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Application of fluidized bed film coating for membrane encapsulation of catalysts

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ABSTRACT

Fluidized bed film coating is considered as an efficient method to coat membranes onto catalytic particles producing a micro/mesoporous composite structure. These composite materials described as Membrane Encapsulated Catalysts (MECs) have the potential to increase reaction yield and selectivity by controlling the diffusion of products and reactants to and from the catalytic core. MECs were synthesized by film coating spherical zeolite particles with a nano-alumina suspension in hydroxylpropyl cellulose (HPC) using a conventional fluidized bed (Mini-Glatt). Coated particles were subsequently calcined in a furnace to remove the HPC leaving a porous alumina membrane. The fluidized bed coating process was evaluated by its ability to coat uniformly and defect-free as well as to control the membrane coating thickness. Scanning electron microscopy (SEM), Near Infrared Spectroscopy (NIR), and surface area and pore size distribution analysis (BET) were used to characterize the coated catalyst. Results show that membrane coatings were uniformly applied and free of defects upon optimization of fluidization parameters for the range of membrane thicknesses (6.0 μm–26.0 μm) produced in this study. The coating thickness estimated from the experimental techniques was in good agreement with the theoretically predicted thickness demonstrating the precision and controllability of the process. The alumina membrane was also shown to adhere well to the catalyst after removal of HPC and its thickness remained unchanged after calcining. Analysis of the membrane coated zeolite showed both microporous and mesoporous properties which may be particularly advantageous in separation processes. It was shown that NIR spectroscopy may be used as a method to replace image analysis for fast characterization of the membrane thickness. NIR spectra were shown to correlate coating thickness with absorbance at 1184 nm ($R^2 = .9920$).

1. Introduction

Catalytic and inert membrane reaction engineering is a concept that has gained intense interest due to its far-reaching applications in many industries [1–4]. This novel concept incorporates membrane separation as an active part of the reaction process as opposed to a separate unit operation. The design of the membrane reactor (MR) combines the enhanced chemical kinetics provided by the catalyst and controlled diffusion of chemical species provided by the membrane to create higher selectivity, yield, and reaction rate. The opportunities presented by MRs to increase productivity while decreasing feed and energy costs warrant the ever increasing research on the subject.

There are several catalyst/membrane arrangements that are compatible with various rectors (e.g. fixed bed, plug flow, fluidized bed, plate reactor) that have been studied thus far. Most common are physically separated catalysts [5,6], dispersed catalysts [7,8], and catalytic membranes [9–11]. In the first arrangement, the catalyst is usually packed or fluidized on the membrane. In the second, the catalyst is dispersed within the pores of the membrane. In the third, the membrane is inherently catalytic controlling both the catalysis and separation of the process. The actual arrangement used will depend on the need of the membrane to act as an extractor, distributer, or active contactor.

While these configurations have had promising results in hydrogenation, dehydrogenation, oxidation, and other reactions common in many chemical and petrochemical processes [12–17], use of MRs has largely remained at the laboratory scale. Many technical obstacles such as scalability, cost, and reliability still prevent large scale industrial practice of the technology. Saracco et al. state that producing large defect-free membranes, preventing coking or poisoning, and sealing of membranes at high temperatures as three of the many problems in scale up [2,3]. Catalyst/membrane arrangements mentioned thus far all succumb to these present limitations.

Membrane encapsulated catalysts (MECs) involve an innovative catalyst/membrane structure. Sometimes referred to as a hybrid or composite catalyst, a catalytic particle is coated with a membrane shell as illustrated in Fig. 1A. This concept has had previous success as a method to prevent coalescence of catalyst particles as well as a method to add thermal protection to a catalytic core [18,19]. Additionally, the membrane shell can be used as a method to control the diffusion of products and reactants to and from the catalytic core

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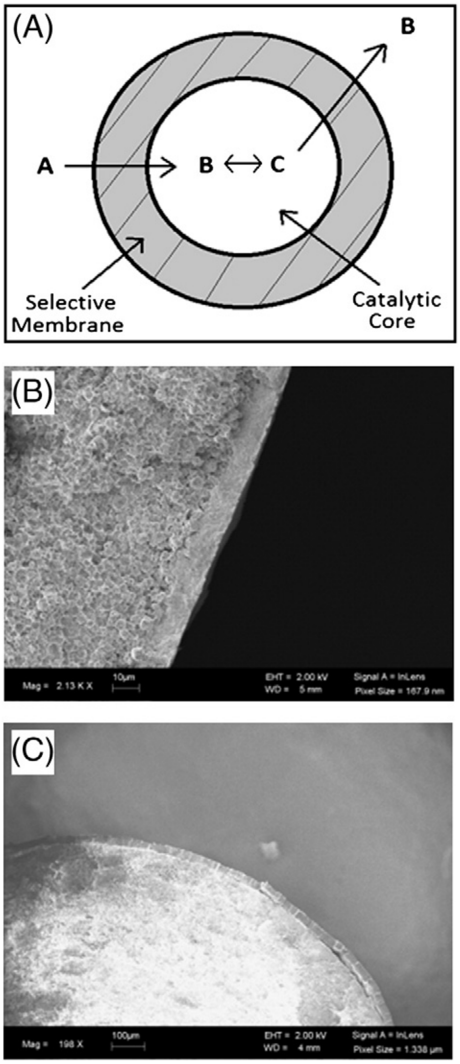

Fig. 1. (A) Illustration of Membrane Encapsulated Catalyst (MEC) with potential application. SEM image of zeolite cross section with coated membrane at (B) high magnification (2.13K×) and (C) low magnification (198×).

[20–22]. MECs used for this purpose offer many distinct advantages over the more conventional MR arrangements previously discussed.

The structure of the MEC yields a much higher membrane surface area than conventional rector membranes containing large membrane sheets. This allows for increased flux across the membrane suitable for industrial needs. This structure also avoids many of the problems associated with scale up previously mentioned. Because each catalyst particle is encapsulated with a membrane coating, the need for preparing a large-scale membrane is eliminated. This effectively limits or avoids defects associated with the production of large-scale membranes. The need for membrane sealing is also eliminated as each catalyst is coated with an individual membrane. The membrane layer may also be engineered to prevent poisoning of the catalyst. Fouling and coking may be avoided, as it would be feasible to replace the catalyst and membrane simultaneously after a certain process life. For these reasons, the development of MECs is essential to the industrial integration of membrane reactors.

Results of chemical reactions using MECs have been promising. Nishiyama reported complete para-selectivity in the production of xylene using a silica–alumina catalyst coated with a silicalite membrane [20]. Similar success has been reported as well [21,22]. Publications, however, have focused on the catalytic activity neglecting study on an efficient method of preparing and applying the membrane coating. Methods used in these previous studies include sol–gel, seed-film, dip-coating, thermal spraying, and slurry coating. Although these are adequate at laboratory scale, a method is required to produce membrane-coated catalysts for large-scale industrial use.

Fluidized bed particle processing has been studied extensively for its coating ability. Short particle circulation time and high heat and mass transport make fluidized beds ideal for film coating applications for large batches. Fluidized beds are also highly controllable processes allowing it to be automated if needed. Past literature has also brought to attention the complexity of the process [23–27]. Difficulties in optimizing the process may introduce unwanted agglomeration, attrition, or spray drying. This may prevent its use for controllable and uniform membrane coating applications.

This paper focuses on fluidized bed film coating as a controllable method to efficiently encapsulate a spherical catalyst particle with a porous membrane layer. This study utilizes a conventional fluidized bed to film coat a nano-alumina suspension onto zeolite particles. Controllability of the membrane thickness as well as the ability to coat defect-free membranes is explored. Scanning electron microscopy (SEM), Near Infrared Spectroscopy (NIR), and surface area and pore size distribution analysis (BET) are used as methods to characterize the membrane coated catalyst.

2. Materials and methods

2.1. Nano-alumina suspension preparation

Hydroxylpropyl cellulose (MW 80,000, Sigma Aldrich) is a hydrophilic water soluble polymer used as a binder in this study. Hydroxylpropyl cellulose (HPC) was dissolved in de-ionized water to make a 1.50% HPC (w/v) solution. Alumina (Al_2O_3, Aeroxide AluC, 13 nm), used as a test material for the porous ceramic membrane coating, was dispersed in the prepared 1.50% HPC (w/v) solution to make a 2.86% Al_2O_3 (w/v) suspension. The suspension was well mixed and no sedimentation was observed throughout the course of experiments. The nano-alumina suspension as described above was used in all coating experiments.

2.2. Fluidized bed film coating procedure

A conventional bench-top fluidized bed (Mini-Glatt, Glatt Air, USA) and a peristaltic pump (Masterflex L/S, Cole-Parmer Company, USA) were used to film-coat zeolite 13X (Sigma-Aldrich) with the nano-alumina suspension described above. 8–12 mesh spherical zeolite with a reported micro-pore volume of $.25 cm^3 g^{-1}$ [28] was used. It should be clarified that although the zeolite used in this study is not catalytic, it is a common catalyst support in many applications. Zeolite, 10 g, was charged into the fluidization vessel and fluidized without spray until the predetermined temperature was reached. Once the appropriate fluidizing air temperature was reached, the fluidized material was film coated using a bottom spray configuration with a 0.8 mm diameter nozzle. The nano-alumina suspension was sprayed at a constant rate throughout the duration of the experiment. Once the nano-alumina suspension was exhausted, fluidization was allowed to continue until the particles were dried. Fluidization and spray conditions were chosen to avoid agglomeration of catalyst particles, particle adhesion to the wall of the fluidization vessel, premature spray drying, and attrition. Process conditions affecting such unwanted phenomena are studied extensively in literature [23–27]. A temperature probe was used to measure the fluidizing air temperature in the vessel during coating. The optimized conditions pertinent to the fluidized bed film coating procedure are as follows. The fluidization and atomizing air pressure were set at 0.80 bar and 0.60 bar respectively. The spray rate was set at 1.00 ml/min and the fluidizing air temperature was set at 60 °C.