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Experiments and modeling of membrane microreactors

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Abstract

Two types of membrane reactors, the packed-bed membrane reactor (PBMR) and catalytic membrane reactor (CMR) were successfully miniaturized. Zeolites were incorporated as catalyst for reaction and membrane for separation. The membrane microreactors were tested for Knoevenagel condensation reaction between benzaldehyde and ethyl cyanoacetate to produce ethyl 2-cyano-3-phenylacrylate. Supra-equilibrium conversion and high product purity were obtained from selective removal of water during the reaction. A simple computation model was developed to simulate the reaction in the multichannel membrane microreactor using kinetic data from batch reaction, correlated data from membrane separation and published transport data. The influence of reactor geometry (i.e. channel width and membrane location), membrane separation and catalyst properties were evaluated and the results compared well with experimental data. The information provided by the model suggests several ways of improving the reactor performance.

Keywords: Miniature reactor; Base catalysis; Knoevenagel condensation; Zeolite; Pervaporation

1. Introduction

Miniaturization of chemical engineering processes is motivated by the quest for clean and efficient on-site, on-demand and on-time, distributed production of chemicals. The reactor being the heart of chemical production process has received a lot of attention. It has been shown that miniaturization can improve heat and mass transfer by decreasing the diffusion distance within the microreactor and increasing the interfacial area per unit reactor volume [1]. Rapid mass and heat transfer rates were obtained even at laminar flow regime [2] making microreactor an excellent choice for fast or highly exothermic reaction systems. Microreactors can suppress formation of hot spots and prevent runaway reaction enabling safe operation under otherwise dangerous conditions [3–5]. The precise spatial and temporal control over temperature, residence time, fluid flow and mixing is another advantage of microreactors [6]. Miniaturization also benefits membrane processes. A large membrane area in a small compact unit is obtained by simply assembling small membrane pieces. This is important for inorganic membranes, which are often brittle and difficult to form. The small membrane size also avoids many of the problems that plague large membrane units such as deformation and cracks introduced during processing and operation. The shorter diffusion length means enhanced mass transfer rate and an improved membrane separation as shown by the zeolite micromembranes reported by Leung and Yeung [7].

Multifunctional reactors that combine reaction and separation in a single process unit offer advantages in performance and operation. The selective removal of one or more products during reaction benefits reactions that are constrained by unfavorable thermodynamics. Supra-equilibrium conversion, improved selectivity and product purity are some of the observed benefits [8]. Membrane reactor also helped prevent catalyst poisoning and deactivation by removing undesirable byproducts from the reaction [9]. This work investigates the miniaturization of a packed-bed membrane reactor and catalytic membrane reactor for Knoevenagel condensation reaction of benzaldehyde and ethyl cyanoacetate. Zeolite catalysts and membranes are used to catalyze the reaction and

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Nomenclature

C	concentration of benzaldehyde (mol m^{-3})
$[C_7H_6O]$	concentration of benzaldehyde (M)
d	depth of channel (μm)
D	diffusion coefficient of bulk fluid ($m^2\ s^{-1}$)
D_{eff}	effective diffusivity of the catalyst ($m^2\ s^{-1}$)
[ECA]	concentration of ethyl cyanoacetate (M)
k	kinetic constant ($m^3\ mol^{-1}\ s^{-1}$)
l	channel length (mm)
r	rate of benzaldehyde conversion per unit catalyst surface area (mol $m^{-2}\ s^{-1}$)
S_a	surface area per unit mass of catalyst ($m^2\ g^{-1}$)
T	reaction temperature (K)
U_m	mean velocity ($m\ s^{-1}$)
U_z	fluid velocity along the z-axis ($m\ s^{-1}$)
w	channel width (μm)
x	radial dimension (m)
y	radial dimension (m)
z	dimension along channel length (m)

Greek letters

ΔP	pressure drop in microchannel (Pa)
ΔP_m	pressure drop across the zeolite membrane (Pa)
ρ	catalyst density ($g\ m^{-3}$)

separate the water byproduct. Zeolite and molecular sieve materials were incorporated as catalyst [10–13], membrane [7,14,15] and structural material [16] in miniature chemical devices such as microreactors and microseparators [17,18]. A recent review by Coronas and Santamaria [19] summarized the use of zeolite films in micro-scale applications. Very precise and localized addition of zeolite materials was obtained using new preparation techniques with a clear demonstration of direct engineering of the deposited zeolite's microstructure and chemistry [17,18]. Membrane microreactors using zeolite catalysts and membranes were successfully designed and fabricated. Reactions conducted in these membrane microreactors included Knoevenagel condensation [13,20,21] and selective oxidation reactions [22]. Supra-equilibrium conversion was obtained in the former, while the latter displayed improved performance against catalyst deactivation.

Computational modeling and simulation are important tools for the design of microreactor systems [23]. Microfluidic calculations provide invaluable information for designing the architecture of the microreactor [24]. Detailed simulation and modeling studies conducted by various researchers [25,26] have provided important insights to the reaction behavior in a microsystem environment. In this work, we present a simple reactor model for predicting the behavior of the Knoevenagel condensation reaction in a multichannel membrane microreactor. The kinetic data for the model were obtained from separate batch experiments, while the membrane separation was conducted on the actual miniature membrane unit and the transport data were taken from the literature. The influence of reactor geometry (i.e. channel width and membrane location), membrane separation and catalyst properties were evaluated and the results compared well with experimental data. The information provided by the model suggests several ways of improving the reactor performance.

2. Experiments

2.1. Microreactor design and fabrication

The microreactor design emphasizes on flexibility and ease of use. It consists of a microreactor plate and stainless steel housing. The plate contains the microfluidic components, the active catalyst and the separation membrane, while the housing unit provides a convenient interface between the microreactor and the macroscale laboratory environment. The detailed description of the microreactor housing can be found in the work of Lai et al. [21]. The modular design enables the rapid fabrication and testing of different microreactor architectures, catalysts and membranes. Fig. 1 summarizes the preparation and test procedures for the two types of multichannel microreactor plates. The membrane–catalyst plates consist of catalyst-coated microchannels with a membrane layer deposited on the back of the plate. The catalytic membrane plates have a layer of catalytic membrane deposited on the wall of the microchannels where the reaction and separation can take place simultaneously.

2.1.1. Membrane–catalyst plates

The *porous multichannel plates* were made from porous SS-316L plates (0.2 μm) purchased from Mott metallurgical corporation. Stainless steel was selected because of its good compatibility with most reactions, excellent machinability and low cost. Thirty-five straight channels measuring 300 μm wide, 600 μm deep and 25 mm long were cut into the 1 mm thick, 25 mm × 25 mm porous plates using electrical discharge micromachining (EDM, AGIE Wirecut 120). After fabrication, the plates were cleaned with detergent and rinsed with water to remove oils and dirt. The plates were further treated with dilute 0.05 M nitric acid to remove rust, before rinsing with deionised, distilled water and ethanol.

Zeolite membranes were grown on the back of the multichannel plate by pre-seeding the stainless steel with zeolite nanocrystals. The 100 nm Sil-1 and 150 nm NaA seeds were used to prepare ZSM-5 and NaA membranes, respectively. Mercapto-3-propyltrimethoxysilane was first coated on the back of the plate to provide the seeds with a strong anchor to the surface. The plate was then brushed with a water mixture containing 1 wt.% zeolite seeds. The process was repeated four times to obtain a uniform seed coating. After drying, the seeded plate was heat-treated at 523 K for 24 h to ensure good adhesion of the seed layer. The ZSM-5 zeolite membranes were grown from a synthesis solution containing a molar composition of 80 SiO_2:4 Al_2O_3:5 Na_2O:1 tetrapropylammonium hydroxide (TPAOH):20,000 H_2O. The aluminum hydroxide prepared by dissolving aluminum sulfate (98+%, Aldrich) in excess ammonium hydroxide solution was filtered, washed and weighed, before adding to a solution of 0.04 M sodium