Enhancement of esterification conversion using novel composite catalytically active pervaporation membranes

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ABSTRACT

A catalytically active pervaporation membrane with a novel composite structure has been prepared by using the immersion phase inversion method. SEM images show its structure containing three layers: the top layer is a porous catalytic layer, the middle layer is the dense PVA selective layer and the bottom layer is the commercially available PES support layer. Esterification reaction of acetic acid and n-butanol is used as a model reaction to test its performance. Batch reaction results show that its catalytic activity is comparable to that of catalyst beads. The result of esterification reactions in pervaporation membrane reactors (PVMRs) shows that the acetic acid conversion reaches 91.4% in 20 h at 85 °C by using the catalytically active membrane, while the equilibrium conversion is around 71.9% under the same condition. The increase of temperature also facilitates the enhancement of acetic acid conversion. The catalytic activity and structure stability of the catalytically active membrane are further confirmed by consecutive experiments and SEM analyses.

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1. Introduction

Esterifications are typical examples of reactions controlled by thermodynamic equilibrium, and they are usually performed in batch reactors with the presence of liquid mineral acid catalyst. They usually suffer from limited product conversion, acid corrosion to equipment, and the difficulty of catalyst separation [1].

In this regard, catalytic pervaporation membrane reactor (PVMR) has drawn an increasing attention recently because of its ability to integrate the functions of catalytic reaction and perva-poration into one single unit [4–10,23–31], in which the product can be selectively removed right after it is formed at the vicinity of catalyst, and therefore, effectively driving the reaction to the product side. In contrast to the traditional reactive distillation process [2,3], where the preferred temperatures for reaction process and the separation process are usually different, the separation process in catalytic PVMR can be carried out at one optimal reaction temperature [11], and its separation efficiency is not limited by relative volatility.

Up to date, most of the membranes used in PVMRs only play the role of separation without any catalytic activity [14,26,30].

Several studies [27–29] demonstrate that the equilibrium shifting could be enhanced if a catalytically active membrane is used. However, in those literatures, separation and catalytic function are integrated into a single layer membrane with dense structure [20], which will lead to a low catalytic activity, as most catalysts sites are wrapped in the membrane with dense structure. Therefore, it has been suggested to use composite multi-layer catalytically active membranes to optimize the separation and the catalytic performance independently [13].

Peters et al. reported an attractive and inspiring result by applying zeolite or Amberlyst coated composite catalytically active membranes in a pervaporation-assisted esterification between acetic acid and n-butanol [20,21]. They demonstrated that their membrane was able to couple catalytic activity and water separa-tion capability together. The catalytic activities of their membranes were comparable to that of catalyst particle. In their study, the catalytic layer was simply deposited on the separation layer using the adhesion method, the membrane pre-treatment and the properties of binder appeared to have great influences on the performances of the membrane [21]. Therefore, new techniques for preparing the composite catalytically active membrane should be further studied to improve membrane performance from its structure.

In this article, we report a catalytically active membrane with a novel composite structure using the technique of immersion phase inversion. The membrane is prepared by coating a porous catalytic layer containing polyvinyl alcohol and ion-exchange resins on a

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dense polyvinyl alcohol (PVA)/ polyethersulfone (PES) separation membrane. The esterification of acetic acid and *n*-butanol is used as a model reaction to investigate its performance. The catalytic activities of the membranes prepared by blending and immersion phase inversion are compared. The catalytic and the pervaporation–esterification performances of the optimized membrane are further investigated by batch experiments and pervaporation experiments.

2. Experimental

2.1. Materials

Ethanol, acetic acid, *n*-butanol, maleic acid and PVA (with the degree of polymerization and saponification of 1750 ± 50 and 99%) were purchased from Beijing Chemicals Plant (Beijing, China). 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. (Shanghai, China) were served as the support layer of catalytically active membrane. All the chemicals were at analytical grade and were used without further purification. Deionized water was used in this study.

Ion-exchange resin consisting of highly cross-linked styrene–divinyl benzene copolymer beads was obtained from Guangfu Fine Chemical Research Institute (Tianjin, China), and it was used as a heterogeneous catalyst in esterification. The commercial resins were washed with methanol and water to remove impurities, then dried in vacuum at 50 °C for 12 h; after that, these resins were milled and sieved to obtained small resin beads with size less than 150 μm. During the preparation of catalytic layer, different size fractions of the resin beads were further separated by sieving (13–25 μm, 25–48 μm, 48–75 μm, and 75–100 μm).

2.2. Membrane preparation and characterization

The composite catalytically active membrane consists of three layers: a support layer (commercial PES porous membrane), a separation layer (PVA pervaporation membrane) and a porous catalytic layer with the loading of catalysts.

2.2.1. Preparation of separation layer

The separation layer (PVA/PES membrane) was prepared first by dissolving PVA powder in deionized-water at 90 °C for 6 h to obtain a PVA aqueous solution. Then a cross-linking agent, maleic acid with a concentration of 0.05 mol maleic acid per mole of PVA, was added to the PVA solution. The mixtures were vigorously stirred at 90 °C for another 12 h till a homogeneous solution was obtained, the PVA concentration in the cast solution is 2 wt%. After that, the PES support layer was dipped into the PVA casting solution for 5 min, and then dried at room temperature for 2 h. Four dip-coating processes were conducted in order to avoid morphological defects. At last, the crosslinked PVA/PES membrane was dried overnight at room temperature and then treated at temperature 120 °C for another 1 h to ensure the esterification reaction between maleic acid and PVA complete.

2.2.2. Preparation of catalytic layer

The catalytic layer was prepared by two different methods.

2.2.2.1. Blending. A catalyst suspension was first obtained by mixing a preset amount of catalysts in deionized-water under mechanical agitation, and then mixed with various concentrations of PVA aqueous solution containing maleic acid (with a concentration of 0.05 mol maleic acid per mole of PVA). A casting suspension was obtained by stirring the mixture overnight to break the clusters of resin particles and then sonicated for 1 h to remove all bubbles. Afterwards, casting suspensions were carefully cast on the PVA/PES membrane prepared in Section 2.2.1, then dried at room temperature for overnight to obtain the catalytically active membrane.

2.2.2.2. Immersion phase inversion. A casting suspension was first prepared as described in Section 2.2.2.1. Then suspensions were cast carefully on the PVA/PES membrane prepared in Section 2.2.1. The casting membrane was immediately immersed into an ethanol coagulation bath at room temperature for 1 h to obtain the catalytically active membrane. At the last step, the membrane was taken out of the coagulation bath and dried at room temperature.

2.2.3. Characterization

The catalyst loading, denoted as the weight of catalysts in per unit membrane area, was varied by adjusting the catalysts concentration in casting suspension, and it was determined by membrane weight increase during the casting process. SEM images of the catalytically active membranes were taken using a JEOL JSM-6710F with an acceleration voltage of 10 kV. SEM images of composite membrane before and after esterification reaction were taken to evaluate the stability of the membrane.

2.3. Performance of the catalytically active membrane

2.3.1. Batch experiments

Batch experiments were carried out in a 50 mL glass flask under agitation at different temperatures to determine the catalytic property of the catalytically active membrane. In a typical experiment, the glass flask loaded with 17 mL of *n*-butanol and a desired amount of catalysts were heated up to the reaction temperature first, after which the pre-heated acetic acid (10.7 mL) was added, catalyst beads (size range of ≤ 150 μm) were directly used in the reaction and the membrane was cut into pieces to achieve better contact with reactants. The glass flask was immersed into an oil bath immediately to start the reaction and this process was considered as the zero-time of reaction. Samples were taken periodically and then titrated by 0.2 M NaOH/ethanol solution to determine the residual acid content according to China Standard of GB/T 1628-2008. The conversion was calculated according to the following equation:

$$\text{Conversion (\%)} = \frac{C_0 - C_i}{C_0} \times 100\% \qquad (1)$$

where C_0 and C_i are referred to the initial acid concentration and the acid concentration at determined reaction time respectively.

2.3.2. Dehydration of n-butanol with pervaporation

Dehydration experiments of *n*-butanol were conducted first in a pervaporation module depicted in Fig. 1 to evaluate the separation performance of the catalytically active membrane [22]. In a typical experiment, a PVA/PES membrane or a catalytically active membrane was sealed in the middle of the module with the effective membrane area of 19.85 cm², then it was charged with a certain amount of water and *n*-butanol, the operation temperature was maintained at 75 °C. At the permeate side vacuum (4–5 kPa) was maintained by a cascade of a liquid nitrogen cold trap and a vacuum pump, magnetic stirring was used to avoid concentration polarization. The permeate was collected periodically and analyzed using Karl–Fischer titration. The separation performance of a