Structured catalyst-reactor for the selective reduction of nitrites and nitrates to N_2 in water

R. Brunet Espinosa[1*], D. Rafieian[2*], R. Lammertink[2], L. Lefferts[1]
[1]*Catalytic Processes and Materials (CPM);* [2]*Soft Matter, Fluidics and Interfaces (SFI); MESA+, University of Twente, P.O. Box 217, 7500 AE, Enschede, The Netherlands*
**corresponding author:r.brunetespinosa@utwente.nl*

Introduction

The removal of contaminants from drinking water is a technological and societal priority for the coming decennia. Among them, nitrites and nitrates still present a challenge. Even though their catalytic reduction is being investigated since the beginning of the nineties, the formation of the ammonia by-product has not yet been sufficiently prevented.

The aim is to selectively reduce nitrites and nitrates from water to N_2 avoiding NH_4^+ formation (major by-product) using hydrogen as reducing agent. An attractive option is to use carbon nano-fibers (CNF)-based catalysts since they are superior in activity as compared to conventional support materials. The main drawback is that their selectivity towards N_2 is low [1]. Therefore, the target is to synthesize CNF-based catalysts that maintain high activity while maximizing the N_2 selectivity. It has been proved that low H/N ratio of reaction intermediates on the catalyst surface can enhance N_2 formation. Thus, decreasing hydrogen concentration would favor N_2 selectivity. However, this would induce mass transfer limitation and very low reactions rates.

Therefore, a new reactor concept has been designed and synthesized in which the gas is fed through a membrane. This reactor consists of a hollow alumina fiber coated with a PDMS membrane outside. The nitrite and nitrate solutions flow from the tube side while the gas containing H_2 is supplied from the outside through the gas permeable membrane. N-containing contaminants and H_2 meet at the Pd particles. These particles are deposited at the CNFs grown in the macro-pores inside the wall of the alumina reactor. This provides a good accessibility of the active sites thanks to the open morphology of the CNF layer. The anticipated advantage of this membrane reactor is to allow a low and homogeneous H_2 concentration in the axial direction avoiding mass transfer limitations.

Materials and Methods

Membrane reactors were prepared from 6cm long hollow α-alumina fibers with 1 and 2mm of inner and outer diameter respectively. CNFs were grown via chemical vapor deposition technique from Ni particles previously deposited on the alumina. After depositing Pd as catalyst, PDMS was coated on the outside of the alumina via dip coating technique.

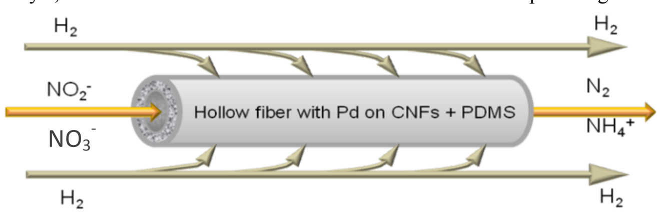

Figure 1. Scheme of the operation of the membrane reactor

Experiments were conducted on these membrane reactors at room temperature and atmospheric pressure. Nitrite and nitrate concentration ranged from 1 to 50ppm and H_2 partial pressure from 0.05 to 1bar. The liquid flow rate used was 0.2ml/min and experiments were run for more than 10h making sure that steady state was reached. Nitrite, nitrate and ammonium concentrations in the reactants and products were measured with Ion Chromatography.

Results and Discussion

Three different tests were performed in nitrite reduction in order to demonstrate the advantage of the membrane reactor. In the first experiment, H_2 was fed through the membrane (H_2 outside) and the nitrite solution to the tube according to the original concept. In the second case, liquid pre-saturated in H_2 was supplied to the tube and no H_2 was fed via the membrane (H_2 inside). In the third experiment, a reactor without PDMS was crushed and tested as a fixed bed reactor with liquid pre-saturated in H_2 (Packed bed). Residence time was constant for all three experiments.

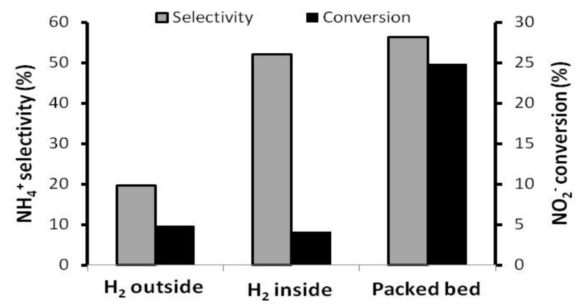

Figure 2.Comparison of the ammonia selectivity and the nitrite conversion for three different reactor concepts.

Figure 2 shows considerably low ammonia selectivity for the H_2 outside experiment demonstrating the advantage of this reactor concept. However, the conversion is significantly lower, which can be attributed to the by-pass of reactants when they flow from the tube side. Lower ammonia selectivities were obtained by tuning the thickness of the membrane as well as reducing the partial pressure of the H_2.

Significance

Considerably low ammonia selectivities are obtained with the new reactor concept. This is possible due to its unique design that allows a low and homogeneous H_2 concentration along the reactor.

References

1. Chinthaginjala, J.K.; Lefferts, L. Applied. Catalysis. B 101 (2010) 144-149.