



Research Paper

New Polymer Catalytic Membranes for Nitrite Reduction: Experimental Assessment

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Highlights

- Pd catalyst was successfully supported on PP and PES Hollow fibers.
- High stability of the supported catalyst was observed after 500 hrs.
- Pd was supported on the surface of the HF, defining the reaction zone.
- P_{H_2} and P_{CO_2} showed strong influence on the kinetics in the nitrite reduction.
- 90% of selectivity to nitrogen gas is achieved at 80 % of nitrite conversion.

Abstract

In this work, the experimental assessment of the performance of a new catalytic hollow fiber reactor with supported Pd catalyst for nitrite removal from polluted waters has been reported. The proposed reactor configuration facilitates working at low flowrate and hydrogen concentrations in order to improve the selectivity of the reduction reaction towards nitrogen, thus, inhibiting the formation of ammonia. Pd catalyst was supported on propylene and polyethersulfone hollow fibers following a simple impregnation method; the stability of the supported catalyst was checked along the operation time. Experiments of nitrite reduction were carried out in the range of 0.075-1 bar of H_2 partial pressure, 0.3-0.4 bar of CO_2 partial pressure, 200-400 mL/min of water flowrate and 20-200 mL/min of gas flowrate with an initial nitrite concentration of 150 mg/L. Under the experimental conditions, a selectivity to N_2 close to 90% with 80% conversion of nitrites was achieved.

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1. Introduction

In recent years, intensive agriculture activities, especially over-fertilization and the discharge of industrial wastewater have resulted in the increasing concentration of nitrogen species in groundwater, particularly the nitrate, which transforms into nitrite in the human body. Nitrites may cause methemoglobinemia in new-born children, usually denominated 'Blue Baby Syndrome'. In the body, it can be also converted to carcinogenic N-nitroso compounds which can cause hypertension and cancer [1]. Thus, nitrate, nitrite and ammonium concentrations in drinking water are limited to 50, 0.1 and 0.5 mg/L, respectively, by the European Community, EC, and to 10, 0.03 and 0.4 mg/L by the World Health Organization. The EC has also issued a directive that recommends a level of only 25 mg/L for nitrates, while for babies, it should be less than 10 mg/L [2].

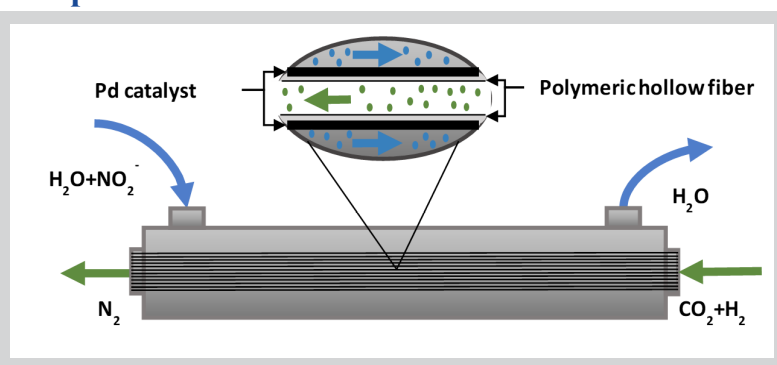
Nowadays, nitrate and nitrite removal from water is carried out by several physicochemical and biological denitrification processes [3]. Among them, electrodialysis, reverse osmosis or ion-exchange, lead to important volumes of brine or regeneration solutions that require post-treatment with high associated costs. Biological denitrification, on the other hand, avoids the high concentrated nitrate and nitrite wasted streams. However, the possibility

of bacterial contamination of drinking water, or the sludge formed during the process, make this biological process not competitive compared to physicochemical processes.

To solve these problems, Vorlop & Tacke [4] studied, for the first time, a catalytic reduction method that avoided the formation of the waste stream produced by other processes. Hörold et al. [2] reported a reaction mechanism based on the catalytic reduction over monometallic and bimetallic catalysts using Pd and a transition metal (Cu, Sn or In) in the presence of hydrogen as reductant. The transition metal reduces NO_3^- to NO_2^- , and then the converted NO_2^- is transferred to the adjacent Pd surface and further reduced to N_2 or NH_4^+ [5]. Thus, it has been widely known that selectivity towards N_2 production versus NH_4^+ production is mostly determined by the NO_2^- reduction stage on the Pd surface [6].

Conventional reactors, e.g., slurry reactors [7-13], fixed bed [14-18] and trickle-bed reactors [19-22] suffer strong diffusional limitations due to the low solubility of hydrogen in water and the limited accessibility of H_2 to the catalyst surface. Catalytic membrane reactors (CMRs), which have been developed in the past decades, combine reaction and separation in a single

Graphical abstract



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step where one (or more) reactant or product species is removed and separated, selectively. CMRs are intensified reactors that allow for easier catalyst optimization, smaller reactor sizes and lower energy consumption and especially suitable for industrial processes in which the performance is limited by the reaction equilibrium [23]. CMRs have been proposed as an alternative to overcome previous drawbacks and to enhance the performance of the catalytic reduction of nitrites. In this way, the membrane acts as a support for the metal catalyst and as a gas-liquid-solid contactor, promoting the contact between reactants and catalyst.

Nitrite hydrogenation has been mainly studied with the catalyst supported on commercial ceramic and carbon based membranes. The unique surface properties characteristic of carbon based supports, make them particularly useful with metals (e.g., high loading, good dispersion and easy recovery of metals) as well as the ability to control the porosity and good stability at low pH; being a better choice against traditional metaloxides supports. The use of carbon materials as catalyst supports for nitrite reduction has been mainly studied in the literature with active carbon (AC) or carbon nanofibers (CNFs) [13–16, 24–29].

Table 1 shows a summary of the results of different supports for nitrite reduction. Although the good properties of polymeric materials, only few references to polymeric supports with Pd have been reported due the poor stability of the metallic particles on polymeric supports. Volkov et al. [30] reported a good deposition of Pd on polypropylene hollow fibers. Other authors [31, 32] employed PEI and polyamide supports, for nitrates reduction; they reported good stability of Pd and nitrogen selectivity close to 80%.

In this work, a new catalytic membrane reactor based on catalytic polymeric hollow fibers (PHFs), hydrophobic polypropylene (PP) and hydrophilic polyethersulfone (PES), has been designed to achieve a high selectivity reduction of aqueous nitrites to nitrogen. Membrane stability, distribution of the palladium catalyst on the polymer pores, the influence of different operation variables (P_{H_2} , P_{CO_2} and flowrate) and the selectivity towards nitrogen have been experimentally studied.

2. Experimental

2.1. Materials and methods

2.1.1. Chemicals

$PdCl_2$ was purchased from Sigma-Aldrich with a purity of 99.999 %. KNO_2 , Ethanol 96 % v/v, HCL 37 % and NaOH were supplied by Panreac. Epoxy resin Loctite EA 9455 was provided by Loctite. Polypropylene, Celgard X-20, hollow fibers membranes were purchased by CELANESE and polyethersulfone, MicroPES 0.3/2, hollow fibers were supplied by MEMBRANA (3M). The properties of the polymeric hollow fibers are shown in Table 2.

2.1.2. Catalytic hollow fibers preparation

$PdCl_2$ was dissolved in MeOH solution with 0.2 M HCl at 50 °C for 2 h. MeOH was used to improve the deposition of the catalyst on the polymeric hollow fibers (PHFs) and HCl to solubilize the $PdCl_2$. To also improve the adhesion between the metallic particles and the hollow fibers surface a pretreatment of the PHFs with ethanol and NaOH (12.5 %) was carried out [30]. The palladium was deposited on the hollow fibers by direct impregnation. The solution was poured homogeneously over the pores of each fiber with a micropipette (1–10 μ L). The first half of the solution was supported on one face of the fibers. Afterwards, the fibers were turn upside down, and the other half of the solution was added. Once the fibers were impregnated, they were dried at room temperature in order to have them ready to reduce the metal of the catalyst. Finally, the palladium was reduced under hydrogen atmosphere for 1 hour.

2.1.3. Experimental setup

Fig. 1. depicts the scheme of the experimental set-up where the fibers already impregnated with the catalysts have been assembled in a stainless steel tubular reactor and sealed with an epoxy resin. The reactor, detail in Fig. 2., has two inlets and two outlets, the uprights for the fluid and the flat ones for the gas. Aqueous nitrite solution was fed to the reactor through the shell side whereas a gas stream, composed of hydrogen, carbon dioxide (to control pH) and the carrier gas (N_2) was fed to the lumen side. The gas and liquid flow counter-currently developing a controlled interphase on the surface of the hollow fibers. Moreover, Table 3 collects the experimental conditions.

Table 1
Different supports for nitrite reduction.

Support	Catalyst	Mode	X (%)	S_{N_2} (%)	Ref.
Al_2O_3	Pd, Pt, Pd-Cu, Ir, Ru, Rh	batch, flow-through	>90	>95	[2,12,14,15,33–47]
TiO_2	Pd	Batch	>90	>90	[48]
CeO_2	Pd	Semi-batch	>90	>90	[49]
Pumice	Pd, Pd-Cu	Batch	>90	>95	[50]
Silica	Pd, Pt, Pd-Cu, Ir, Ru, Rh	Flow-through, batch	>90	>95	[2,14,15]
AC	Pd	Batch, semi-batch, flow-through	>90	>80	[13–15,24,25]
CNF	Pd	Batch, flow-through	>90	>20	[14–16,26–29]
Graphite	Pd	Flow-through	>90	>10	[14,15]
Lignocelulose fiber	Pd	Batch	>90	-	[51]

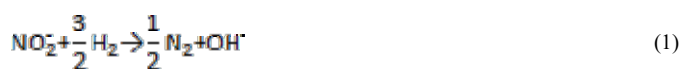
Table 2
Properties of PES and PP PHF.

Membrane type	Supplier	Pore size (μ m)	Inner diameter (μ m)	Wall thickness (μ m)	Membrane properties
Celgard X-20	CELANESE	0.115	400	50	Hydrophobic
MicroPES 0.3/2	MEMBRANA	0.2	300	100	Hydrophilic

Table 3
Range of experimental conditions.

Reaction temperature, °C	Room temperature
Hydrogen partial pressure, bar	0.075-1
Carbon dioxide partial pressure, bar	0.3-0.4
Catalyst loading, mg	35.83
Reactor volume, mL	30
Gas flowrate, mL/min	20-200
Initial nitrite concentration, mg/L	150
Number of hollow fibers	25
Liquid flowrate, mL/min	200-400
Liquid volume, mL	150
Flow current	Counter-current

Before the reaction started, the reactor was purged with nitrogen and then washed with water. A concentrated solution of nitrites, prepared with KNO_2 , was poured into the stirred water feed tank and then recirculated to the hollow fiber contactor, where the H_2 reduces the nitrites on the catalyst surface. Nitrite hydrogenation over Pd catalyst can be represented by the following reactions:



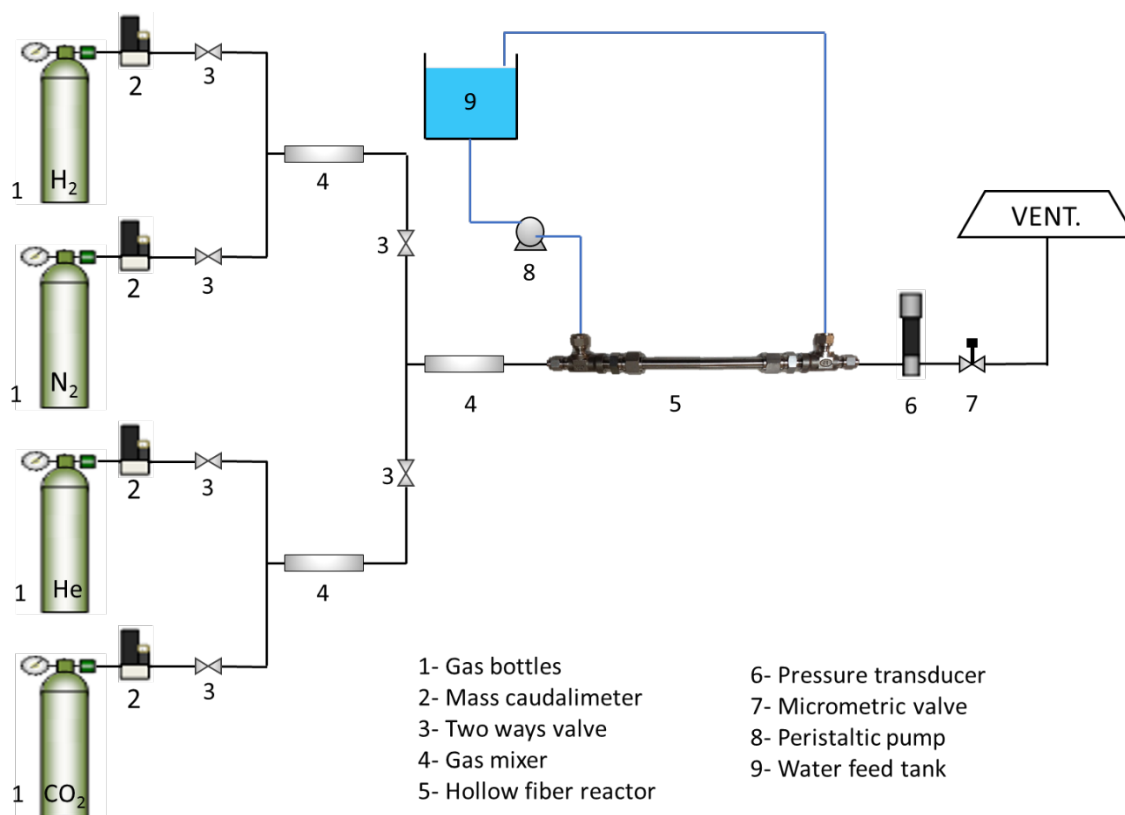


Fig. 1. Experimental set up of the system to reduce nitrites.

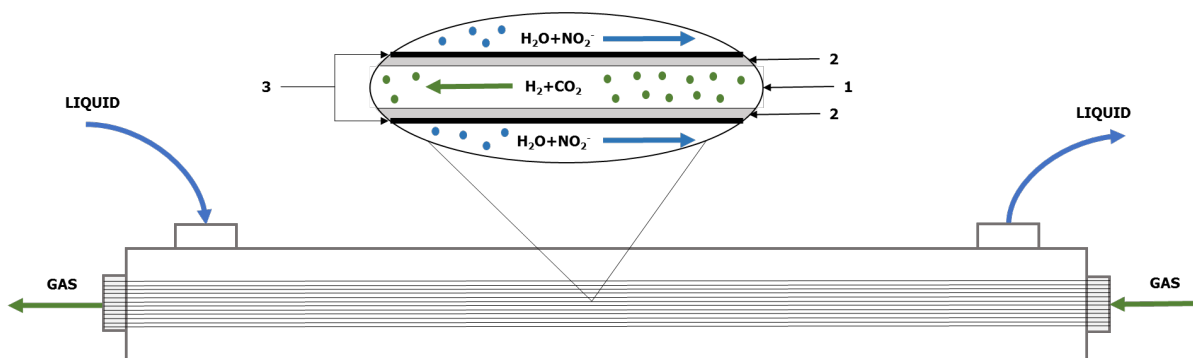


Fig. 2. Scheme of a membrane contactor and zoom in of a hollow fiber (1- lumen side of the PHFs; 2- wall of the PHFs; 3- Pd supported on the surface of the PHFs).

During hydrogenation of nitrites OH^- are released, inhibiting the reaction. In order to control the concentration of OH^- , the pH value of the aqueous phase was kept in the range between 4.86 and 5.72 by flowing CO_2 and provoking the following reactions [12]:



To monitor the progress of the reaction under consideration, representative samples were withdrawn periodically and the pH was measured.

2.2. Analytical techniques

Temperature degradation of the polymeric hollow fibers was studied using thermogravimetric analysis (TG-DTA 60H Shimadzu). The degradation was studied in the presence and absence of palladium in order to determine the influence of this catalyst in the hollow fiber temperature resistance.

Scanning electron microscope (SEM) (Carl Zeiss, EVO MA15) was used to determine the catalyst distribution in the cross-section of the Pd-PHF.

For further knowledge of the membrane structure, EDX analysis was carried out. EDX makes use of x-ray spectrum emitted by the solid sample bombarded with a focused beam of electrons to obtain a localized chemical analysis. When the sample is hit by the electron beam, electrons are ejected from the atoms of the sample surface. The resulting electron vacancies are filled by electrons from a higher energy state, and an x-ray is emitted to balance the energy difference between the two electrons' states. The x-ray energy is characteristic of the element from which it was emitted.

The linear spectrum of energy dispersive X-ray spectroscopy (EDX) was applied to the same samples of SEM to assess the palladium dispersion profile on the membrane cross-section.

The catalyst loading and the palladium stability in the PHFs were studied from leaching experiments determining the Pd concentration in an inductively coupled plasma mass spectrometry (ICP-MS). To study the stability, a constant water flow was recirculated to the hollow fiber contactor. Once the samples were taken at different periods of time, they were dissolved with a microwave digestion system (Milestone, Ethos One) to have them ready for the ICP-MS analyzer.

Two ion chromatography systems (Dionex ICS-1100 and Dionex DX-120) were used to analyze NO_2^- and NH_4^+ ions from the samples taken during the experiments.

3. Results and discussion

3.1. Fibers characterization

3.1.1. Thermal analysis

First, the thermal behavior of the membranes was analyzed by using a TG-DTA analyzer. Samples of PES/PP hollow fibers and Pd-PES/PP were heated between 25 °C and 800 °C. The results obtained from TG-DTA for PES and PP are shown in Fig. 3. TG analysis shows that the decomposition temperature (T_d , defined as the temperature where at least 3% weight loss is detected) increased in the presence of Pd for PP membranes from 320°C to 450 °C, while for PES membranes is just the opposite, it decreased from 550°C to 500 °C. This is attributed to the presence of Pd that has a degradation temperature higher than PP but lower than the PES materials.

3.1.2. Membrane composition

SEM spectra of the catalyst supported on PP and PES hollow fibers were analyzed in order to determine the distribution of palladium in the cross-section of the membrane. The white color in

Fig. 4. corresponds to the coating of palladium on the surface of the polymeric hollow fibers. In both hollow fibers palladium is mostly observed on the surface, therefore, we can assume that the reaction will take place on the outer radius of the membrane.

In this work, EDX was used in conjunction with SEM to obtain the composition at different locations of the cross-section of the membranes.

Two different areas were analyzed with EDX analysis, the inner radius (Spectrum 1) and the surface of the hollow fiber (Spectrum 2). The results from EDX analysis are shown in Table 4. It can be seen in both cases that the palladium concentration is higher on the surface of the hollow fibers, which is

in agreement with the information obtained from SEM spectra.

Table 4
Elemental composition of the PdCl₂ supported PES/PP-PHF membranes.

Element	PES		PP	
	Spectrum 1	Spectrum 2	Spectrum 1	Spectrum 2
C	51.06	43	83.32	67.56
O	30.72	26.95	-	-
Na	-	1.59	-	-
S	14.41	9.93	-	-
Cl	0.99	3.24	3	4.68
Pd	2.82	15.29	13.68	27.77

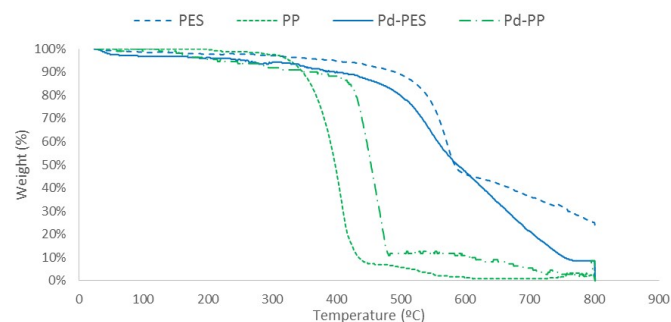


Fig. 3. Weight loss in the PES/PP-PHF with 5/10 wt% Pd (Pd-PES/PP) and in the absence of catalyst (PES/PP) as temperature rises.

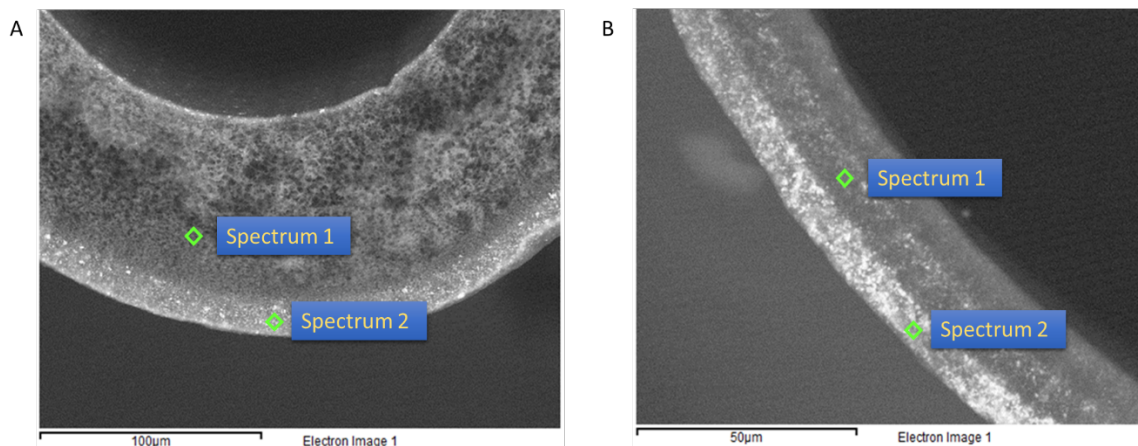


Fig. 4. SEM images of the cross-section of a 5 wt % wt Pd-PES hollow fiber (A) and 10 wt % Pd-PP hollow fiber (B).

3.1.3. Catalyst deposition stability

In order to check the stability of the Pd-PHF's catalytic membrane, the membranes were washed flowing a constant water flowrate. Aqueous samples were taken at different periods of time and the metallic concentration was analyzed via inductively coupled plasma mass spectrometry (ICP-MS) to check the robustness of the impregnation method. From a mass balance the metallic concentration on the fibers was calculated. Fig. 5. reports in both cases, PP and PES, the stability along time of the Pd impregnation method on the PHFs. The weight increase is attributed to a non-homogeneous distribution on the hollow fibers. Despite this, we conclude that Pd is firmly deposited on the surface of the PHFs after 500 hours treatment under constant water flow.

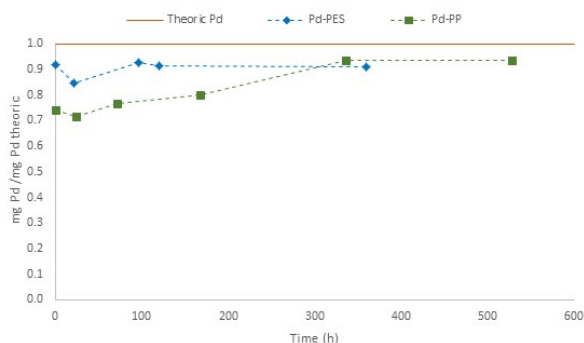


Fig. 5. Normalized catalyst loading results from ICP-MS. In green Pd-PP samples and in blue Pd-PES samples taken during time under constant water flow.

3.2. Catalytic reduction of nitrites

Catalytic reduction experiments were carried out in the experimental system described before working with Pd-PP hollow fibers. The experiments were designed to analyze the influence of the following variables, H_2 partial pressure (0.075-1 bar), CO_2 partial pressure (0.3-0.4 bar), liquid flowrate (200-400 mL/min) and gas flowrate (20-200 mL/min); the rest of operation variables were kept constant. Table 3 depicts the detailed operations conditions, parameter values and testing parameters.

3.2.1. Influence of the H_2 partial pressure

Fig. 6. shows the influence of the hydrogen partial pressure in the gas phase on the membrane reactor performance for water denitrification, where the H_2 partial pressure was adjusted by mixing H_2 , CO_2 and N_2 at atmospheric pressure. As expected, the increase in H_2 partial pressure caused an increase in the nitrite reduction rate. But it also caused a decrease in the selectivity to nitrogen as it is shown in Table 5. However, as the hydrogen partial pressure approaches 1, the nitrite reduction rate decreased dramatically. Increasing the nitrite-to-hydrogen ratio results in decreasing ammonia selectivity; this is in agreement with previous works which report that ammonia selectivity can be decreased by operating under lower surface hydrogen concentration [2, 12, 25].

3.2.2. Influence of the CO_2 partial pressure

The influence of CO_2 partial pressure in the gas feed phase was also analyzed. Results are reported in Fig. 7. and show, contrary to the work of M. D'Arino et al. [52], that an increase in the partial pressure of carbon dioxide leads to an increase in the reaction rate and, at the same time, a slight decrease in the selectivity to nitrogen gas. This different behavior can be due to the different H_2/CO_2 ratios that were used in the latter work. D'Arino et al.

changed the H_2/CO_2 ratio (1/2, 1/4, 1/8, 1/12) by varying the hydrogen and carbon dioxide partial pressure. This means that while the P_{CO_2} increases, the P_{H_2} decreases, leading to lower reaction rates and ammonia formation. In our case, only the carbon dioxide partial pressure is changed keeping the hydrogen partial pressure constant. Fig. 8. shows the change of the pH in the reduction experiments. It can be seen that once the pH has been stabilized the nitrogen selectivity starts a smooth decay. With lower CO_2 partial pressure the stabilization occurs at longer times and the ammonium formation is delayed. This can be explained by the inhibitory effect exerted by OH^- on the surface of the catalyst. CO_2 reacts with OH^- giving CO_3^{2-} , as it shown in Eq. 3 and Eq. 4, increasing the possibilities for NO_2^- to react in the active sites. To optimize this process a trade-off between the denitrification rate and nitrogen selectivity has to be considered.

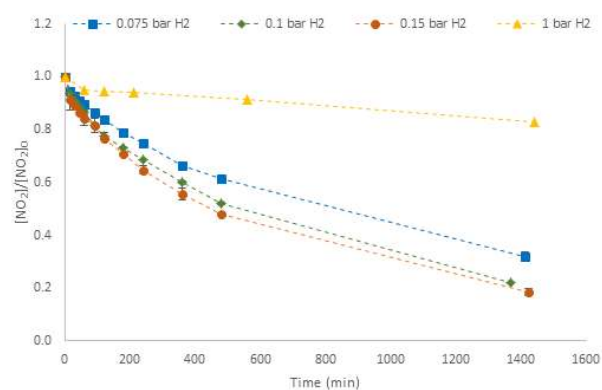


Fig. 6. Influence of the partial pressure of hydrogen in nitrite reduction (■: 0.075 bar H_2 ; ◆: 0.1 bar H_2 ; ●: 0.15 bar H_2 ; ▲: 1 bar H_2). $P_{CO_2} = 0.3$; $Q_{gas} = 20$ mL/min; $Q_l = 200$ mL/min; $T = 20$ °C.

Table 5

Nitrite conversion and nitrogen selectivity at different hydrogen partial pressures.

P_{H_2} (bar)	Nitrite conversion (%)	S_{N_2} (%)
0.075	70	90
0.1	80	88
0.15	80	84
1	20	13

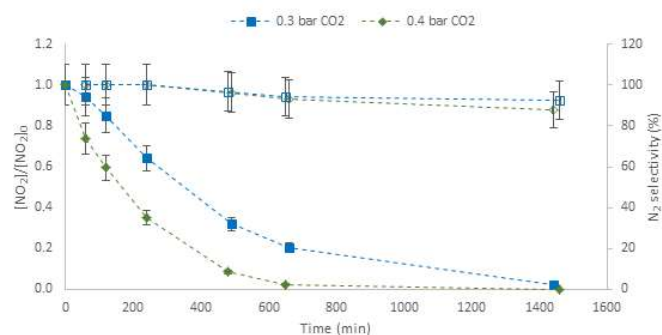


Fig. 7. Influence of the partial pressure of CO_2 in nitrite reduction (■: 0.3 bar CO_2 ; ◆: 0.4 bar CO_2) and nitrogen selectivity (□: 0.3 bar CO_2 ; ◇: 0.4 bar CO_2). $P_{H_2} = 0.1$; $Q_{gas} = 20$ mL/min; $Q_l = 200$ mL/min; $T = 20$ °C.

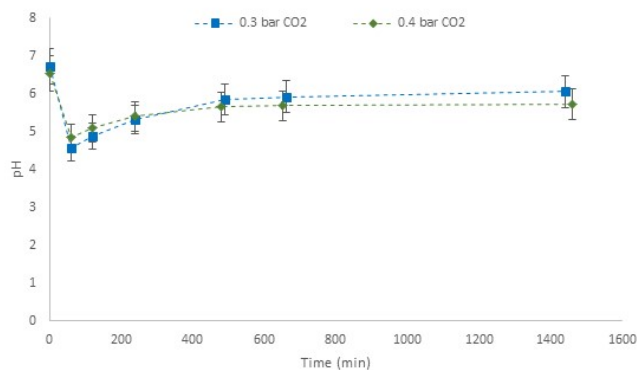


Fig. 8. Change of pH along time as a function of different CO₂ partial pressures. $P_{H_2} = 0.1$; $Q_{gas} = 20$ mL/min; $Q_l = 200$ mL/min; $T = 20$ °C.

3.2.3. Influence of the liquid flowrate

The effect of the liquid feed flow rate on the kinetics of nitrite removal is shown in Fig. 9. A slight difference on the kinetics and a slightly worse behavior on the selectivity for the higher flowrate value is observed. Generally, high feed flow rates decrease the mass transfer resistance in the boundary film of the liquid phase; this could lead to higher denitrification rates in the case of mass transport control. However, on the other hand, the higher feed flow rate may also generate a higher pressure drop in the fiber lumen and favor membrane flooding in the pores of the hollow fibers. As a result, part of the membrane and the active sites could have less contribution to denitrification, leading to poorer membrane reactor performance. So that the positive and negative effects of the aqueous phase flowrate are counterbalanced in the range of experimental variables.

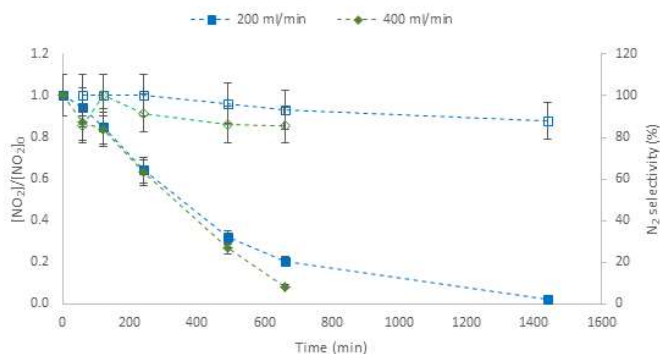


Fig. 9. Influence of the liquid flowrate in nitrite reduction (■: 200 mL/min; ◆: 400 mL/min) and nitrogen selectivity (□: 200 mL/min; ◇: 400 mL/min). $P_{H_2} = 0.1$; $P_{CO_2} = 0.3$; $Q_{gas} = 20$ mL/min; $T = 20$ °C.

3.2.4. Influence of the gas flowrate

The effect of the gas feed flow rate on the kinetics of nitrite removal is shown in Fig. 10. As could be observed, the reaction rate increases with the gas flow rate. The positive influence of the gas flow rate on the mass transfer kinetics through this phase is considered negligible in this case; however, higher gas flow rates may result in higher gas pressure in the inner fiber helping to maintain the gas-liquid interphase hindering liquid flooding in the pores of the hollow fiber membranes; this effect is just the opposite to the effect resulting from the increase in the liquid flow rate.

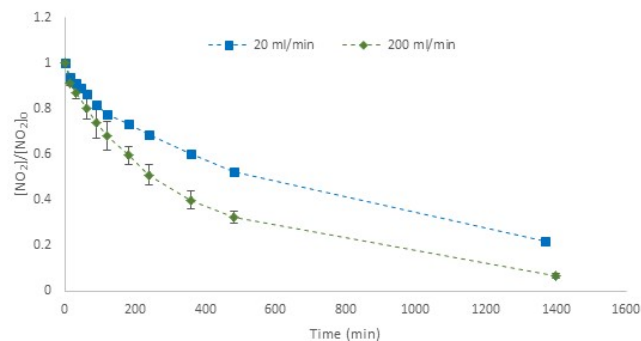


Fig. 10. Influence of the liquid flowrate in nitrite reduction (■: 20 mL/min; ◆: 200 mL/min). $P_{H_2} = 0.1$; $P_{CO_2} = 0.3$; $Q_l = 200$ mL/min; $T = 20$ °C.

4. Conclusions

A catalytic membrane reactor based on Pd particles supported on porous PHFs has been designed for the first time and applied to nitrite reduction from polluted waters. First, the microstructure and stability of the catalytic membranes along time were determined. The catalyst was mostly deposited on the outer radius (SEM spectra) of the PHFs allowing the reaction to take place on the surface of the hollow fibers.

The performance of the catalytic reactor has been experimentally assessed working in the range of variables P_{H_2} (0.075-1 bar), P_{CO_2} (0.3-0.4 bar), liquid flow rate (200-400 mL/min) and gas flow rate (20-200 mL/min). For high P_{H_2} (0.15 bar H₂), the reaction rate and the ammonia formation increase, but as the P_{H_2} approaches 1, the nitrite reduction rate decreases dramatically. At the lowest P_{CO_2} (0.3 bar CO₂) the reaction rate decreases, but the ammonia formation is delayed. The variation in the liquid flow rate does not have effect due to the counterbalance between the higher pressure drop in the fiber lumen and the decrease in the mass transfer resistance. At highest gas flow rate (200 mL/min), the denitrification rate also increases. The gas pressure in the inner fiber maintains the gas-liquid interphase closer to the catalyst active sites.

Finally, in this work the best results in terms of nitrite reduction rate and nitrogen selectivity (90% of selectivity to nitrogen gas at 80 % of nitrite conversion) were achieved working at 0.1 bar partial pressure of H₂, 0.3 bar partial pressure of CO₂, 200 mL/min of liquid flow rate and 20 mL/min of gas flow rate.

Acknowledgements

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References

- [1] G. Gulis, M. Czompolyova, J.R. Cerhan, An ecologic study of nitrate in municipal drinking water and cancer incidence in Trnava District, Slovakia, Environ. Res. 88 (2002) 182-187. doi:10.1006/enrs.2002.4331.
- [2] S. Hörold, K.-D. Vorlop, T. Tacke, M. Sell, Development of catalysts for a selective nitrate and nitrite removal from drinking water, Catal. Today. 17 (1993) 21-30. doi:10.1016/0920-5861(93)80004-K.
- [3] V.B. Jensen, J.L. Darby, C. Seidel, C. Gorman, Nitrate in potable water supplies: Alternative management strategies, Crit. Rev. Environ. Sci. Technol. 44 (2014) 2203-2286. doi:10.1080/10643389.2013.828272.
- [4] K.-D. Vorlop, T. Tacke, Erste Schritte auf dem Weg zur edelmetallkatalysierten Nitrat- und Nitrit-Entfernung aus Trinkwasser, Chemie Ing. Tech. 61 (1989) 836-837. doi:10.1002/cite.330611023.

- [5] U. Prüsse, K.D. Vorlop, Supported bimetallic palladium catalysts for water-phase nitrate reduction, *J. Mol. Catal. A Chem.* 173 (2001) 313–328. doi:10.1016/S1381-1169(01)00156-X.
- [6] J. Martínez, A. Ortiz, I. Ortiz, State-of-the-art and perspectives of the catalytic and electrocatalytic reduction of aqueous nitrates, *Appl. Catal. B Environ.* 207 (2017) 42–59. doi:10.1016/j.apcatb.2017.02.016.
- [7] A.A.C.M. Beenackers, W.P.M. Van Swaaij, Mass transfer in gas-liquid slurry reactors, *Chem. Eng. Sci.* 48 (1993) 3109–3139. doi:10.1016/0009-2509(93)80199-Z.
- [8] E. Dietrich, C. Mathieu, H. Delmas, J. Jenck, Raney-nickel catalyzed hydrogenations: Gas-liquid mass transfer in gas-induced stirred slurry reactors, *Chem. Eng. Sci.* 47 (1992) 3597–3604. doi:10.1016/0009-2509(92)85075-M.
- [9] E. Alper, B. Wichtendahl, W.D. Deckwer, Gas absorption mechanism in catalytic slurry reactors, *Chem. Eng. Sci.* 35 (1980) 217–222. doi:10.1016/0009-2509(80)80090-X.
- [10] W.J. Bruining, G.E.H. Joosten, A.A.C.M. Beenackers, H. Hofman, Enhancement of gas-liquid mass transfer by a dispersed second liquid phase, *Chem. Eng. Sci.* 41 (1986) 1873–1877. doi:10.1016/0009-2509(86)87066-X.
- [11] V. Hessel, P. Angeli, A. Gavriilidis, H. Löwe, Gas-liquid and gas-liquid-solid microstructured reactors: Contacting principles and applications, *Ind. Eng. Chem. Res.* 44 (2005) 9750–9769. doi:10.1021/ie0503139.
- [12] A. Pintar, J. Batista, J. Levec, Potential of mono- and bimetallic catalysts for liquid-phase hydrogenation of aqueous nitrite solutions, *Water Sci. Technol.* 37 (1998) 177–185. doi:10.1016/S0273-1223(98)00248-0.
- [13] A.M. Perez-Coronado, L. Calvo, J.A. Baeza, J. Palomar, L. Lefferts, J.J. Rodriguez, M.A. Gilarranz, Selective Reduction of Nitrite to Nitrogen with Carbon-Supported Pd-AOT Nanoparticles, *Ind. Eng. Chem. Res.* 56 (2017) 11745–11754. doi:10.1021/acs.iecr.7b02944.
- [14] J.K. Chinthaginjala, L. Lefferts, Support effect on selectivity of nitrite reduction in water, *Appl. Catal. B Environ.* 101 (2010) 144–149. doi:10.1016/j.apcatb.2010.09.023.
- [15] J.K. Chinthaginjala, J.H. Bitter, L. Lefferts, Thin layer of carbon-nano-fibers (CNFs) as catalyst support for fast mass transfer in hydrogenation of nitrite, *Appl. Catal. A Gen.* 383 (2010) 24–32. doi:10.1016/j.apcata.2010.05.013.
- [16] J.K. Chinthaginjala, A. Villa, D.S. Su, B.L. Mojet, L. Lefferts, Nitrite reduction over Pd supported CNFs: Metal particle size effect on selectivity, *Catal. Today.* 183 (2012) 119–123. doi:10.1016/j.cattod.2011.11.003.
- [17] M. Benkhaled, C. Descorme, D. Duprez, S. Morin, C. Thomazeau, D. Uzio, Study of hydrogen surface mobility and hydrogenation reactions over alumina-supported palladium catalysts, *Appl. Catal. A Gen.* 346 (2008) 36–43. doi:10.1016/j.apcata.2008.04.043.
- [18] R. Brunet Espinosa, L. Lefferts, Ni in CNFs: Highly Active for Nitrite Hydrogenation, *ACS Catal.* 6 (2016) 5432–5440. doi:10.1021/acscatal.6b01375.
- [19] A.J. Colombo, G. Baldi, S. Sicardi, Solid-liquid contacting effectiveness in trickle bed reactors, *Chem. Eng. Sci.* 31 (1976) 1101–1108. doi:10.1016/0009-2509(76)85019-1.
- [20] P.L. Mills, M.P. Dudukovic, Evaluation of liquid-solid contacting in trickle-bed reactors by tracer methods, *AIChE J.* 27 (1981) 893–904. doi:10.1002/aic.690270604.
- [21] A. Attou, C. Boyer, G. Ferschneider, Modelling of the hydrodynamics of the cocurrent gas-liquid trickle flow through a trickle-bed reactor, *Chem. Eng. Sci.* 54 (1999) 785–802. doi:10.1016/S0009-2509(98)00285-1.
- [22] I. Iliuta, F. Larachi, B.P.A. Grandjean, G. Wild, Gas-liquid interfacial mass transfer in trickle-bed reactors: State-of-the-art correlations, *Chem. Eng. Sci.* 54 (1999) 5633–5645. doi:10.1016/S0009-2509(99)00129-3.
- [23] N. Diban, A.T. Aguayo, J. Bilbao, A. Urriaga, I. Ortiz, Membrane reactors for in situ water removal: A review of applications, *Ind. Eng. Chem. Res.* 52 (2013) 10342–10354. doi:10.1021/ie3029625.
- [24] Y. Zhao, W. Liang, Y. Li, L. Lefferts, Effect of chlorine on performance of Pd catalysts prepared via colloidal immobilization, *Catal. Today.* 297 (2017) 308–315. doi:10.1016/j.cattod.2017.01.028.
- [25] Y. Matatov-Meytal, Y. Shindler, M. Sheintuch, Cloth catalysts in water denitrification III. pH inhibition of nitrite hydrogenation over Pd/ACC, *Appl. Catal. B Environ.* 45 (2003) 127–134. doi:10.1016/S0926-3373(03)00126-7.
- [26] N. Jarrar, Nitrite hydrogenation over palladium-carbon nanofiber foam: a parametric study using factorial design of experiments, *React. Kinet. Mech. Catal.* 125 (2018) 287–301. doi:10.1007/s11444-018-1384-2.
- [27] T. Ye, D.P. Durkin, M. Hu, X. Wang, N.A. Banek, M.J. Wagner, D. Shuai, Enhancement of Nitrite Reduction Kinetics on Electrospun Pd-Carbon Nanomaterial Catalysts for Water Purification, *ACS Appl. Mater. Interfaces.* 8 (2016) 17739–17744. doi:10.1021/acsami.6b03635.
- [28] D. Shuai, J.K. Choe, J.R. Shapley, C.J. Werth, Enhanced Activity and Selectivity of Carbon Nanofiber Supported Pd Catalysts for Nitrite Reduction, *Environ. Sci. Technol.* 46 (2012) 2847–2855. doi:10.1021/es203200d.
- [29] H.C. Aran, S. Pacheco Benito, M.W.J. Luiten-Olieman, S. Er, M. Wessling, L. Lefferts, N.E. Benes, R.G.H. Lammertink, Carbon nanofibers in catalytic membrane microreactors, *J. Memb. Sci.* 381 (2011) 244–250. doi:10.1016/j.memsci.2011.07.037.
- [30] V. V. Volkov, V.I. Lebedeva, I. V. Petrova, A. V. Bobyl, S.G. Konnikov, V.I. Roldughin, J. Van Erkel, G.F. Tereshchenko, Adlayers of palladium particles and their aggregates on porous polypropylene hollow fiber membranes as hydrogenation contractors/reactors, *Adv. Colloid Interface Sci.* 164 (2011) 144–155. doi:10.1016/j.cis.2010.10.008.
- [31] K. Lütke, K.-V. Peinemann, V. Kasche, R.-D. Behling, Nitrate removal of drinking water by means of catalytically active membranes, *J. Memb. Sci.* 151 (1998) 3–11. doi:10.1016/S0376-7388(98)00227-0.
- [32] O.M. Ilinich, E.N. Gribov, P.A. Simonov, Water denitrification over catalytic membranes: Hydrogen spillover and catalytic activity of macroporous membranes loaded with Pd and Cu, *Catal. Today.* 82 (2003) 49–56. doi:10.1016/S0920-5861(03)00201-3.
- [33] A. Devard, M.A. Ulla, F.A. Marchesini, Synthesis of Pd/Al₂O₃ coating onto a cordierite monolith and its application to nitrite reduction in water, *Catal. Commun.* 34 (2013) 26–29. doi:10.1016/j.catcom.2013.01.005.
- [34] S.D. Ebbesen, B.L. Mojet, L. Lefferts, Effect of pH on the nitrite hydrogenation mechanism over Pd/Al₂O₃ and Pt/Al₂O₃: Details obtained with ATR-IR spectroscopy, *J. Phys. Chem. C.* 115 (2011) 1186–1194. doi:10.1021/jp106521t.
- [35] H.C. Aran, J.K. Chinthaginjala, R. Groote, T. Roelofs, L. Lefferts, M. Wessling, R.G.H. Lammertink, Porous ceramic mesoreactors: A new approach for gas-liquid contacting in multiphase microreaction technology, *Chem. Eng. J.* 169 (2011) 239–246. doi:10.1016/j.cej.2010.11.005.
- [36] S.D. Ebbesen, B.L. Mojet, L. Lefferts, Mechanistic investigation of the heterogeneous hydrogenation of nitrite over Pt/Al₂O₃ by attenuated total reflection infrared spectroscopy, *J. Phys. Chem. C.* 113 (2009) 2503–2511. doi:10.1021/jp8081886.
- [37] S.D. Ebbesen, B.L. Mojet, L. Lefferts, In situ ATR-IR study of nitrite hydrogenation over Pd/Al₂O₃, *J. Catal.* 256 (2008) 15–23. doi:10.1016/j.jcat.2008.02.013.
- [38] M. Vospemik, A. Pintar, G. Berčić, J. Levec, Experimental verification of ceramic membrane potentials for supporting three-phase catalytic reactions, *J. Memb. Sci.* 223 (2003) 157–169. doi:10.1016/S0376-7388(03)00320-X.
- [39] M. Reif, R. Dittmeyer, Porous, catalytically active ceramic membranes for gas-liquid reactions: A comparison between catalytic diffuser and forced through flow concept, *Catal. Today.* 82 (2003) 3–14. doi:10.1016/S0920-5861(03)00197-4.
- [40] V. Höller, K. Radevik, I. Yuranov, L. Kiwi-Minsker, A. Renken, Reduction of nitrite-ions in water over Pd-supported on structured fibrous materials, *Appl. Catal. B Environ.* 32 (2001) 143–150. doi:10.1016/S0926-3373(01)00139-4.
- [41] A. Pintar, G. Bereic, J. Levec, Catalytic Liquid-Phase Nitrite Reduction: Kinetics and Catalyst Deactivation, *AIChE J.* 44 (1998) 2280–2292. doi:10.1002/aic.690441017.
- [42] R. Brunet Espinosa, D. Rafeian, R.S. Postma, R.G.H. Lammertink, L. Lefferts, Egg-shell membrane reactors for nitrite hydrogenation: Manipulating kinetics and selectivity, *Appl. Catal. B Environ.* 224 (2018) 276–282. doi:10.1016/j.apcatb.2017.10.058.
- [43] R. Brunet Espinosa, D. Rafeian, R.G.H. Lammertink, L. Lefferts, Carbon nanofiber based membrane reactor for selective nitrite hydrogenation, *Catal. Today.* 273 (2016) 50–61. doi:10.1016/j.cattod.2016.02.057.
- [44] Z. Zhao, G. Tong, X. Tan, Nitrite removal from water by catalytic hydrogenation in a Pd-CNTs/Al₂O₃ hollow fiber membrane reactor, *J. Chem Technol Biotechnol.* 91 (2016) 2298–2304. doi:10.1002/jctb.4816.
- [45] Y. Zhao, N. Koteswara Rao, L. Lefferts, Adsorbed species on Pd catalyst during nitrite hydrogenation approaching complete conversion, *J. Catal.* 337 (2016) 102–110. doi:10.1016/j.jcat.2016.02.007.
- [46] A.H. Pizarro, C.B. Molina, J.J. Rodriguez, F. Epron, Catalytic reduction of nitrate and nitrite with mono- and bimetallic catalysts supported on pillared clays, *Biochem. Pharmacol.* 3 (2015) 2777–2785. doi:10.1016/j.jece.2015.09.026.
- [47] C. Franch, R.G.H. Lammertink, L. Lefferts, Partially hydrophobized catalyst particles for aqueous nitrite hydrogenation, *Appl. Catal. B Environ.* 156–157 (2014) 166–172. doi:10.1016/j.apcatb.2014.03.020.
- [48] H. Shin, S. Jung, S. Bae, W. Lee, H. Kim, Nitrite reduction mechanism on a Pd surface, *Environ. Sci. Technol.* 48 (2014) 12768–12774. doi:10.1021/es503772x.
- [49] J. Lee, Y.G. Hur, M.S. Kim, K.Y. Lee, Catalytic reduction of nitrite in water over ceria- and ceria-zirconia-supported Pd catalysts, *J. Mol. Catal. A Chem.* 399 (2015) 48–52. doi:10.1016/j.molcata.2015.01.012.
- [50] F. Deganello, L.F. Liotta, A. Macaluso, A.M. Venezia, G. Deganello, Catalytic

- reduction of nitrates and nitrites in water solution on pumice-supported Pd-Cu catalysts, *Appl. Catal. B Environ.* 24 (2000) 265–273. doi:10.1016/S0926-3373(99)00109-5.
- [51] D.P. Durkin, T. Ye, E.G. Larson, L.M. Haverhals, K.J.T. Livi, H.C. De Long, P.C. Trulove, D.H. Fairbrother, D. Shuai, Lignocellulose Fiber- and Welded Fiber-Supports for Palladium-Based Catalytic Hydrogenation: A Natural Fiber Welding Application for Water Treatment, *ACS Sustain. Chem. Eng.* 4 (2016) 5511–5522. doi:10.1021/acsschemeng.6b01250.
- [52] M. D'Arino, F. Pinna, G. Strukul, Nitrate and nitrite hydrogenation with Pd and Pt/SnO₂ catalysts: The effect of the support porosity and the role of carbon dioxide in the control of selectivity, *Appl. Catal. B Environ.* 53 (2004) 161–168. doi:10.1016/j.apcatb.2004.05.015.