



A novel catalytically active membrane with highly porous catalytic layer for the conversion enhancement of esterification: Focusing on the reduction of mass transfer resistance of the catalytic layer



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ABSTRACT

A composite catalytically active membrane was prepared focusing on the reduction of membrane mass transfer resistance to achieve a better esterification-pervaporation coupling performance. The effect of membrane preparation conditions on the membrane morphology was first evaluated. Under an optimized membrane preparation conditions, a “sandwich-like” composite membrane with a highly inter-connected sponge-like catalytic layer on a polyvinyl alcohol / polyethersulfone bilayer was obtained. The porosity of the membrane was found to be as high as 81.6%. A simple resistance-in-series model was developed to analyze the mass transfer resistance distribution in a traditional inert membrane reactor (IMR), a catalytically active membrane reactor (CAMR) with *dense* catalytic layer and a catalytically active membrane reactor with *porous* catalytic layer, respectively. Results showed that the preparation of a highly porous catalytic layer decreased the resistance of catalytic layer from 48.5% to 20.6% of overall resistances, leading to an enhanced water removal ability for the composite membrane. Finally, reaction-separation coupling experiments in IMR, CAMR with *porous* catalytic layer and CAMR with *dense* catalytic layer showed that, with a faster reaction kinetics and water removal rate, CAMR with *porous* catalytic layer exhibited a best coupling performance.

1. Introduction

Pervaporation membrane reactor (PVMR) has been considered as a promising *in-situ* product removal technology for conversion enhancement of equilibrium limited reactions [1,2]. Integrating both the functions of catalytic reaction and pervaporation into one single unite, PVMR can efficiently *in-situ* remove one of product out of the system, thus driving the reaction to the product side to achieve a much higher conversion.

Up to date, most of the membranes used in PVMRs only play the role of separation without any catalytic activity [3–8], the catalyst is generally suspended or dissolved in the bulk solution [9–12], usually this type of PVMR was also denoted as an inert membrane reactor (IMR). However, Yeung et al. [13] concluded that the reaction should take place as close to the selective membrane surface as possible since a Dirac delta distribution of the catalyst placed at the feed side outperforms a uniform catalyst distribution of catalyst placed in the bulk solution. A number of reports have [14–18] supported this conclusion by using a catalytically active membrane reactor (CAMR) where the membrane was made catalytically active, they observed an enhanced

equilibrium displacement for their reactions.

Generally, the structures of catalytically active membranes in the existing literatures could be classified to two categories: 1). The straightforward ones where both separation and catalytic functions are simply integrated into one single layer, the catalytic activity of the membrane was hardly satisfactory because the catalyst loading is difficult to increase in a very thin selective layer. 2). The others where a composite multi-layer structure was employed, usually with a catalytic layer on top of a selective layer. Over the years, this structure design has been attracting increasing attentions since it allows independent optimization of the separation and catalytic properties [14,19–21]. For example, Peters et al. [14,15] reported a composite catalytically active membrane by dip-coating zeolite or Amberlyst on selective layer using adhesion approach. They demonstrated that the catalytic activity of the membrane was comparable to that of bulk catalysts because of a much controllable catalyst loading, also the coupling performance of CAMR outran that of IMR. However, they also found that, with an increasing of catalyst thickness (higher mass transfer resistance in catalytic layer), this superior performance for CAMR disappeared due to an increased diffusion resistance within the catalytic layer [16].

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To be more specific, in IMR, total mass transfer resistance for the product removal comes from resistances of boundary layer and selective membrane layer. Whereas, in CAMR, the mass transfer resistance for product removal is only from the composite membrane (i.e. catalytic layer and selective layer combined) since the reaction actually takes place in the membrane [22]. In this way, if the mass transfer resistance of catalytic layer is too large (resulting from either high catalytic layer thickness or dense structure) [23] and thus resulting in a higher resistance than that of boundary layer in IMR, the total mass transfer resistance for product removal and reactant diffusion would be higher in CAMR, thus the reaction-separation coupling performance in CAMR would be significantly compromised. As a result, the essential to achieve a superior reaction-separation coupling performance for CAMR is actually relied on an elaborate preparation of a catalytic layer with low mass transfer resistance and high catalytic activity.

Immersion phase inversion is a most widely used versatile technique for preparation of polymeric membranes. A variety of morphologies could be obtained by adjusting the thermodynamics (liquid-liquid demixing or liquid-solid demixing mechanisms) or the kinetics (solvent-nonsolvent mass exchange rate) of the process. In our previous studies [24,25], we reported the use of heterogeneous catalysts to prepare porous catalytic layer by immersion phase inversion. However, with the presence of heterogeneous catalyst particles inside the layer, it was difficult to adjust the structure of catalytic layer since the catalyst particle seemed to interfere with the membrane formation process. As a result, the porosity of the catalytic layer could not be further increased for a lower mass transfer resistance. Moreover, the distributions of mass transfer resistance in IMR or CAMRs were not studied.

For a significant reduction of mass transfer resistance of the membrane, we reported a composite catalytically active membrane where a highly porous catalytic layer was coated on a dense polyvinyl alcohol (PVA) selective layer by immersion phase inversion. Specifically, the porous catalytic layer was made by adding catalyst $Zr(SO_4)_2 \cdot 4H_2O$ and pore-forming additive in a PVA host polymer. A unique feature of the catalyst is that $Zr(SO_4)_2 \cdot 4H_2O$ itself, when free of immobilization, is usually used as a heterogeneous catalyst for esterification since it is insoluble in the reactants [26,27], however, this catalyst can be completely dissolved in PVA aqueous solution to form a homogeneous and transparent catalytic casting solution. Thus there were no particles inside the catalytic casting solution and an easier manipulation of the membrane structure could be allowed. Moreover, various additives including polyethylene glycol (PEG) 2000, lithium chloride (LiCl) and polyvinylpyrrolidone (PVP) were applied into the casting solution to further increase the porosity of the membrane. Dehydration of *n*-butanol aqueous solution was carried out to evaluate the effect of membrane preparation conditions on the membrane morphology. The optimized membrane structure and surface morphology were then analyzed by SEM images. A resistance-in-series model was developed to analyze the total mass transfer resistance and membrane resistance in IMR, and CAMRs. Finally, reaction-pervaporation coupling for esterification of acetic acid and *n*-butanol were carried out in IMR and CAMRs to compare the conversion enhancement in different reactors.

2. Materials and methods

2.1. Materials

$Zr(SO_4)_2 \cdot 4H_2O$ with particle size of 20–40 μm was purchased from Tianjin Guangfu Fine Chemical Research Institute, the number of acid sites in $Zr(SO_4)_2 \cdot 4H_2O$ beads was found to be 0.53 mmol / g catalyst [28]. PVP, PEG 2000 and LiCl was from Shanghai Aladdin-Reagent Co., Ltd. PVA powder with the degree of polymerization and saponification of $1750 \pm 50\%$ and 99% were purchased from Beijing Yi Li Fine Chemicals Co. Ltd., Commercially available PES membranes (pore diameter 0.1–0.4 μm , porosity 65–70%, thickness 100 μm) from Shanghai Blue King Membrane Technology Engineering Co., Ltd. were served as the

support layer of catalytically active membrane. Ethanol, acetic acid, *n*-butanol, maleic acid were purchased from Beijing Chemicals Plant (Beijing, China). All the chemicals were at analytical grade and were used as received.

2.2. Membrane preparation and characterization

Three types of membranes with different structures were prepared in this section: PVA pervaporation membrane, catalytically active membrane with dense catalytic layer (dCAM), catalytically active membrane with porous catalytic layer (pCAM).

2.2.1. Preparation of PVA pervaporation membrane for IMR

A PVA pervaporation membrane was prepared for experiments related to IMR. A dense PVA selective layer was casted on a commercially available PES layer by dip-coating method, the detailed preparation procedure could be found in our previous studies [24,25].

2.2.2. Preparation of composite catalytically active membrane for CAMR

Multi-layer catalytically active membranes were prepared for experiments related to CAMR. It should be noted here that, in order to compare mass transfer resistance for various membrane structures, catalytically active membrane with porous catalytic layer (pCAM) and catalytically active membrane with dense catalytic layer (dCAM) were prepared respectively in this study.

For pCAM preparation: Since composite catalytically active membrane combines multi-layers, the adherence between different layers especially the adherence between selective layer and catalytic layer has a great impact to the stability of the composite membrane. In this study, PVA, the same material of separation layer, was chosen to be the host polymer for catalyst for the preparation of catalytic layer. First, a homogeneous casting solution containing PVA, additive and 5 wt% $Zr(SO_4)_2 \cdot 4H_2O$ was prepared by mixing a pre-dissolved $Zr(SO_4)_2 \cdot 4H_2O$ / additive aqueous solution (20 g) and a PVA aqueous solution (80 g), maleic acid was then added into the casting solution for cross-linking (with a concentration of 0.05 mol maleic acid per mole of PVA). The casting solution was stirred at 90 °C for 4 h and then allowed to stand for another 1 h to remove all bubbles. Afterwards, 0.75 g casting solution were carefully cast on a PVA pervaporation membrane (7 cm \times 7 cm) prepared in Section 2.2.1, and immediately immersed into an ethanol coagulation bath maintained at selected temperatures for 1 h to obtain the membrane. At the last step, the membrane was taken out of the coagulation bath and dried at room temperature.

For dCAM preparation: A modified homogeneous casting solution containing 10 wt% PVA and 5 wt% $Zr(SO_4)_2 \cdot 4H_2O$ was first prepared, other preparation condition were similar to the Section 2.2.2. Afterwards, 0.75 g casting solution were carefully cast on a PVA pervaporation membrane (7 cm \times 7 cm) prepared in Section 2.2.1, and immediately taken to a vacuum oven to dry at 37 °C for 24 h to obtain the membrane.

2.2.3. Characterization

The catalyst loading on the membrane was varied by adjusting the catalysts concentration in casting suspension, and it was determined by membrane weight increase during the casting process. Scanning electron micrographs (SEMs) of the membranes were taken using a JEOL JSM-6710F with an acceleration voltage of 10 kV. Viscosity of cast solution was measured using a rotational viscometer (DV-1, China) at room temperature.

Porosity of the catalytically active membrane was determined based on wet / dry method. First, the weight of a composite membrane was measured after it was dried in an oven at 40 °C for 24 h, then the dry membrane was immersed into *n*-butanol at room temperature for 4 h, afterward, the wet membrane was taken out and softly wiped out using a tissue and weighted quickly. Porosity of the membrane could be calculated using the following equation:

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