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Carbon nano-fiber based membrane reactor for selective nitrite hydrogenation

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ABSTRACT

Catalytic hydrogenation of nitrite in drinking water demands control over the selectivity towards nitrogen, minimizing the formation of ammonia. This selectivity is strongly influenced by the H/N ratio of reaction intermediates at the catalyst surface. Therefore, we fabricated a membrane reactor that feeds separately hydrogen gas and a nitrite solution. This allows dosing low but homogeneous hydrogen concentrations along the axial direction of the catalyst bed. As a consequence, low H/N ratios can be achieved, favouring the formation of nitrogen without limiting the nitrite conversion. We demonstrate that this reactor concept offers better nitrogen selectivity than conventional reactor configurations where hydrogen is pre-dissolved in the nitrite solution.

1. Introduction

During the last few decades, the use of microreactors for chemical conversion and analysis has experienced spectacular advances. With these miniaturized reaction systems, it is possible to explore wider pressure, temperature and concentration ranges as compared to conventional macroscopic reactors. Due to their small characteristic length, microreactors exhibit a high surface to volume ratio, where surface active forces dominate volume forces. This entails an enhancement in mass and heat transport that can improve activity and selectivity because the local concentrations and temperature at the active sites can be better controlled. Additionally, the small volume of the microreactors allows a safer operation, especially for the formation of hazardous and toxic chemicals [1–8].

Suppression of heat and mass transfer limitations in microreactors makes them ideal for three phase catalytic reactions. These reactions generally suffer from transport limitations caused, for example, by stagnant film resistance at the external surface area of the solid catalyst and internal diffusion in porous catalyst bodies. These effects are more prominent when the reactions are fast. To minimize resistance at the gas-liquid interface, a good dispersion of the gas in the liquid is required. This can be achieved via the use of membrane microreactors [6–10].

Micro/macro membrane reactors are usually divided in three categories, namely extractors, distributors and contactors. Extractors selectively remove a product of an equilibrium-restricted reaction to obtain higher yields as compared to conventional reactors. Distributors allow dosing the gas reactant along the reaction zone generating an optimum concentration profile. This becomes important for reaction networks where side reactions are strongly influenced by the concentration of one of the reactants. Contactors present a catalytic membrane, creating a well-defined reaction interface between two different medias [11–15].

Nitrite (NO_2^-) and nitrate (NO_3^-) hydrogenation are fast liquid phase reactions that can benefit from micro-membrane technology

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[16–19]. These compounds are typical water contaminants that can lead to health problems. Although nitrate is not directly harmful for humans, it can be converted in the body to nitrite via reduction processes leading to health diseases such as methemoglobinemia (blue baby syndrome) or to the formation of carcinogenic nitrosamines [20–25]. A very efficient way to remove nitrite is via catalytic hydrogenation [26]. This reaction converts nitrite to nitrogen and ammonia (NH_4^+, by-product). European Environment Agency (EEA) established a maximal ammonia concentration in water of 0.5 mg/L [27]. Therefore, significant efforts focus on the prevention of ammonia formation. The selectivity of nitrite hydrogenation is influenced by various parameters such as temperature, pH and the H/N ratio of reactant intermediates at the catalyst surface. This last parameter can be tuned by regulating the concentration of the reactants (nitrite and hydrogen). Higher H/N ratios will lead to higher ammonia selectivity while low ratios would lead to higher nitrogen selectivity [22,27–30]. However, low hydrogen concentrations could also generate mass transfer limitations, resulting in low efficient use of the catalyst and consequently very low activity.

In the current work, we explore the use of a distributor membrane reactor for the nitrite hydrogenation reaction. This reactor consists of a hollow alumina structure partly filled with carbon nano-fibers (CNFs) loaded with palladium nanoparticles. The outer structure is covered with a polydimethylsiloxane (PDMS) membrane. This reactor can regulate the hydrogen dosed in the reaction zone by hydrogen dilution with argon to achieve low H/N ratios. The reactor configuration allows low and homogeneous hydrogen concentration along the catalyst bed, preventing hydrogen depletion since hydrogen is continuously supplied through the membrane. Although membrane reactors have been studied for nitrate and nitrite hydrogenation [18,19,31–33], tuning of the selectivity via manipulation of the H/N ratio has not yet been demonstrated. Operation at low H/N ratio with nitrite solution pre-saturated with hydrogen would not be efficient, as exhaustion of dissolved hydrogen would cause very low nitrite conversion.

2. Experimental

2.1. Reagents and materials

Porous ceramic α-alumina (α-Al_2O_3) hollow fibers with a mean pore size of 800 nm were obtained from Hyflux CEPAration Technologies, Europe. These hollow fibers have an inner and outer diameter of 0.9 and 1.9 mm respectively and were cut in pieces 55 mm long. They were used as catalyst support and at the same time used to construct the reactor. Nickel was deposited using nickel nitrate hexahydrate (Merck), urea (Merck) and nitric acid (65%, Merck). CNFs were grown using ethylene (99.95% PRAXAIR), hydrogen and nitrogen (99.999% INDUGAS) without any further purification. Palladium was deposited using palladium acetylacetonate (Alfa Aesar) and toluene (>99.9%, Merck). PDMS coating was performed using toluene (>99.9% Merck) as solvent and a two component PDMS RTV 615 kit (Permacol B.V.) consisting of a vinyl terminated pre-polymer and a Pt-catalyzed cross-linker named RTV-A and RTV-B respectively. The catalytic tests were performed using sodium nitrite (>99%, Merck) as nitrite source.

2.2. Fabrication of the reactors

The synthesis of the membrane reactors consisted of several steps. Initially, nickel was deposited in the macropores of the alumina hollow fiber, followed by CNF growth. Any loose CNFs were removed by sonication. In the next step, palladium was deposited on the CNFs and then was calcined and reduced. Finally, the outer wall of the alumina fiber was coated with a viscous PDMS solution, forming a dense layer after curing. Several parameters of the process were studied to optimize the reactor (shown in Table 1).

2.2.1. Nickel deposition

Homogeneous deposition-precipitation technique was used to deposit nickel on the walls of the macropores of the hollow alumina fiber. The hollow fibers were immersed as-received in a stirred nickel nitrate solution of 80 mL. Several concentrations were used: 0.02, 0.2, 1.0 and 5.0 g Ni/L. The temperature was kept constant at 100 °C and a reflux system was connected to avoid evaporation of the water. The initial pH of the solution was adjusted at pH 3.5 using a diluted nitric acid solution. To precipitate the nickel on the alumina, 20 mL of concentrated urea solution (1.06 g/20 mL) were added drop-wise during the first 15 min. After 2 h of deposition time, the sample was removed from the nickel solution, rinsed thoroughly with miliQ water and dried at 85 °C during 2 h in vacuum.

2.2.2. CNF growth

Catalytic chemical vapour deposition technique was used to grow CNFs from the nickel particles deposited in the previous step. The synthesis of the CNFs was performed using an in-house build quartz tube reactor with an inner diameter of 10 mm. The hollow fiber was reduced in a mixture of 20% H_2 and 80% N_2 for 2 h at different temperatures (450, 550, 750 or 850 °C) to vary the nickel particle size. The temperature was raised from 20 °C to the target temperature at 6 °C/min under 100 ml/min of N_2. After the reduction, the system was cooled down in 80 mL/min N_2 flow to the CNF synthesis temperature (350, 450, 550, 600, 700, 750 °C). The CNF synthesis was performed during 30 min with a gas mixture containing 7% H_2, 20% ethylene (C_2H_4) and 73% N_2 with a total flow rate of 100 mL/min. Finally, the system was cooled down in nitrogen flow rate of 80 mL/min.

In the last step, the sample was sonicated in miliQ water for 30 min to remove any CNFs poorly attached to the alumina fiber. After this treatment, the sample was dried at 85 °C during 2 h in vacuum.

2.2.3. Pd deposition

A solution of palladium acetylacetonate in toluene with a concentration of 6 mg Pd/mL was prepared for depositing palladium. The hollow fiber with CNFs was immersed in 25 mL of the prepared solution for 17 h. Next, it was removed from the solution and dried during 2 h at 85 °C in vacuum. In the next step, the sample was oxidized in air for 1 h at 250 °C and reduced for 2 h in a gas mixture of 50% H_2 and 50% N_2 also at 250 °C. Finally the system was cooled down to room temperature in nitrogen flow.

2.2.4. PDMS coating

Adapted from Aran et al. [19], a two component PDMS kit (RTV-A and RTV-B, 10:1 weight ratio) was dissolved in toluene at 85 wt% and heated at 60 °C in a home-made reflux setup for pre-crosslinking the PDMS/toluene solution. The viscosity of the solution was measured by a Brookfield DV-II + Pro viscometer equipped with a nr-61 spindle. When a viscosity of 100 mPa.s was reached, the cross-linking was stopped by immersing the solution in ice. The hollow alumina fiber was dip-coated with the partially cross-linked solution at a constant speed of 2.5 mm/s. To prevent the presence of PDMS inside the alumina fiber, one end of the alumina was sealed by glue and the open end was kept above the PDMS solution during the coating. In the last step, the coated sample was completely cross-linked in an oven at 80 °C for 2 h. Finally, both ends of the alumina were cut to remove the glue at one side and the non-coated part at the other side.