 50 vol% ethanol, but selectivity increased to 9.5 at the azeotropic mixture of 95%. In practice, membrane efficiency improved with ethanol concentration, but as separation was achieved over the entire concentration range, inorganic membranes may be applied to various dehydration applications.

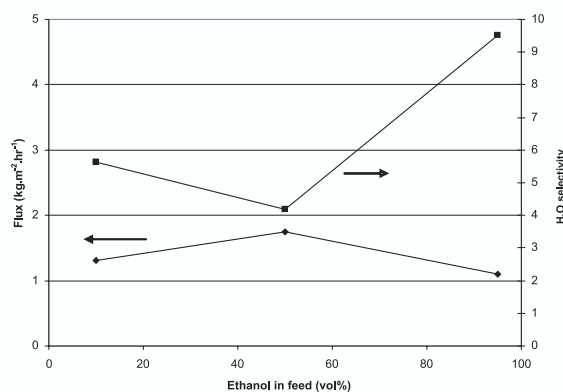


Figure 6: Effect of feed concentration of ethanol on flux and selectivity of CTMSS membrane at 25°C.

Increasing feed pressure increased flux slightly from 1 to above $2 \text{ kg}\cdot\text{m}^{-2}\cdot\text{hr}^{-1}$ as shown in Figure . The increase in driving force however was not advantageous to selectivity, as a drop from 9.5 to around 3 was observed. In other words, pressurising the feed solution assisted the ethanol diffusion over water. Operating at slightly above ambient pressure feeds is therefore favourable to achieve higher selectivities.

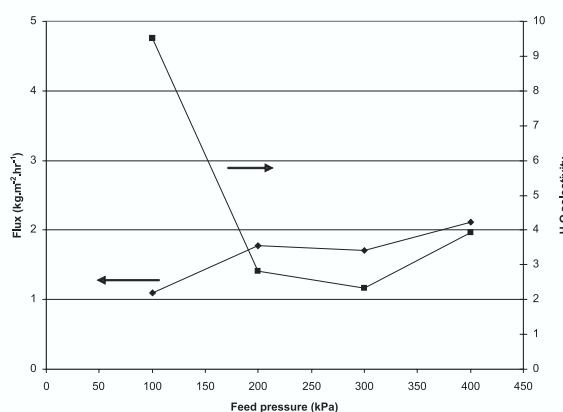


Figure 7: Permeate flux and selectivity trends with pressure applied to feed solution of 95 vol% ethanol at 25°C.

CONCLUSION

A CTMSS membrane was developed and tested for dehydration of ethanol using pervaporation. The top layer consists of a silica film of 20nm thickness, which subsequently enters the γ -alumina in excess of 90nm. Increases to selectivity were observed after 200 minutes of continuous operation due to water and ethanol chemisorption into the pores of the membrane, blocking ethanol diffusion. Best separation efficiencies were achieved at the azeotropic mixture of 95 vol% where selectivity was highest, but separation was achievable at all concentrations. Pressurising the feed up to 400kPa increased the flux slightly, but reduced the selectivity of the membrane. These results show the potential of CTMSS membranes as an enabling technology in ethanol and water separation.

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