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Hydrogenation of nitrates in water using mesoporous membranes operated in a flow-through catalytic contactor

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ABSTRACT

The hydrogenation of nitrates in aqueous solution has been studied using Pd–Cu catalysts deposited in mesoporous ceramic membranes operated in a flow-through catalytic membrane reactor. The effect of the top-layer pore size (5, 10 or 25 nm) on the catalytic activity was explored. The activity increased with trans-membrane flow rate for the three membranes, although moderately with the 25 nm pore membrane. At a similar flow rate, the activity increased when the pore size decreased. Concentration polarization of nitrates was evidenced by ultrafiltration experiments with bare membranes, and was enhanced when the pore size decreased. Concentration polarization appeared effective in improving the catalytic activity, due to a local increase in nitrate concentration in the catalytic top-layer of the membranes.

1. Introduction

Nitrates are the main components of agricultural fertilizers, and their intensive use leads to a regular increase of nitrate concentration in surface and ground waters. Because of their toxicity, the European Commission has set to 50 mg/L the maximum nitrate concentration allowed in drinking water [1]. This limit is now largely exceeded in many ground waters, which therefore require treatment to meet the requirements for potable water. Current physico-chemical processes used for nitrate removal from drinking water are ion exchange and membrane processes (reverse osmosis or electrodialysis). A general limitation of these technologies is the formation of concentrated brines, which have to be treated before disposal.

Catalytic hydrogenation of nitrates offers an elegant solution to water denitrification, since the nitrates are reduced into a harmless product, nitrogen. Supported palladium catalysts promoted by copper have been the most studied catalysts for nitrate hydrogenation in water [2,3]. Mechanistic and kinetic studies showed that the reduction of nitrates is a stepwise reaction, in which nitrates are first converted into nitrites on copper by a redox mechanism. The palladium ensures subsequent catalytic reduction of nitrites into nitrogen and/or ammonium, which is an un-desired by-product [4,5].

The reaction has been investigated mainly in fixed bed reactors, operating in batch or semi-batch conditions. As often in three-phase reactions, the reaction rate is strongly limited by mass transfer of hydrogen to the catalyst surface, related to the low solubility of hydrogen in water. Strong external and/or internal diffusion limitations have been evidenced, depending on the catalyst particle size and the porosity [6,7]. In addition, diffusion limitations of hydroxyl ions formed during the reaction are also detrimental to the selectivity towards nitrogen.

Membranes are widely used for water and beverage processing, whereas catalytic membrane reactors (CMRs) are particularly adapted to control activity and selectivity issues in gas/liquid catalytic reactions [8,9]. In the contactor configuration, the porous membrane provides a contact area between the solid catalyst, incorporated in the membrane, and the gas/liquid phases (interfacial configuration) or between the solid catalyst and the reactants dissolved in the liquid phase (flow-through configuration). As regards the catalytic reduction of nitrates, the expected benefits of membrane reactors, compared to conventional reactors, are: (i) better efficiency, due to an improved contact between the reactants and the catalyst (absence of diffusion limitations due to short diffusion path length), (ii) higher selectivity (in interfacial configuration, the hydrogen supply can be controlled by dosing through the membrane, whereas the contact time can be accurately controlled in flow-through configuration), and (iii) there is no need to separate the catalyst from the treated water. Additionally, membrane reactors are particularly adapted to continuous processes in a simple and compact reactor design.

Ilinitch et al. [10] compared the catalytic reduction of nitrates with Pd–Cu catalysts deposited on γ-alumina powders or on disk-

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shaped alumina membranes with a pore size around 1 μm. Indeed, pronounced diffusion limitations were evidenced with powder catalysts, whereas the mass transfers were improved with the catalytic membranes operated in forced-through mode, as shown by a multifold increase in the reaction rates.

Similarly, Strukul et al. [11] compared the behavior of Pd–Cu or Pd–Sn catalysts supported on zirconia or titania powders or on porous ceramic membranes coated with a porous layer of titania or zirconia by sol–gel method. The catalytic membranes, tested in recirculation or as interfacial contactor, were found less active and selective than the powder catalysts. The pore size of the membranes, however, was not controlled, and cracks in the top-layer were observed by SEM. High selectivities towards NH_4^+ (>50%) were obtained.

Nitrate and nitrite hydrogenation in membrane reactors has been essentially studied using macroporous membranes (pore size 60–400 nm [12], and up to 10 μm [13]). Both interfacial contactor and flow-through configurations have been applied and sometimes compared [14–16]. The flow-through configuration showed a higher activity and selectivity towards nitrogen than the interfacial diffuser, due to a more efficient contact between the reactants and the catalyst [15].

In one study, a microporous polymer membrane has been operated for the hydrogenation of nitrates in forced-through mode [17]. A Pd–Cu/Al_2O_3 powder catalyst was dispersed in the polymer precursor solution, and incorporated in the membranes during their preparation. A high selectivity (70–80%) towards nitrogen was obtained in all experiments, in which the pH, the temperature and the flow rate were varied.

In the present work, we used Pd–Cu catalysts supported on mesoporous membranes (pore size 5–25 nm) for nitrate hydrogenation. The flow-through configuration was chosen to study the membrane performances and the influence of pore size on the hydrogenation of nitrates.

2. Experimental

The membranes used were commercial porous alumina tubes (Pall Exekia, length 25 cm, outer diameter 1 cm), with an asymmetric structure composed of 3 α-alumina layers of decreasing pore size (12, 0.8 and 0.2 μm) from shell to lumen side, and a final mesoporous layer (lumen side) made of γ-alumina with pores of 25, 10 or 5 nm. Pd and Cu were deposited simultaneously in the membrane using the evaporation–crystallization technique [18]. $Pd(NO_3)_2$ (10 wt.% in aqueous 10 wt.% HNO_3, Aldrich) and $Cu(NO_3)_2{\cdot}3H_2O$ (Aldrich) were used as precursors and dissolved in demineralized water at a concentration of 0.077 mol/L Pd and 0.031 mol/L Cu (Pd/Cu = 2.5). The tubes were rotated vertically in this solution for 15 h, then removed and dried at room temperature in horizontal position under rotation (60 rpm) for 24 h. The metal nitrates were thermally decomposed at 250 °C (heating rate 1 °C/min), followed by metal reduction under pure hydrogen at the same temperature 250 °C for 15 h.

The hydrogenation of nitrates was carried out at room temperature (20 °C) by pumping a solution of $NaNO_3$, saturated with dissolved hydrogen, through the catalytic membrane with an HPLC pump.

In the present study, we chose to work with low initial nitrate concentrations (10–50 mg/L range), although 50 mg/L corresponds to the maximum legal limit for nitrates in drinking water. This choice was imposed by the fact that, in a flow-through membrane reactor configuration, only dissolved hydrogen is available for nitrate reduction. The reaction is therefore limited by the low solubility of hydrogen in water (0.81 mmol/L at 20 °C under 1 bar H_2 [19]). Since the H_2/NO_3^- stoichiometry required for reducing nitrates into nitrogen is 2.5 (Eq. (1)), the reaction will indeed be limited by the hydrogen supply as soon as the nitrate concentration exceeds 0.32 mmol/L (20 mg/L), provided that 100% conversion of nitrates into N_2 is achieved in a single pass.

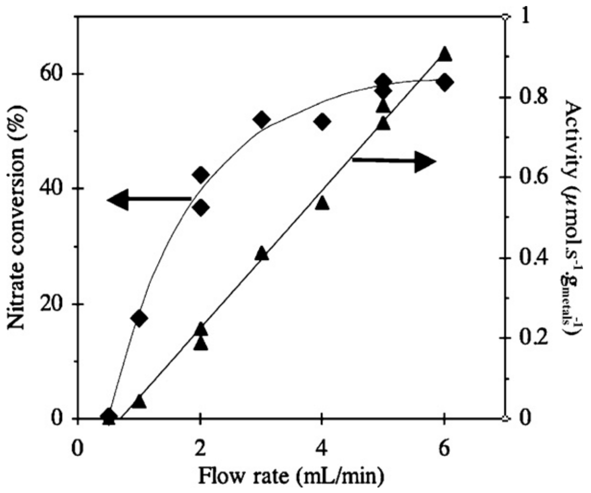

Fig. 1. Conversion of nitrates in single pass and reaction rate versus trans-membrane flow rate. *Conditions*: Al_2O_3 membrane with 5 nm pores, Pd/Cu = 2.5, 1 bar H_2, 33 ppm (0.53 mmol/L) NO_3^-.

$$2NO_3^- + 5H_2 \rightarrow N_2 + 4H_2O + 2OH^- \qquad (1)$$

The nitrate solution was fed by the lumen side, i.e. on the mesoporous side, and the permeate collected on the shell side was analyzed using two ion chromatographs (Dionex ICS-90) equipped for the analysis of anions (NO_3^-, NO_2^-) and cations (NH_4^+, Na^+), respectively. The selectivity towards nitrogen was calculated from the material balance for N-containing salts in solution, assuming that only N_2 is formed as gaseous product (negligible N_2O formation).

Ultrafiltration experiments were performed on bare alumina membranes, previously calcined at 600 °C under air to remove any possible contaminant. The nitrate solution (fed by the lumen side) was pumped through the membranes with an HPLC pump, the permeate being collected and analyzed at regular time intervals. When necessary, the whole retentate volume (≈10 mL) was collected and analyzed.

3. Results

3.1. Activity of catalytic membranes with 5 nm top-layer pores

The catalytic activity was evaluated in forced-through configuration, in which the nitrate solution saturated with hydrogen is pumped through the catalytic membrane, and the products composition was analyzed after a single pass. Several factors influencing the catalytic activity were studied: trans-membrane flow rate, initial nitrate concentration and hydrogen saturation pressure.

3.1.1. Influence of trans-membrane flow rate

The trans-membrane flow rate directly determines the contact time between the reactants and the catalyst deposited in the membrane. The expected behavior, as in most catalytic reactions, is that the reaction rate decreases when the contact time decreases, i.e. when the trans-membrane flow rate increases. Using a catalytic membrane with 5 nm pores, however, the opposite behavior is observed (Fig. 1): the conversion of nitrates increases with the trans-membrane flow rate, and the reaction rates increases linearly when the trans-membrane flow rate increases.

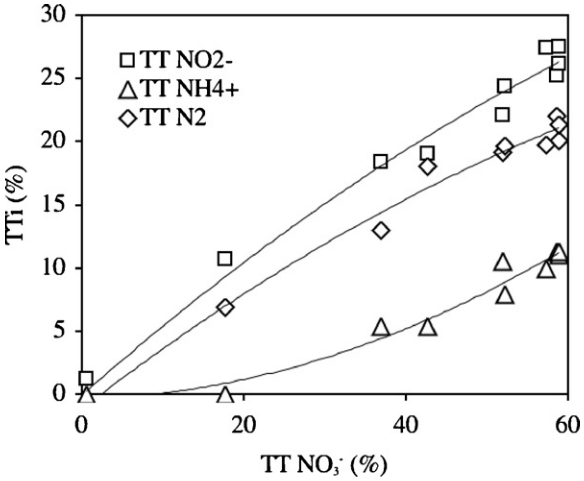

Fig. 2. TTi/TTg plot of products selectivity in single pass versus nitrate conversion. *Conditions*: Al_2O_3 membrane with 5 nm pores, Pd/Cu = 2.5, 1 bar H_2, 33 ppm (0.53 mmol/L) NO_3^-.

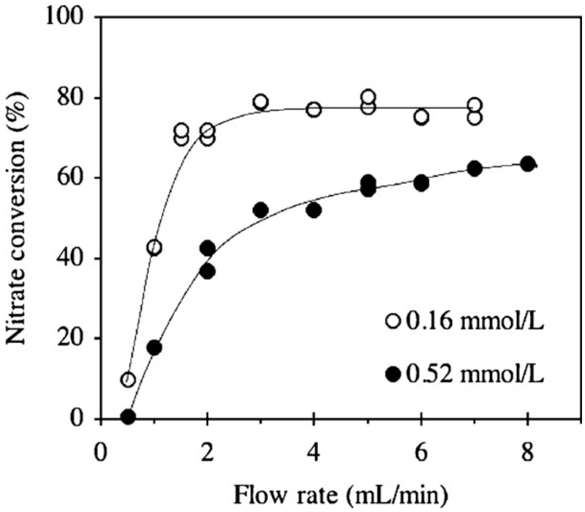

Fig. 3. Nitrate conversion in a single pass as a function of trans-membrane flow rate, at two initial nitrate concentrations. *Conditions*: Al_2O_3 membrane with 5 nm pores, Pd/Cu = 2.5, 1 bar H_2.

In single pass, NO_2^- (first step of the reduction) is the main product (Fig. 2). At low conversion of nitrates (<20%), the selectivity is essentially into NO_2^- and N_2, no ammonium being detected. NO_2^- reduction into N_2 appears to be faster than its hydrogenation into NH_4^+.

It should be mentioned that the selectivity towards N_2 was calculated from the N-containing compounds balance, and might include the possible formation of N_2O. Some authors indeed analyzed N_2O in the gas phase during the catalytic reduction of nitrates with Pd–Cu catalysts [20,21], whereas others actually did not [22,23], and therefore N_2O formation still appears a matter of debate. Since the gas phase is seldom analyzed in literature, and was not in the present study, the nitrogen selectivity should be considered with caution.

3.1.2. Influence of initial nitrate concentration

The conversion of nitrates in a single pass at different trans-membrane flow rates, starting with two different initial concentrations, is shown in Fig. 3. The corresponding rates of nitrates disappearances are plotted in Fig. 4.

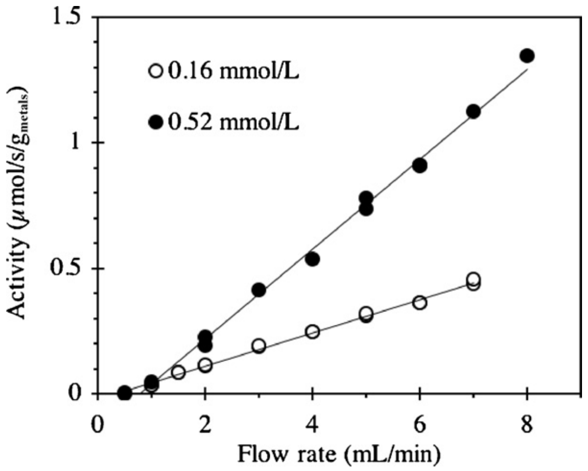

Fig. 4. Rate of nitrate disappearance in a single pass as a function of trans-membrane flow rate, at two initial nitrate concentrations. *Conditions*: Al_2O_3 membrane with 5 nm pores, Pd/Cu = 2.5, 1 bar H_2.

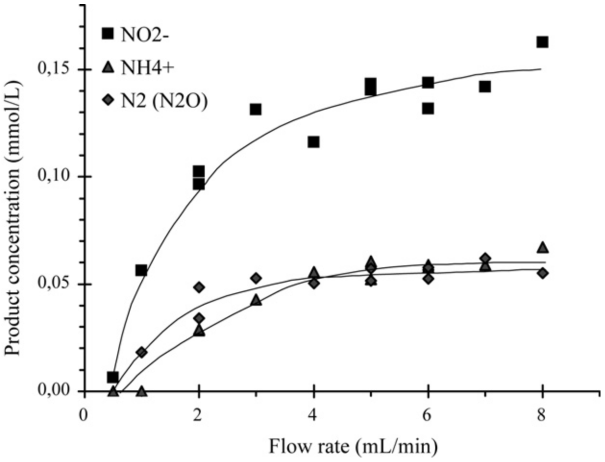

Fig. 5. Permeate composition after a single pass versus flow rate, at an initial nitrate concentration 0.52 mmol/L. *Conditions*: Al_2O_3 membrane with 5 nm pores, Pd/Cu = 2.5, 1 bar H_2.

The reaction rate increases with initial nitrate concentration, in good agreement with previous kinetic studies showing that, for low initial nitrate concentrations (<100 ppm), the apparent reaction order is positive and ≈1 with respect to nitrates [3]. In both cases, the reaction rate increases linearly with the trans-membrane flow rate.

The product composition, however, is very different depending on initial nitrate concentration (Figs. 5 and 6). When the initial nitrate concentration is 0.52 mmol/L, the nitrates are mainly converted into nitrites, whereas ammonium and N_2 are formed in similar amounts. Starting with an initial nitrate concentration of 0.16 mmol/L, there is only formation of nitrites and ammonium when increasing the permeation flow rate. Low catalyst surface coverage by N-species probably prevents N_2 formation, whereas the hydrogen excess should favor the formation of NH_4^+.

3.1.3. Influence of hydrogen saturation pressure

In flow-through configuration and in a single pass through the membrane, only dissolved H_2 is available for nitrate reduction. According to the product formed, the NO_3^-/H_2 stoichiometric ratio is different (Eqs. (2)–(4)):

$$NO_3^- + H_2 \rightarrow NO_2^- + H_2O \qquad (2)$$

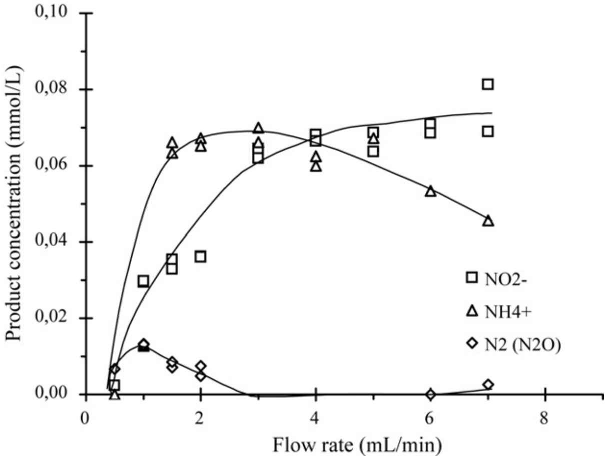

Fig. 6. Permeate composition after a single pass versus flow rate, at an initial nitrate concentration 0.16 mmol/L. *Conditions*: Al_2O_3 membrane with 5 nm pores, Pd/Cu = 2.5, 1 bar H_2.

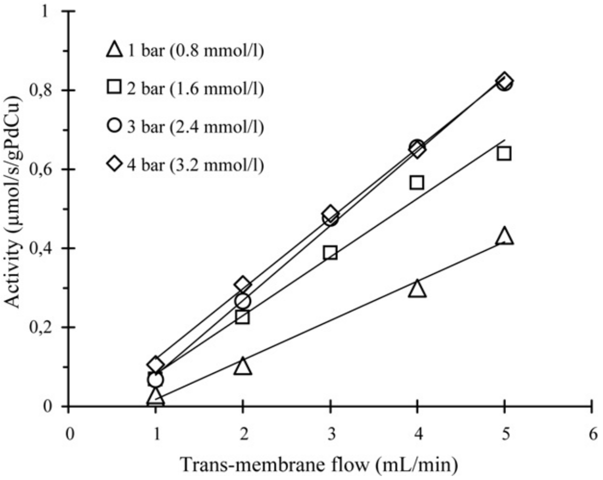

Fig. 7. Rate of nitrate disappearance versus trans-membrane flow rate, at different H_2 saturation pressures. *Conditions*: single pass, initial nitrate concentration 0.42 mmol/L, Al_2O_3 membrane with 5 nm pores, Pd/Cu = 2.5.

$$NO_3^- + 2.5H_2 \rightarrow 0.5N_2 + OH^- + 2H_2O \quad (3)$$

$$NO_3^- + 4H_2 \rightarrow NH_4^+ + 2OH^- + H_2O \quad (4)$$

The solubility of hydrogen in water at 20 °C and under 1 atm H_2 is 0.81 mmol/L [19]. According to Henry's law, the hydrogen solubility is proportional to the hydrogen partial pressure in the gas phase. Table 1 reports the calculated hydrogen concentrations required in solution to achieve the reduction of various amounts of nitrates into NO_2^-, N_2 or NH_4^+, assuming that only one reaction (2), (3) or (4) occurs with 100% conversion of nitrates.

At increasing initial nitrate concentrations, the reaction will be rapidly limited by hydrogen availability, unless gas phase hydrogen is pressurized to increase its concentration in solution. Starting with 30 ppm dissolved nitrates and under 1 bar H_2, the concentration of dissolved hydrogen allows at maximum 67% conversion of NO_3^- into N_2 in a single pass.

Fig. 7 shows the effect of hydrogen saturation pressure on the activity, at different trans-membrane flow rates. The initial nitrate concentration was 0.42 mmol/L (26 ppm).

The hydrogen conversion, calculated on the basis of nitrate conversion and products formed, does not exceed 50% in all experiments, so the activity should not be limited by hydrogen. The activity increases with the concentration of hydrogen in solution, which suggests a positive reaction order with respect to H_2. The maximum activity is obtained at H_2 pressure ≥3 bar: the nitrate conversion in a single pass reaches 92% at a trans-membrane flow rate of 5 mL/min, but NO_2^- is the main product (Fig. 8). No ammonium is detected at conversions <20%.

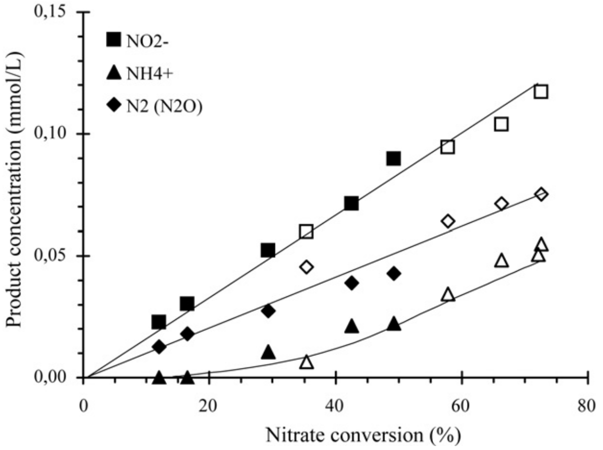

Fig. 8. Permeate composition versus nitrate conversion, at two H_2 saturation pressures. Full symbols: 1 bar H_2; open symbols: 2 bar H_2. *Conditions*: single pass, initial nitrate concentration 0.42 mmol/L, Al_2O_3 membrane with 5 nm pores, Pd/Cu = 2.5.

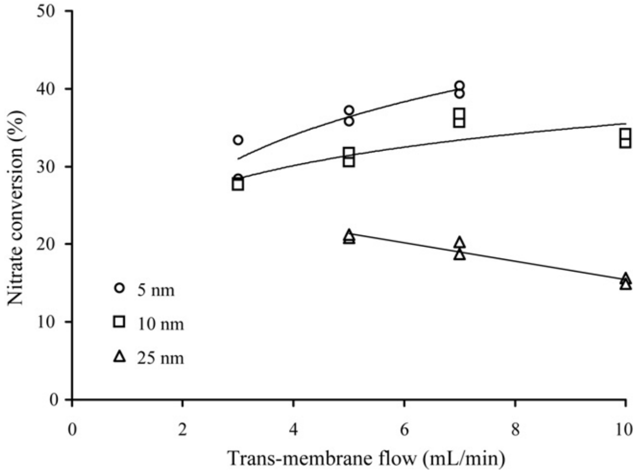

Fig. 9. Conversion of nitrates in single pass, at different trans-membrane flow rates. *Conditions*: Pd–Cu/Al_2O_3 membranes with 5, 10 or 25 nm top layer pore size, Pd/Cu = 2.5, 30 ppm (0.48 mmol/L) NO_3^-, 1 bar H_2 in the gas phase.

3.2. Effect of membrane top-layer pore size on the catalytic activity

The effect of the top layer pore size was investigated using membranes with pores of 5, 10 or 25 nm, in which the same amount of Pd–Cu catalyst was deposited. The conversion of nitrates as a function of trans-membrane flow rate in different membranes is shown in Fig. 9. With the 5 and 10 nm pores membranes, the conversion of nitrates increases with the flow rate, i.e. when the contact time decreases. This is not observed with the 25 nm pores membrane, in which the conversion decreases when the flow rate increases.

The reaction rate, however, increases with the trans membrane flow rate for the three membranes, but only moderately with the membrane with 25 nm pore size (Fig. 10). At similar flow rates, the activity is higher when the pores size decreases.

At a flow rate of 3 mL/min, the reaction rates are 0.22 µmol $(NO_3^-)\,s^{-1}\,g_{PdCu}^{-1}$ (or 1.25 mmol$(NO_3^-)\,min^{-1}\,mol_{PdCu}^{-1}$) with the 5 nm pores membrane, and 0.19 µmol$(NO_3^-)\,s^{-1}\,g_{PdCu}^{-1}$ (or

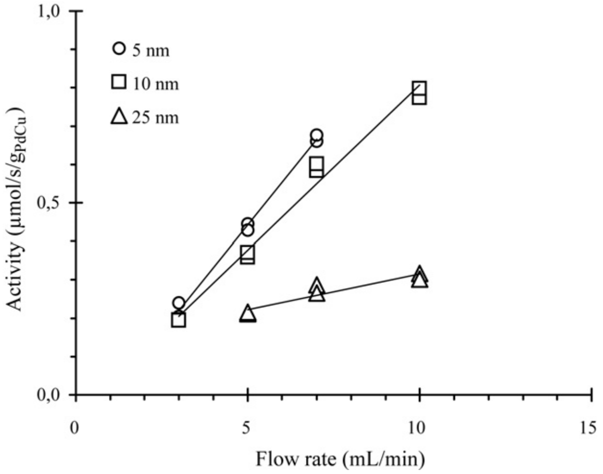

Fig. 10. Rate of nitrates disappearance at different trans-membrane flow rates. *Conditions*: Pd–Cu/Al_2O_3 membranes with 5, 10 or 25 nm top layer pore size, Pd/Cu = 2.5, 30 ppm (0.48 mmol/L) NO_3^-, 1 bar H_2 in the gas phase.

1.1 mmol(NO_3^-) min^{-1} mol$_{PdCu}$$^{-1}$) with the 10 nm pores membrane. In comparison, Ilinich et al. [24], using Pd–Cu catalysts deposited in macroporous membranes (pore diameter 0.4 µm) in forced-though mode at a trans-membrane flow rate of 2.4 mL/min, obtained a reaction rate of 0.56 mmol(NO_3^-) min^{-1} mol$_{PdCu}$$^{-1}$ for an initial nitrate concentration of 200 ppm. Decreasing the pores size significantly enhances the catalytic activity of the membrane.

3.3. *Concentration polarization of nitrates and ultrafiltration experiments*

Concentration polarization is a well-known phenomenon in nano- or ultra-filtration [25] processes like reverse osmosis or electro-dialysis. One or several dissolved salts are rejected by the membrane, and since the convective flow through the membrane is larger than the backflow diffusion to the bulk feed solution, an accumulation of the rejected components takes place at the membrane surface.

The ceramic membranes used in the present work fall in the range of ultra-filtration membranes, which corresponds to pore sizes in the 2–100 nm range. Therefore, the flow-through configuration of the CMR may lead to concentration polarization of nitrates. In order to check this point, nitrate solutions were filtered through bare alumina membranes with 5, 10 and 25 nm pores, and the nitrate concentrations were measured in the permeate and retentate sides after 8 h of filtration (Fig. 11).

Significant variations in the nitrate concentrations are evidenced after filtration experiments, in the absence of any catalytic reaction: the nitrates are more concentrated in the retentate than the feed solution, whereas they are less concentrated in the permeate. The difference between the two concentrations increases as the pore size decreases. This reveals that concentration polarization takes place during the filtration, and that it is more important with small pores membranes.

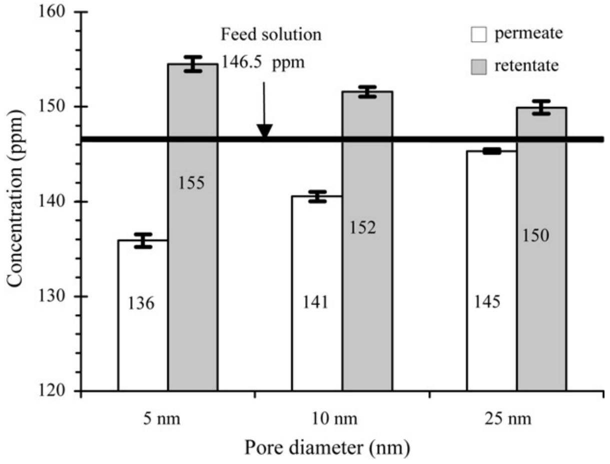

Fig. 11. Nitrate concentration in the permeate and retentate sides, after 8 h forced flow of a feed solution at 146.5 ppm NO_3^- (1 mL/min, bare Al_2O_3 membranes). Each bar represents the average value of 3 different analyses, the error bar shows the standard deviation of the measurements.

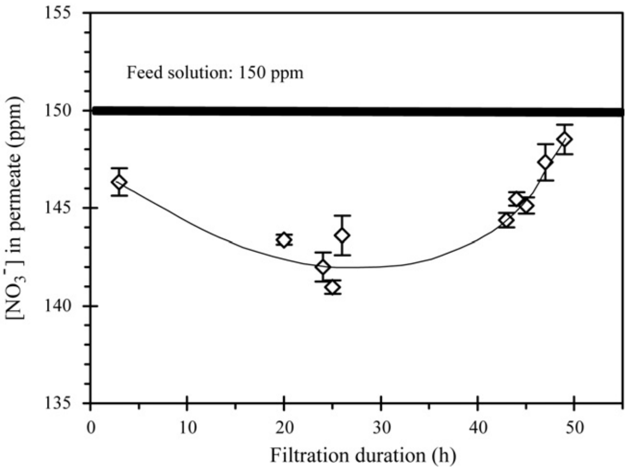

Fig. 12. Evolution of nitrate concentration in the permeate as a function of filtration duration. *Conditions*: Membrane with 5 nm pores, [NO_3^-] = 150 ppm in the feed solution, trans-membrane flow rate 1 mL/min.

Since nitrates cannot accumulate indefinitely and the system must reach steady state, the time dependence of concentration polarization was studied. Fig. 12 shows the evolution of nitrate concentration in the permeate with the filtration time. Nitrate retention increases with time and reaches a maximum after 20–25 h of filtration, then its concentration in the permeate slowly tends back to the concentration of the feed solution after ≈50 h. Integration of the area between the feed solution and the nitrate concentration curve in the permeate leads to a total mass of 17 mg NO_3^- accumulated in the membrane. If these nitrates were exclusively concentrated in the porous volume of the membrane, this would correspond to a concentration of 0.1 mol/L, i.e. ≈40 times more concentrated than the feed solution. A more realistic picture,

Table 1
Theoretical hydrogen concentration in solution and corresponding gas phase hydrogen pressure required for reduction of various amounts of nitrates into NO_2^-, N_2 or NH_4^+.

[NO_3^-]		[H_2] for reaction (2)		[H_2] for reaction (3)		[H_2] for reaction (4)	
ppm	mmol/L	mmol/L	bar	mmol/L	bar	mmol/L	bar
10	0.16	0.16	0.2	0.4	0.5	0.64	0.8
30	0.48	0.48	0.6	1.2	1.5	1.92	2.4
50	0.80	0.8	1.0	2	2.5	3.2	4
100	1.61	1.61	2.0	4	5	6.4	8.1

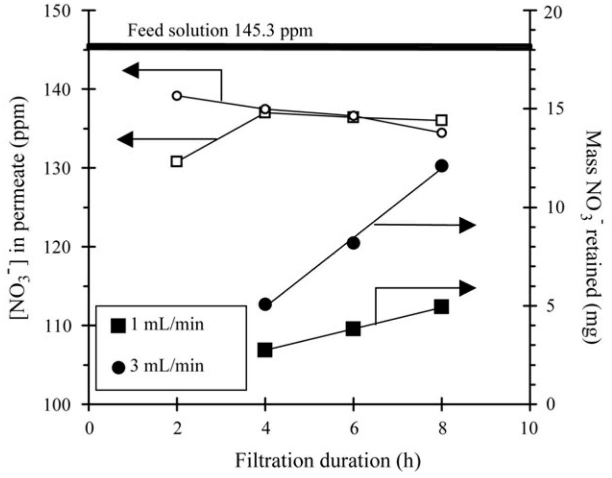

Fig. 13. Dependence of nitrate concentration in permeate and of nitrate retention on filtration duration, at different trans-membrane flow rates. *Conditions*: two membranes with 5 nm pores, initial nitrate concentration 145 ppm.

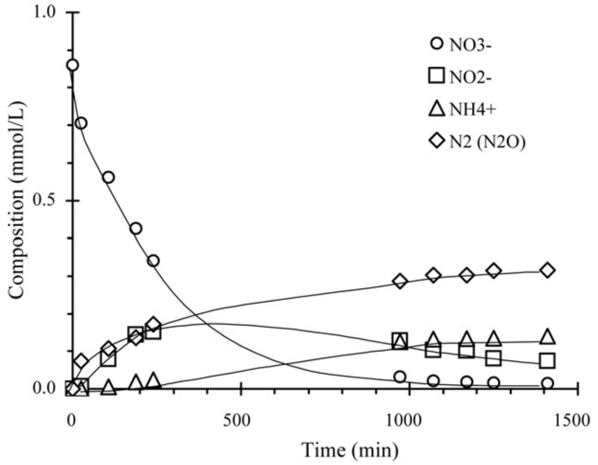

Fig. 14. Composition profile with recirculation time, membrane with 5 nm pores. *Conditions*: 50 ppm nitrates, trans-membrane flow rate 5 mL/min, 1 bar H_2 in the gas phase. The lines are visual guides.

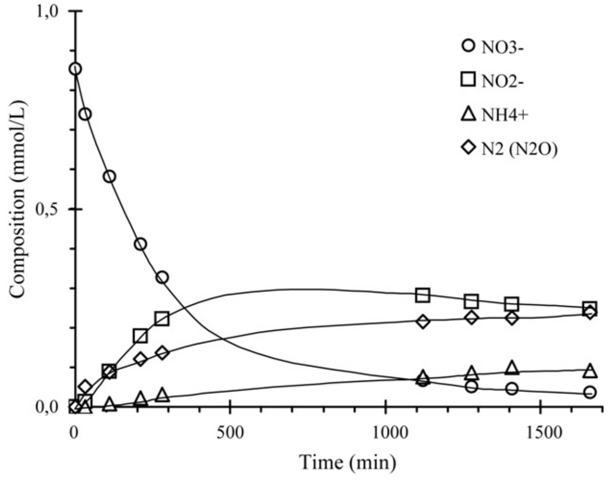

Fig. 15. Composition profile with recirculation time, membrane with 10 nm pores. *Conditions*: 50 ppm nitrates, flow rate 5 mL/min, 1 bar H_2 in the gas phase. The lines are visual guides.

however, is that the nitrates are concentrated in a film at the surface of the mesoporous layer.

The effect of trans-membrane flow rate on the concentration polarization of nitrates is shown in Fig. 13. Two different membranes with a pore size of 5 nm were used, in order to start each experiment with a clean membrane.

The difference in nitrate concentration between the permeate and the feed solution is similar at the two flow rates tested. However, since the initial nitrate concentration is the same, the cumulated mass of nitrates retained is more or less tripled when the flow rate changes from 1 to 3 mL/min, as shown in Fig. 13.

3.4. *Effect of membrane top-layer pore size on the catalytic activity in recirculation*

The objective of the CMR process being to eliminate the nitrates from potable water, the catalytic activity was also studied with recirculation of the solution, until total conversion of nitrates was reached. The most active membranes, i.e. with 5 and 10 nm top-layer pore size, were tested in recirculation (Figs. 14 and 15).

Initial rates of nitrate disappearance are roughly similar with the two membranes, but the product selectivity is different. The main product is nitrite (intermediate reduction product) with the 10 nm pore size membrane, even at high conversions of nitrates. After 1410 min, the conversion of nitrates is 98.3% with the 5 nm pores membrane, but only 94.6% with the 10 nm pores membrane. The membrane with 10 nm pores appears less active than the 5 nm pores membrane. The amount of ammonium formed at total conversion of nitrates (0.14 mmol/L or 2.5 ppm, with the 5 nm pores membrane) exceeds by a factor of five the European standards for ammonium concentration in drinking water (0.5 ppm [1]). Because of polarization concentration, controlling the reaction selectivity by controlling the contact time between the nitrates and the catalyst appears difficult. However, these objectives could be achieved from the optimal control of the whole system after adequate modelling of the reactor.

4. Discussion

Mesoporous catalytic membranes with 5 and 10 nm pores exhibit an unusual behavior in the catalytic reduction of nitrates: the conversion of nitrates reaction increases when the reaction contact time decreases. The same trend, although not explained, has been observed by Lüdtke et al. [17], using microporous polymer membranes in forced-through mode: the activity increased linearly from ≈40 to ≈210 $\mu mol\, min^{-1}\, m^{-2}$ (NO_3^- reacted) when the volume flow density was changed between 5 and 25 $L\, h^{-1}\, m^{-2}$, whereas the selectivity towards N_2 remained more or less constant. Using macroporous membranes (1 μm pore size), Ilinich et al. [7,10] also observed an increase in the reaction rate with the trans-membrane flow rate. It was attributed to an improved mass transfer in the pores. The mass transfer coefficient is indeed related to the hydrodynamic properties of the system. It is improved by increasing the flow rate and, for a similar flow rate, by decreasing the hydrodynamic diameter.

With the mesoporous membranes used in the present work (membranes with a top-layer pore size of 5, 10 and 25 nm), a linear increase in the activity as a function of trans-membrane flow rate is observed, but the slope decreases as the pore size increases (Fig. 10). Although the pore size could affect the mass transfer of reactants, filtration experiments of sodium nitrate solutions also clearly evidence concentration polarization of nitrates. In a porous material, the diffusion of solutes is restricted by the porosity of the solid and by the pore tortuosity. When the size of the solute molecule is comparable to the pore size, hydrodynamic particle/wall interactions play a dominant role. The diffusion coefficient of solutes is therefore smaller in the pores than in the bulk solution [26]. The ratio λ

Table 2
Calculation of nitrate diffusion coefficient ratio in solution and in the pores.

Pore diameter (nm)	$\lambda^{a} = Ø(NO_3^-)/Ø$pores	D_p/D_{bulk} from Eq. (5)[b]
5	0.089	0.57
10	0.045	0.65
25	0.018	0.71

[a] Size of the nitrate ion with its immobilized hydration shell: 0.446 nm, from Ref. [28].

[b] Tortuosity factor = 1.3, from the tube manufacturer.

of the molecule size on the pore size has been directly related to ratio of the diffusivity in the pores D_p on the molecular diffusivity in the bulk solution D_{bulk}, through the relations [27]:

$$\frac{D_p}{D_{bulk}} = \frac{1 + 1.13\lambda\,\mathrm{Ln}\lambda - 1.54\lambda}{\tau_p(1-\lambda)^2} \quad \text{for } \lambda < 0.2 \tag{5}$$

or

$$\frac{D_p}{D_{bulk}} = \frac{1 - 2.10\lambda + 2.09\lambda^3 - 0.98\lambda^5}{\tau_p} \quad \text{for } \lambda > 0.2 \tag{6}$$

Calculation of the D_p/D_m ratio for different membrane pore sizes is shown in Table 2. Whatever the pore size, the diffusivity of nitrates in the pores is lower than the diffusivity in the bulk solution. The nitrate diffusivity in the pores also decreases with the pore size.

The diffusion coefficients of aqueous chromium nitrate [29] or nickel nitrate [30] into porous materials have been measured for materials with pore diameters in the 2–20 nm range. When the pore diameters are larger than 5 nm, the structural resistance to the diffusion of ions was negligible [30]. The pore diffusion coefficient D_p was proportional to the pore size, but only 2–3 times smaller than the bulk diffusion value. These results are in agreement with the calculations presented in Table 2. However, in pores with diameter of ≈3–5 nm, physical restrictions to the diffusion appeared because the size of the hydrated ion (0.45 nm for Cr^{3+}) became close to the pore size, and D_p decreased steeply (i.e. $D_p/D_{bulk} = 0.1$ in pores of 3.16 nm [diameter [29]], $D_p/D_{bulk} = 0.18$ in pores with diameter of 4 nm [30]). When the pore size was close to micropores, the diffusion of the metal salt was strongly restricted and D_p decreased by orders of magnitudes (i.e. $D_p/D_{bulk} = 0.02$ in pores with diameter of 2.6 nm [29], $D_p/D_{bulk} < 4 \times 10^{-3}$ in pores with diameter of 2.1 nm [30]). The pore size of ≈5 nm appeared the critical limit to the diffusion of aqueous ions.

When the catalytic reduction of nitrates is performed with mesoporous catalytic membranes, the restriction of nitrate diffusion into the mesopores leads to nitrate accumulation on the top layer of the alumina membrane, which is essentially the catalytic zone, as shown previously: because of the asymmetric structure of the porous support and of capillary forces, the solution of metal precursors migrates from the large to the small pores during the preparation of the catalytic membranes, leading to metal concentration in this area [31–33]. Therefore, the nitrate concentration increases locally in the catalytic zone and the reaction rate increases similarly, as long as hydrogen transfer does not limit the reaction. The effect on the catalytic activity is particularly strong with the 5 and 10 nm pore membranes (Fig. 10), in which the concentration polarization of nitrates is important (Fig. 11). In contrast, with the 25 nm pores membrane the polarization concentration is modest, and the catalytic activity is only slightly improved when the flow rate increases.

As far as nitrate reduction in a flow-though CMR is concerned, the concentration polarization has an immediate effect: it improves the reactivity of nitrate ions by increasing their concentration in the catalytic zone. High amounts of nitrites, however, are formed in a single pass, and recirculation of the solution is required to push forward the reaction towards N_2. As a perspective, a two-stage membrane reactor could be foreseen, to first convert nitrates into nitrites, and then perform nitrite reduction in a second stage. The negative effect of concentration polarization, however, is that one of the main advantages of CMRs, i.e. the control of contact time, is cancelled. Consequently, the ammonium selectivity remains an issue, like in other previously published studies where the amounts of ammonium at total nitrate conversion are always too high [10–16,23]. It should be mentioned, however, that the low initial NO_3^- concentrations used in the present study do not favor the selectivity towards nitrogen.

5. Conclusion

Tubular mesoporous membranes supporting Pd–Cu catalysts were operated as CMRs in forced-through configuration for the hydrogenation of nitrates in water. We have explored the effect of pore size (5, 10 and 25 nm) on the catalytic activity. The conclusions drawn from this study are as follows:

- In forced-through configuration, the membranes exhibit an unusual catalytic behavior: the rate of nitrate disappearance increases with the trans-membrane flow rate, i.e. when the contact time decreases. At a similar trans-membrane flow rate, the rate of nitrate disappearance follows the order 5 nm > 10 nm > 25 nm.
- Concentration polarization of nitrate ions was evidenced by ultrafiltration experiments, the amounts of nitrates retained in the pores following the order 5 nm > 10 nm > 25 nm. Increasing the trans-membrane flow rate also increases the amount of nitrates accumulated in the membrane. The concentration polarization is only moderate with the 25 nm pore membrane.
- Concentration polarization of nitrates appears correlated with the catalytic activity: nitrate accumulation in the catalytic zone results in an increase in the reaction rate. A high activity is obtained with small pores membranes (92% nitrate conversion in a single pass with the 5 nm pores membrane at a flow rate of 5 mL/min), which also exhibit the strongest concentration polarization effect. The main product, however, is nitrite, an intermediate product of the reaction.
- Despite the improvement in activity imparted by concentration polarization, it has a detrimental effect on the selectivity because the control of contact time becomes impossible and too many ammoniums are formed.

More generally, these results suggest that mesoporous catalytic membranes could take advantage of polarization concentration to simultaneously concentrate traces of pollutants and enhance their destruction.

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