



## Research paper

## Egg-shell membrane reactors for nitrite hydrogenation: Manipulating kinetics and selectivity



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## ABSTRACT

A method to fabricate catalytic membrane contactor reactors with a Pd-egg-shell distribution has been developed on  $\alpha$ -alumina tubes, allowing excellent control over the distribution of the active phase through the wall of the alumina tube. The performance of these catalytic membrane reactors has been assessed for nitrite hydrogenation. We have shown that manipulation of the thickness of the zone containing active phase induces different diffusion lengths for nitrite and hydrogen, strongly influencing activity and selectivity. Thick active layers have proved to be more selective to nitrogen, the desired product for purification of drinking water. Surprisingly, a thick layer with active phase also induced a negative apparent order in hydrogen, which is tentatively assigned to the fact that the ratio of concentrations of reactants, hydrogen and nitrite, varies extremely in the active zone.

## 1. Introduction

Catalysts in contact with reactants and/or products in both gas- and liquid-phase are highly relevant for the chemical industry [1–4]. Conventional multiphase reactors comprise slurry reactors operating with catalyst particles of typically tens of microns, *i.e.* stirred tanks or bubble columns, as well as packed bed trickle-phase reactors [4–8] with catalyst particles of a few mm typically. The most common problems encountered with slurry catalysts concerns the filtration section which is expensive and not very robust, since *e.g.* attrition of the catalyst particles creates fines that are difficult to separate from the liquid [4]. Catalytic packed bed trickle-phase reactors usually suffer from internal mass transfer limitations due to the relatively large catalyst support particles, necessary to limit the pressure drop. Additionally, the random packing of the catalyst bodies easily results in flow mal-distribution including stagnant zones and by-passes [4,5,9]. Structured catalytic reactors based on *e.g.* monoliths [10,11], foams [12–15], and cloth [16,17] have attracted special attention in the last decades since these circumvent the necessity of filtration combined with short diffusion lengths, similar to slurry catalysts.

Catalytic membrane reactors are an interesting alternative for

multiphase reactions. One of their main advantages is the well-defined gas-liquid interface independent of the flow rates of both phases [6,18–23]. Several reviews have been published describing and classifying catalytic membrane reactors. The most commonly used classification is based on the role of the membrane and is divided in three categories, namely extractor, contactor and distributor [21,24,25]. Extractors are used to suppress consecutive reactions or to increase conversion of equilibrium-restricted conversions, by selectively extracting one of the products through the membrane, integrating catalytic conversion with separation. Contactors promote a good contact between the catalyst and the reactant *via* the use of catalytically active membranes, integrating catalytic conversion and mixing. Contactors are a specific version of distributors, enabling well controlled distribution of one of the reactants to the reaction zone, avoiding variations in concentration in the axial direction of the reactor. This type of operation is relevant in cases that the selectivity is strongly influenced by the concentration of one of the reactants, *e.g.* in nitrite hydrogenation [26] and selective oxidation reactions operating with low oxygen concentration because of safety concern [21].

The major disadvantage of catalytic membrane reactors in three-phase operation is poor mixing in the liquid phase, caused by the

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laminar regimes of the liquid stream in the relatively narrow channel. Recent work carried by Pashkova et al. [27] and Vospornik et al. [28] showed how to improve mixing and transport in the liquid channel by introducing glass beads or a static mixer inside the membrane tube. A different approach to minimize transport limitations in the liquid reactants is miniaturizing the membrane reactor, thus decreasing the diffusion length [1,29].

Nitrate is a common inorganic contaminant that can be found even in drinking water. In the human body, it can easily convert to nitrite, endangering health *via* methemoglobinemia (blue baby syndrome) or *via* formation of some carcinogenic nitrosamines [4,30,31]. Catalytic hydrogenation is a very promising technique to eliminate nitrate and nitrite from drinking water since it can convert these inorganic contaminants into harmless nitrogen. However, avoiding the formation of the undesired by-product ammonia still presents a challenge. It is known that the selectivity of nitrite hydrogenation is strongly influenced by the H/N of reaction intermediates on the catalyst surface [32–36]. Therefore the selectivity of the nitrite hydrogenation can be manipulated via the local concentrations of hydrogen and nitrite at the active sites, which depend on the transport rate of both hydrogen and nitrite. Thus, nitrite hydrogenation is a suitable model reaction to study the mass-transfer performance of catalytic membrane reactors.

In previous work we have shown that the selectivity to  $N_2$  of the reaction benefits from the use of a membrane contactor reactor, based on Pd supported on CNFs inside the macro-pores of an  $\alpha$ -alumina membrane, as compared to different reactor configurations co-feeding hydrogen and nitrite to the reaction zone [37]. In short, the membrane reactor allows decreasing the H/N ratio in the reaction zone via hydrogen dosing through the membrane, resulting in higher nitrogen selectivity, without compromising the conversion level. The catalytic membrane contactor reactors used so far contained CNFs and palladium distributed throughout the  $\alpha$ -alumina tube. Here, we report on the effect of the distribution of palladium and CNFs inside the wall of the alumina tube, investigating the influence on conversion and selectivity. Differences are to be expected because of variation of the diffusion lengths to the active sites for both reactants, similar but not identical to egg-shell structures in conventional catalyst particles, as will be discussed in detail.

## 2. Experimental

### 2.1. Materials used

Porous ceramic alumina ( $\alpha$ - $Al_2O_3$ ) hollow fibers with a length of 200 mm and an inner and outer diameter of 0.9 and 1.9 mm respectively, were purchased from Hyflux CEPARATION Technologies, Europe. They were cut in pieces of 55 mm long to be used as catalyst support and as the skeleton of the reactor. Nickel nitrate hexahydrate (Merck), urea (Merck) and nitric acid (65%, Merck) were used to deposit nickel on the alumina hollow fibers. Ethylene (99.95% PRAXAIR), hydrogen and nitrogen (99.999% INDUGAS) were used to grow CNFs without any further purification. Palladium acetylacetonate (Alfa Aesar) and toluene (> 99.9%, Merck) were used to deposit palladium. Toluene (> 99.9% Merck) and a two component PDMS RTV 615 kit (permacol B.V.) consisting of a vinyl terminated pre-polymer (RTV-A) and a Pt-catalysed cross-linker (RTV-B) were used for the preparation of the PDMS solution. Sodium nitrite (> 99%, Merck) was used as nitrite source for the catalytic tests.

### 2.2. Fabrication of the reactors

The membrane reactors were synthesized as described elsewhere (submitted to Catalysis Today). In short, a hollow  $\alpha$ -alumina fiber was loaded with small nickel particles using nickel deposition-precipitation technique. Afterwards, CNFs were grown using a quartz tube reactor of 10 mm diameter. The hollow alumina fiber was placed inside the quartz

tube and the temperature was raised to 850 °C at 6 °C/min using 100 ml/min of nitrogen gas. After 1 h at 850 °C, a hydrogen/nitrogen mixture (50/50) was fed to the system for 2 h. Next, the temperature was cooled to 600 °C under 80 ml/min of nitrogen gas. The CNF growth was performed at 600 °C under a gas mixture containing 20% ethylene ( $C_2H_4$ ), 7%  $H_2$ , and 73%  $N_2$ . Three different CNF growth times were studied: 15, 22.5 and 45 min. Next, the temperature was cooled to room temperature under 80 ml/min of nitrogen gas. Any loose CNFs were removed via sonication with miliQ water. After drying the sample, palladium was deposited on the CNFs using palladium acetylacetonate precursor and was then calcined and reduced at 250 °C. In the final step, the outer wall of the alumina fiber was coated with a home-made PDMS membrane. One of the reactors with CNFs grown for 45 min and without PDMS coating was crushed and sieved to a particle size of 125–250  $\mu m$ .

### 2.3. Catalytic test

The synthesized membrane reactors were tested using the nitrite hydrogenation reaction under identical conditions. A nitrite solution (44  $\mu mol/L$   $NO_2^-$ ) saturated with argon was introduced inside the tube with a flowrate of 0.05 ml/min, while the shell of the membrane reactor was exposed to a gas mixture containing between 0.02 and 1.0 bar of hydrogen, balanced with argon. In this configuration, hydrogen is allowed to diffuse to the reaction zone through the PDMS membrane located at the outer wall of the reactor. Hydrogen and nitrite meet and react at the palladium particles located at the CNFs.

The crushed reactor without PDMS was tested in a packed bed reactor. A nitrite solution (217  $\mu mol/L$   $NO_2^-$ ) was pre-saturated in different hydrogen partial pressures (0.2, 0.5 and 1.0 bar) and fed to the catalytic bed.

All the tests were conducted at room temperature (20 °C). Nitrite and ammonium ( $NH_4^+$ ) concentrations were measured at the inlet and outlet of the reactor with an in-line Ion Chromatograph (Dionex, ICS 1000). These values allowed calculating nitrite conversion and ammonia selectivity according to equations 1 and 2 respectively. The solutions were not buffered. Selectivity to nitrogen was calculated based on the mass balance and the fact that exclusively ammonia and nitrogen are formed under these conditions [32,35,38] (Fig. 1).

$$NO_2^- \text{ conversion} = \frac{[NO_2^-]_{\text{initial}} - [NO_2^-]_{\text{final}}}{[NO_2^-]_{\text{initial}}} \cdot 100 \quad (1)$$

$$NH_4^+ \text{ selectivity} = \frac{[NH_4^+]_{\text{final}} - [NH_4^+]_{\text{initial}}}{[NO_2^-]_{\text{initial}} - [NO_2^-]_{\text{final}}} \cdot 100 \quad (2)$$

### 2.4. Characterization

The BET surface areas of the membrane reactors were determined with  $N_2$ -adsorption obtained at 77 K (Micromeritics Tristar) using the BET isotherm. The location and morphology of the CNFs inside the pores in the wall of the membrane reactor as well as the palladium particle size were determined with High Resolution Scanning Electron Microscopy, HR-SEM (Analysis Zeiss MERLIN HR-SEM) equipped with EDX (Aztec, Oxford Instruments). Palladium particle size was determined by averaging 150 measurements on three different positions in the sample. Cross-sections were prepared with the help of a scalpel.

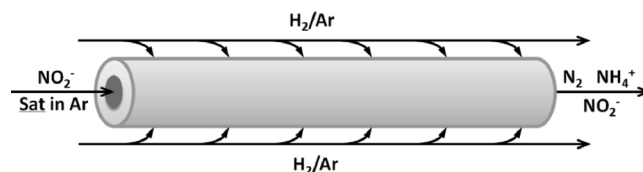


Fig. 1. Flow operation of a membrane reactor.

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