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Preparation of zeolite-coated pervaporation membranes for the integration of reaction and separation

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Abstract

Pervaporation is a promising option to enhance conversion of reversible condensation reactions, generating water as a by-product. In this work, composite catalytic membranes for pervaporation-assisted esterification processes are prepared. Catalytic zeolite H-USY layers have been deposited on silica membranes by dip-coating using TEOS and Ludox AS-40 as binder material. Membrane pre-treatment and the addition of binder to the dip-coat suspension appear to be crucial in the process. Tuning of catalytic layer thickness is possible by varying the number of dip-coat steps. This procedure avoids failure of the coating due to the high stresses, which can occur in thicker coatings during firing. In the pervaporation-assisted esterification reaction the H-USY coated catalytic pervaporation membrane was able to couple catalytic activity and water removal. The catalytic activity is comparable to the activity of the bulk zeolite catalyst. The collected permeate consists mainly of water and the loss of acid, alcohol and ester through the membrane is negligible. The performance of the membrane reactor is mainly limited by reaction kinetics and can be improved by using a more active catalyst.

Keywords: Esterification; Pervaporation; Catalytic membrane; Zeolite coating; Structured catalyst

1. Introduction

Pervaporation is a promising option to enhance conversion of reversible condensation reactions, generating water as a by-product. Pervaporation is attractive because the energy consumption is low, the reaction can be carried out at the optimal temperature, and the separation efficiency in pervaporation is not determined by the relative volatility as in reactive distillation [1]. In most pervaporation-coupled esterification studies presented so far, the membranes used are catalytically inactive [1–6]. Several authors [7–10], however, used membranes with catalytic activity to carry out esterifications of different alcohols. They showed that equilibrium displacement could be enhanced if the membrane selective layer itself provides the catalytic function. In these studies, however, the membranes were neither very catalytically active nor highly selective to water because one single layer provided both the selective and the catalytic function. Therefore, it has been suggested to use a composite catalytic membrane to be able to optimise both layers independently [10,11]. The principle of an esterification reaction in a composite catalytic membrane reactor is schematically shown in Fig. 1.

The acid and the alcohol molecules diffuse into the catalytic layer where they are converted to an ester and water. The formed ester molecule diffuses back towards the bulk liquid whereas water is removed in situ through the membrane due to the close integration of reaction and separation. Consequently, hydrolysis of the formed ester is reduced and the attained conversion will be increased compared to the inert membrane reactor [7–9]. Additionally, heterogeneous catalysts might be used more efficiently due to the thinness of the catalytic layer present on the membrane support [12]. Other advantages are that no catalyst neutralization or recovery is needed.

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Nomenclature

k_{obs}	observed reaction rate constant (m^3 mol^{-1} s^{-1})
k_r	reaction rate constant normalized for catalyst amount (m^3 mol^{-1} g_{cat}^{-1} s^{-1})
t	time (h)
T	temperature (°C)
X	conversion

Subscripts

c	calcination

The present study focuses on the preparation of composite catalytic pervaporation membranes. The esterification reaction between acetic acid and butanol was taken as a model reaction. First, the activity of various catalysts with respect to the esterification reaction was measured. Subsequently, composite catalytic membranes were prepared by applying a zeolite coating on top of ceramic silica membranes. The goal is to attain a strong and tuneable attachment of zeolite crystals on top of the selective microporous silica layer. Finally, the performance of the composite catalytic membrane as a combined reactor and separator in the esterification reaction was examined.

Zeolite coatings have been used as catalyst in various reactions like condensation, acylation and dehydrogenation reactions [12–17]. Zeolite coating is usually done through a crystallization step where the membrane is soaked in a zeolite crystallization mixture [13]. This method gives a strong attachment and possibly an oriented zeolite layer. However, zeolite crystallization takes place in highly alkaline aluminosilicate solutions. In the present case, direct zeolite crystallization was not possible because the microporous silica layer is not stable under these conditions. As a consequence, a dip-coat method was used. The membrane is immersed at a certain speed in a suspension of zeolite crystals that contains binder material followed by evaporation of the solvent by drying and calcination. Without this binder the deposited crystals will only bind to the surface by “Van der Waals” forces. In the dip-coat technique the resulting catalyst loading is satisfactory and easy controllable. This is important because in the preparation of composite catalytic membranes an optimum in catalytic layer thickness exists [11]. Furthermore, it is not necessary to develop a special zeolite synthesis formulation for coating applications, so an already optimized and catalytically active zeolite can directly be applied.

2. Experimental

2.1. Activity of catalysts

The activity of various zeolites was measured in the esterification of acetic acid and butanol. The zeolites investigated were H-ZSM5 and H-USY and were obtained from Zeolyst Int. (Valley Forge, USA). The average particle size was 1 μm as measured by scanning electron microscopy (SEM). Zeolite H-ZSM5 and H-USY, denoted as H-USY-*x*, where *x* represents the silica to alumina ratio, were used after calcination in an air stream for 8 h at 500 °C. For comparison with the zeolite catalysts also sulphated zirconium oxide was studied. A commercial sulphated zirconium oxide sample was acquired from Mel Chemicals (Manchester, UK) and was used after calcination in an air stream for 6 h at 550 °C.

The catalyst activity was studied in a batch reflux system. A three-necked flask equipped with a condenser and stirrer was charged with acetic acid (0.66 mol) and pre-activated catalyst. Then, the system was heated up to the reaction temperature after which pre-heated alcohol (0.66 mol) was added. The reaction temperature was maintained by means of a thermostatic water bath in which the reactor was immersed. For kinetic measurements, samples were taken periodically and analysed by a gas chromatograph equipped with a flame ionisation detector and a thermal conductivity detector. All catalysts were employed under similar reaction conditions. The reaction was performed at a temperature of 75 °C. GC analysis confirmed that no by-products were formed. The reaction rate constants were evaluated from the measured time-dependent concentration curves using the differential method. The non-linear least-squares regression technique was used to minimise the sum of the square differences on the reaction rate for acetic acid.

2.2. Coating and testing of the pervaporation membranes

Ceramic pervaporation hollow fibre membranes (TNO-TPD, The Netherlands) were used. The inner and outer diameter of the membranes is 2.0 mm and 3.2 mm, respectively. The length of the membranes is 20 cm. They consist of γ-alumina layers supported on a porous α-alumina tubular membrane. The permselective layer on the outside of the support is a thin (70 nm) layer made of microporous amorphous silica [18]. In the dehydration of *n*-butanol these membranes have proved to combine a high water flux with a good selectivity [18].

2.3. Standard binder solution

A silica binder solution was prepared as follows: TEOS (Merck, >98%) was mixed with ethanol and water. A small amount of nitric acid (65 wt.% in water) as a silicate oligomerisation catalyst was added and the resulting mixture was heated at 60 °C for 3 h under continuous stirring. The reaction mixture had a molar ratio TEOS/ethanol/water/HNO_3 of 1/3.8/6.4/0.085. Commercial colloidal silica (Ludox AS-40, Aldrich) was also used as a binder solution.

2.4. Zeolite dip-coat suspensions

The dip-coat solutions were prepared by mixing H-USY crystals and ethanol. Dealuminated zeolite H-USY with a