

# PFSA-TiO<sub>2</sub>(or Al<sub>2</sub>O<sub>3</sub>)-PVA/PVA/PAN difunctional hollow fiber composite membranes prepared by dip-coating method

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**Abstract** PFSA-TiO<sub>2</sub>(or Al<sub>2</sub>O<sub>3</sub>)-PVA/PVA/PAN difunctional hollow fiber composite membranes with separation performance and catalytic activity have been prepared by dip-coating method. The good separation performance was brought about by the glutaraldehyde (GA) surface cross-linked PVA/PAN composite membrane, and the good catalytic activity of the membrane was achieved by the perfluorosulphonic acid (PFSA) used. The difunctional hollow fiber membranes were characterized by XRD, TGA, EDX, SEM, and FTIR. The separation performance was measured by dehydration of azeotropic top product of ethanol-acetic acid esterification, and the catalytic activity was obtained by investigating the esterification of ethanol and acetic acid. The FTIR spectra and the morphologies of difunctional hollow fiber composite membranes were similar for samples prior to esterification and post-esterification with ethanol and acetic acid for 24 h. Difunctional hollow fiber composite membranes with 2% PFSA, 8% TiO<sub>2</sub> (named as DM-T1), and 2% PFSA, 8% Al<sub>2</sub>O<sub>3</sub> (named as DM-A1) (all by weights) showed the best catalytic activity. They displayed fluxes of 165 and 173 g/m<sup>2</sup> h, separation factors of water to ethanol of 279 and 161, PFSA contents in difunctional hollow fiber composite membrane of 3.2 and 2.4%, the ratios of PFSA to feed solution (acetic acid–ethanol) of 0.031 and 0.023%, and the

equilibrium conversion of ethanol at 53.5 and 57.6%, in the given order for TiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> containing samples.

**Keywords** Catalysts · Coatings · Esterification · Membranes · Selectivity

## Introduction

Pervaporation, a novel and green separation process, which takes advantage of the difference between solubility and diffusion behavior of various components within the membrane [1], is considered to be a promising alternative to conventional energy intensive separation technologies [2]. Pervaporation has found viable applications in dehydration of organic solvents [3], in removal of dilute organic compounds from aqueous streams [4, 5], and in the separation of organic-organic mixtures [6–8]. Recently, the use of membranes in chemical reaction processes has attracted attention since separation membranes permit selective permeation of one or more product species from the reaction mixture, which helps to enhance the conversions of thermodynamically or kinetically limited reactions [9]. Using membranes to separate products in a reversible reaction is an effective method for producing esters [9].

Esterification of acid and alcohol is a typical example of an equilibrium-limited reaction, which produces water as a by-product. The conversion is generally low due to the limitation imposed by thermodynamic equilibrium. To achieve a high ester yield, it is customary to drive the equilibrium to the ester side by either using a large excess of one of the reactants (usually the alcohol) or using reactive distillation to accomplish in situ removal of product [10].

Up to the present time, pervaporation coupling with esterification has attracted much attention. This can be

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