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Use of palladium based catalysts in the hydrogenation of nitrates in drinking water: from powders to membranes

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Abstract

The behavior of Cu or Sn promoted palladium catalysts supported on zirconia and titania for the hydrogenation of nitrate in drinking water is discussed. Catalysts are prepared either as powders (microspheres) or in the form of membranes deposited on commercial alumina tubes. The performance of the former in terms of activity and selectivity towards the formation of nitrogen in a batch reactor is presented as a function of the preparation procedure, the type of precursor, the Pd/Cu ratio and the type of promoter. The use of catalysts under diffusion controlled conditions allows to reduce significantly the amount of ammonia formed while retaining a high catalytic activity. Membrane catalysts are prepared by sol–gel and characterized by SEM, EDS and hydrogen permeability tests. Their reactivity is studied either in a recirculation reactor or in a continuous flow reactor and the effect of the initial pH, the residence time and the internal hydrogen pressure are reported. ©2000 Elsevier Science B.V. All rights reserved.

Keywords: Hydrogenation; Nitrate; Palladium; Zirconia; Membrane catalysts

1. Introduction

As a result of high rates of nitrogen fertilization and intensive agricultural production, the concentration of nitrate in water supplies in many agricultural areas of the EU exceeds the admissible level for many industrial or human uses (EC Directive 80/778: maximum concentration <50 mg nitrate/l). Future outlooks are even worse because of the continuous decrease of the capacity of the ground to fix nitrate.

Conventional techniques for denitrification of ground water are relatively costly, they need in some cases a secondary post-treatment of effluents and cannot be easily suited to variable nitrate contents, flow of water, and so on. Water treatment technologies using a solid catalyst and a gas-phase reagent (O_2, O_3, H_2) have been proven to offer several advantages in terms of rate of reaction, operating conditions and process economics over conventional techniques of waste or polluted groundwater treatment [1].

In this respect, catalytic reduction of nitrate represents one of the most promising approach to address the problems outlined above [2–15]. Recently, we reported the possible use of Al_2O_3–CuO mixed oxide 1 mm spheres as supports for Pd catalysts for the hydrogenation of nitrate, with the aim of performing the reaction under continuous flow operations [16]. However, one of the main problems associated with

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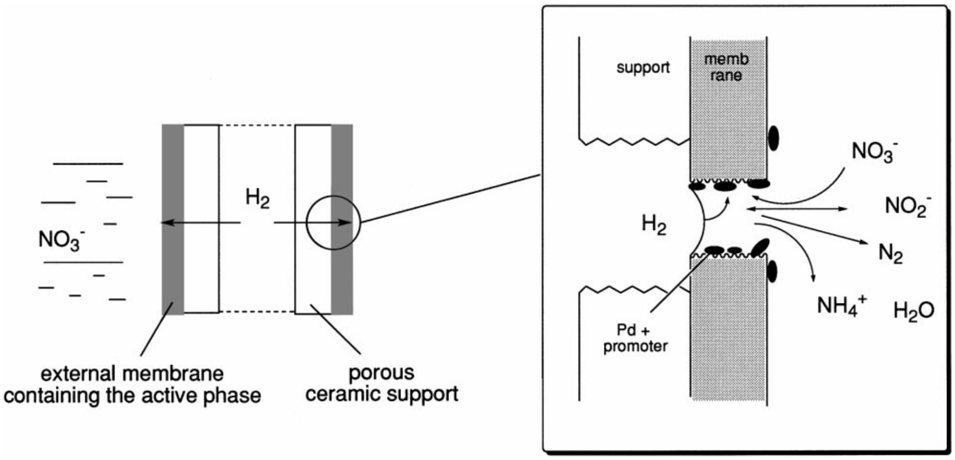

Fig. 1. The concept of tubular membrane catalysts.

catalytic reduction of nitrate is the formation of undesired side products, i.e. ammonia, as the result of over-hydrogenation. It has been observed that the kinetics of the overall process can be severely influenced by diffusion effects and more generally, a limit of such technologies is the necessity of generating an efficient gas/liquid/solid three-phase contact which is crucial not only for the rate of reaction but in several cases also for the selectivity. In this respect, attempts to solve the problem of the three phase contact have included the use of metal colloids immobilized in hollow fiber dialyzer reactors [17] or the use of catalyst particles encapsulated in poly-vinylalcohol hydrogel beads [18,19]. Furthermore, a general problem affecting gas-phase reactants such as H_2 and O_3, is that safety problems may arise in large scale reactors.

The objective of the present work is to evaluate the possibility to develop a viable process for nitrate reduction which relies on the use of porous catalytic membranes (Fig. 1). In this novel catalyst design, hydrogen is fed from inside the membrane (in principle directly on the active phase), while the water solution flows on the outside. The basic idea is to create a highly effective gas/liquid/solid interface and to adjust the pressure differential across the membrane in order to control the hydrogen mass transfer rate, aiming at an improved control of the activity and selectivity. This new approach is intrinsically safer than traditional catalysts, because the hydrogen pressure can be adjusted to avoid hydrogen flow outside the membrane.

Moreover, since the literature reported to date on this subject concerns almost exclusively the use of alumina as the catalyst support, we thought of interest to study the use of zirconia as a non conventional support because of its capability to improve the performance of supported transition (noble) metals in hydrogenation reactions [20].

2. Experimental

2.1. Materials

Zirconia microspheres (32–50 μm) were prepared by Gel-Supported-Precipitation [21,22] azeotropically dried and calcined in air at 550°C for 3 h. Textural parameters were: BET surface area 112 m^2/g; Dpores av 8.2 nm; Vp 0.25 ml/g.

Powder catalysts were prepared by impregnation methods starting from aqueous solutions of $PdCl_2$, $Pd(OAc)_2$, $CuCl_2$, $Cu(OAc)_2$, $SnCl_2$. They were all calcined in air at 500°C for 1 h and reduced in hydrogen flow at 130°C (150°C in the case of the Sn containing catalyst) for 1 h. Their analytical properties are reported in Table 1. Pd and Cu contents were determined by atomic absorption analysis.

Tubular membrane catalysts were prepared from commercial alumina tubes (from Velterop) coated by the appropriate membrane with sol–gel technique. The membrane was prepared by dip-coating using sol-type

Table 1
Analytical data of the ZrO_2 supported powder catalysts

Sample	Precursors	Pd(%) theor (found)	Cu or Sn (%) theor (found)	Pd/Cu or Sn	Preparation method[a]
P1	$PdCl_2 + CuCl_2$	5.0 (4.3)	1.5 (1.3)	3.3	WC
P2		5.0 (4.9)	1.5 (1.5)	3.2	IW
P3		5.0 (4.2)	0.5 (0.47)	8.9	SI
P4		5.0 (3.9)	1.0 (0.86)	4.5	SI
P5		5.0 (3.9)	1.5 (1.3)	3.0	SI
P6		5.0 (4.1)	2.0 (1.8)	2.2	SI
P7	$Pd(OAc)_2 + Cu(OAc)_2$[b]	5.0 (4.4)	1.5 (1.4)	3.1	WC
P8	[c]	5.0 (5.0)	1.5 (1.4)	3.5	WC
P9	$PdCl_2 + SnCl_2$	5.0 (4.7)	1.5 (1.1)	4.2	WC

[a] SI wet subsequent impregnation (Pd + Cu); WC wet coimpregnation; IW incipient wetness impregnation.
[b] Solution in MeOH.
[c] Solution in AcOH.

solutions of zirconia, titania and alumina. After drying at 150°C for 18 h, tubular membranes were calcined at 500°C. After impregnation with $Pd(OAc)_2$ and $Cu(OAc)_2$ in acetic acid, tubular membranes were dried, calcined in air at 500°C for 1 h and finally reduced in hydrogen flow at 130°C.

2.2. Methods

Powder catalysts were all subjected to TPO/TPR analysis to determine the calcination and reduction temperature. They all show a TPO maximum at 330°C and a TPR maximum at 130°C (150°C in the case of the Sn containing catalyst) with evidence for β-hydride decomposition at ~70–80°C. TPO: flow gas 5% O_2 in He (40 ml/min); T ramp 10°C/min. TPR: flow gas 5% H_2 in Ar (40 ml/min); T ramp 10°C/min.

BET nitrogen adsorption and desorption were measured at −196°C with a Micromeritics ASAP 2010 apparatus. The samples were pretreated at 300°C under vacuum (1.33 Pa)

The morphology was studied both by SEM on a Philips 505 instrument and on an optical Reichert Polyvar 2 microscope. Energy Dispersive System (EDS) mapping of Cu, Sn and Pd were made on the cross-section of several microspheres, revealing unvariably a uniform distribution of the element within the zirconia matrix.

X-ray diffraction (XRD) patterns were obtained by a Siemens D 500 powder diffractometer equipped with a graphite crystal monochromator using a Copper Kα X-ray radiation source. Experiments were run in step-scan mode with a step interval of 0.02° 2Θ and a count rate of 1 s per step over the range 5–90° 2Θ.

Hydrogen permeability tests were performed on tubular membrane catalysts fitted with two adaptors at the ends, one of which was connected to H_2. The adaptors were tightened and the tubes immersed in water. The hydrogen line was pressurized at increasing pressures and gas evolution was evaluated by analysis of photographs taken during the experiment. The flow of gas leaving the water bath was measured with a flowmeter.

2.3. Catalytic experiments

Powder catalysts were tested in a thermostatted (25°C) batch reactor equipped with a pH-stat, H_2 inlet and outlet and a sampling port. The catalyst (40 mg) was suspended in pure water (63 ml) and saturated with hydrogen (120 ml/min) for 1 h under vigorous stirring. pH was set at 5.0 and maintained constant throughout the reaction. Then 7 ml of a 1000 ppm solution of NO_3^- were added and time was started. Samples were periodically taken from the suspension and analysis of NO_3^- and NO_2^- concentrations was performed by ion chromatography. Ammonia concentration was determined with the use of an gas sensitive electrode.

Tubular catalysts were tested in a stainless steel reactor, by flowing a 50 ppm solution of nitrate from a reservoir. The reaction was operated under recirculation mode or under continuous flow. In the former case, pH was set at 5.0, the nitrate solution was hydrogen saturated for 60 min (H_2 flow 120 ml/min) and the recirculation rate was 2.5 ml/min. In the latter case, the solution was air saturated and hydrogen was fed from inside the membrane.

3. Results and discussion

3.1. Powder catalysts

In Table 1 a summary is reported of the amounts of Pd and Cu or Sn determined by atomic absorption analysis and the preparation method employed for the different powder catalysts. Powder X-ray diffraction analysis of these samples indicates that zirconia is present as a mixture of tetragonal and monoclinic phases, but no clear evidence of peaks referring to Pd and Cu metals could be observed indicating that the metals are well dispersed with particle size <2–3 nm [23,24].

3.2. Influence of the preparation method

The catalytic behavior of the samples reported in Table 1 in the reduction of nitrate at room temperature was studied in a batch, well mixed reactor, under conditions in which diffusion control limitations could be excluded. A typical reaction profile is shown in Fig. 2. The depletion of nitrate follows an approximately first order decay, appreciable amounts of intermediate nitrite are observed, while ammonia forms regularly from the beginning of the reaction. Complete conversion of both nitrate and nitrite is obtained in about 20–30 min. On the basis of the behavior shown in Fig. 2, five parameters can be defined that will be used for the evaluation of the performance of the catalysts: (i) the initial rate, (ii) the reaction time, (iii) the maximum nitrite formed as intermediate, (iv) the ammonia present at the end of the reaction and (v) the selectivity to nitrogen. As far as the latter is concerned, it was assumed that N_2 and NH_4^+ are the only reaction products.

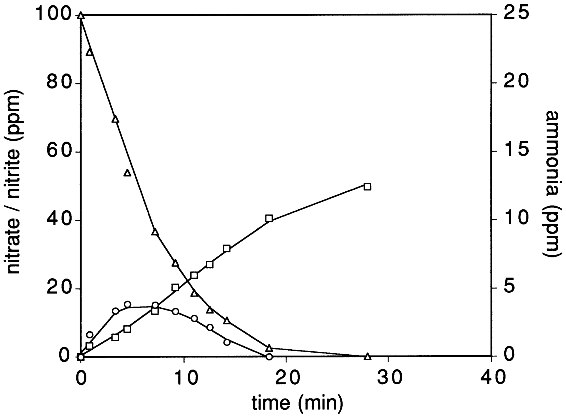

Fig. 2. A typical reaction profile for the hydrogenation of nitrate with powder catalysts (cat P1): triangles (nitrate), circles (nitrite), squares (ammonia).

A summary of the reactivity of the catalysts is shown in Table 2. As can be seen, the effect of the preparation procedure seems negligible (samples P1, P2, P5). Wet subsequent impregnation, wet coimpregnation and incipient wetness impregnation allow to prepare catalysts that display virtually identical performance in terms of ammonia formation and selectivity (Table 2). Slight differences in activity can be easily accounted for on the basis of the slightly different Pd content (Table 1).

The use of metal acetates in different solvents compared to the use of metal chlorides in HCl solution using the wet coimpregnation method (samples P1, P7, P8) allows to prepare catalysts with a slightly better catalytic activity (Table 2) especially when acetic acid is used as the solvent. However, much higher amounts of both intermediate nitrite and ammonia are observed suggesting metal chlorides as the preferred precursors.

Since the early report by Hörold et al. [5], the Pd/Cu ratio is known to affect considerably the activity and selectivity of the catalysts, it is therefore a critical composition parameter and it was evaluated. In Table 1 the range of theoretical Cu content 0.5–2.0% was explored in catalysts containing a nominal 5% fixed amount of Pd all prepared by subsequent impregnation. Table 2 shows that the activity of the catalysts does not change significantly, while the selectivity to nitrogen is considerably increased for Cu contents >1% or for Pd/Cu ratios <5.

3.3. Role of the promoter

Supported catalysts containing only palladium are active in the reduction of nitrite, but not in the reduction of nitrate which can be promoted by the addition

Table 2
Catalytic performance of the Pd–Cu/ZrO_2 powder catalysts

Sample	Initial rate (ppm/min)	Reaction time (min)	Maximum nitrite (ppm)	Ammonia (ppm)	N_2 selectivity (%)
P1	9.1	28	15	12	54
P2	9.1	25	10	11	58
P3	5.0	38	13	24	12
P4	6.2	33	13	13	52
P5	5.1	32	15	12	56
P6	4.9	28	11	14	48
P7	9.2	21	41	19	30
P8	12.5	15	36	22	19

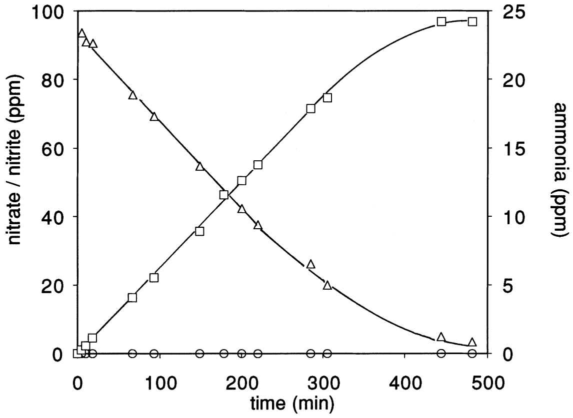

Fig. 3. Reaction profile observed with catalyst P9: triangles (nitrate), circles (nitrite), squares (ammonia).

of a second element such as copper [2–6,8–16]. More recently, the use of Sn instead of Cu as the promoter on catalysts supported on alumina has been reported [7,25] to display both higher activity and higher selectivity to nitrogen which seems to be the key issue for this class of nitrate hydrogenation catalysts. However, no indication is available on the promotion effect of Sn when alternative oxide supports such as titania or zirconia are used, as in the present work. A sample (P9) was prepared starting from $SnCl_2$ deposited by coimpregnation (Table 1) and its catalytic behavior is shown in Fig. 3. The reaction conditions are the same as those used for the experiment reported in Fig. 2 for the corresponding Cu promoted sample (P1) and thus a direct comparison is possible. As can be seen from Fig. 3, nitrate depletion follows an approximately zero order decay and a comparison with Fig. 2 shows a much longer reaction time (>500 min), no formation of intermediate nitrite, and a formation of ammonia that is twice as much. The corresponding selectivity to N_2 is 12% compared to 56% in the case of the corresponding Cu containing catalyst. Therefore, in contrast with the results obtained by other authors [7,25] on alumina supported catalysts, the use of Sn instead of Cu as promoter for Pd is negative in the present case. Reasonably, this could be attributed to the effect of the support, possibly due to the fact that copper reacts with alumina to form a surface spinel-type copper-aluminate phase, in contrast with zirconia [26].

3.4. Effect of the reaction conditions

From the reactivity data reported in Table 2, it appears that all catalysts have a high catalytic activity, but their selectivity is always rather moderate and in any case far from being acceptable for practical purposes. It is known that the selectivity can be significantly improved by operating under poor surface hydrogen concentration [5,16]. Some of the catalysts of Table 2 have been tested under diffusion controlled conditions using a higher amount of catalyst (200 mg) and a lower stirring rate. The typical reaction profile under these conditions is shown in Fig. 4 for sample P6. The reaction time becomes shorter, intermediate nitrite formation is almost suppressed and the final amount of ammonia is much lower. In particular, it can be noticed that ammonia formation increases significantly when the residual amount of nitrate is about to finish. Although, the presence of the ‘induction time’ in the formation of ammonia may be in some cases less pronounced than in Fig. 4, its existence can be noticed in most catalysts tested under these experimental conditions. This allows to define a window in which ammonia formation is still acceptable (and close to the

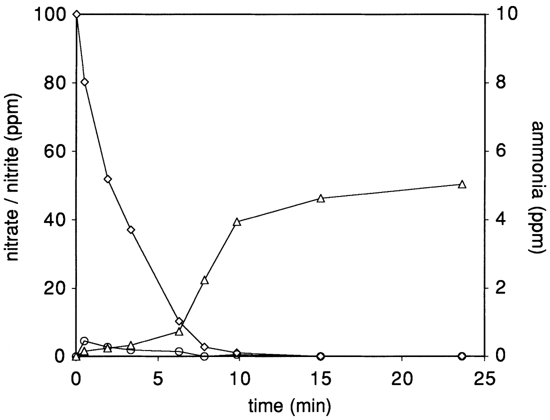

Fig. 4. A typical reaction profile for the hydrogenation of nitrate under diffusion controlled conditions (cat P6): diamonds (nitrate), circles (nitrite), triangles (ammonia).

Table 3
Ammonia formed at 20 ppm residual nitrate for some powder catalysts operating under diffusion controlled limitations

Sample	NH_3 (ppm)
P1	4.0
P3	3.3
P4	1.1
P5	3.8
P6	0.4
P7	4.6
P8	4.2

0.5 ppm maximum admissible level required for practical applications), while nitrate hydrogenation has already proceeded to a significant extent. Representative data obtained for some of the powder catalysts used in this work are shown in Table 3. It is worth noting that, although this behavior has not been optimized, some of the results reported in Table 3 (samples P3, P4, P6) can positively compare with the best performances reported in the literature [13,15,16,25] in the catalytic hydrogenation of nitrate, especially because low ammonia formation can be observed while retaining a high catalytic activity.

3.5. Preparation and characterization of the tubular membrane catalysts

Tubular membrane catalysts have been prepared by sol–gel methods by deposition on commercial alumina tubes, with or without the presence of an intermediate α-alumina layer (thickness ∼100 μm) with small pores, the purpose of which was to ensure a steady deposition of the final membrane. The latter must possess a sufficient porosity and a regular pore distribution to allow a uniform flow of hydrogen. Another important point is that the active phase must be easily accessible in order to observe an acceptable catalytic activity. The theoretical Pd and Cu contents in the active phase was 5 and 2%, respectively. Some analytical and morphological data of the tubular catalysts are reported in Table 4. It has to be noticed that EDS mapping allowed to determine only the actual content of Pd in the active phase, since the Cu signal was too low. Moreover, the amount of catalytic phase present on the 10 cm long tubes was estimated by assuming a value of 3 g/ml for the active phase density. In tubular catalysts having the intermediate α-alumina layer the final catalytic membrane layer is generally more steadily deposited and more mechanically resistant.

Hydrogen permeability tests were performed on the bare alumina tubes, on the tubes coated with the intermediate layer and on the final catalysts with or without the intermediate membrane. The parameters analyzed were the uniformity of diffusion along the tube, the minimal pressure of bubbling and the change of the bubbling area with the internal pressure. Although they are semi-quantitative, as the evaluation of the bubbling area is calculated from photographs of the bubbling tube, these simple tests are quite informative. Some typical results are shown in Fig. 5 where

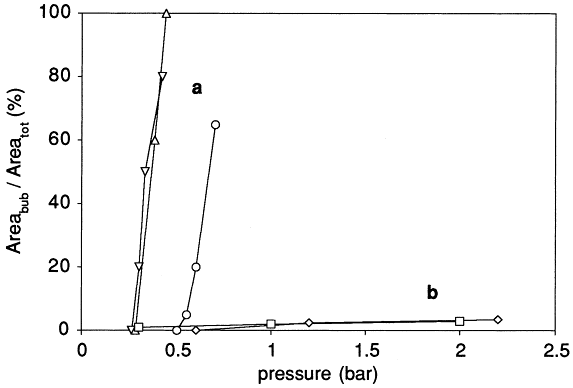

Fig. 5. Hydrogen flow measurements on tubular membrane catalysts: triangles (bare alumina tube), inverted triangles (T1), circles (T2), diamonds (T4), squares (T5).

Table 4
Some analytical and morphological characteristics of the tubular membrane catalysts

Tube	Membrane type	Thickness (μm)	Estimated amount of catal phase (mg)	PdO (%)
T1	ZrO_2	16	180	4.3
T2	TiO_2	17	190	4.6
T3	Al_2O_3	10	110	3.9
T4	Al_2O_3	2.0–2.5	20–30	6.5
T5	Al_2O_3	1.0–1.5	10–17	2.9

the percent of the tube surface evolving bubbles versus the applied internal pressure is reported. The first hydrogen bubble is normally observed in the 0.3–0.6 bar range. Moreover, two different cases can be easily envisaged as far as the behavior with increasing pressure is concerned: in the first one (denoted with **a**), the area evolving bubbles increases regularly with moderately increasing the pressure, bubbles are approximately of the same size, and with a sufficiently low increase of the internal pressure the whole external surface of the tube is covered with regular bubbles; in the second one (denoted with **b**), bubbles are evolved from a limited number of points no matter how large is the pressure applied. These differences in H_2 flow behavior could be explained by assuming that case **a** is related to the presence of a regular array of pores along the tubular membrane, while case **b** is a consequence of preferential channeling of gas, due to local inhomogeneities of the microstructure, or even bulk defects like cracks.

These observations were confirmed by microstructural determinations carried out by SEM. These were taken either on the fractured cross section of a tube or on the polished longitudinal section (Fig. 6). Image A reveals that the bare tube has a microstructure with α-alumina grain dimension around 40–50 μm. Of course, this kind of microstructure affects the smoothness of the inner and outer surfaces, where holes as deep as 30–40 μm are revealed. Addition of the intermediate layer results in the formation of a dense coating with low porosity (image B), as witnessed by the fact that the corresponding hydrogen flow is dramatically reduced to only 4 l/h at 2.5 bar. Finally, the outer ceramic membrane containing the active phase appears as a unique layer, the thickness of which is different depending on the preparation (image C). In some cases, the morphology of the membrane surface reveals the presence of cracks (image D) and its density is proportional to the membrane thickness. Pd content inside the outer ceramic membrane was determined by EDS mapping, as reported above.

3.6. Reactivity of tubular membrane catalysts

Catalytic activity tests on tubular membrane samples were performed under two different modes:

1. A recirculation mode in which the nitrate solution was flown over the tubular catalysts and recirculated through a reservoir in which it was saturated with hydrogen. In this case, the principal aim was to test the tubes under conditions as close as possible to those of the powder catalysts in order to determine the extent of the loss of catalytic activity.
2. A continuous flow mode in which an air saturated solution is continuously flown over the tubular catalyst and hydrogen is fed through the membrane. These experimental conditions allowed to check the effects of the residence time, the initial pH of the solution and the H_2 pressure inside the membrane and are more similar to the possible end use of these catalysts.

Some results obtained in the recirculation mode are shown in Fig. 7 and refer to tubes (T1, T2) without the intermediate alumina layer. In fact, the other tubes show very poor activity as a consequence of their inhomogeneous H_2 flow properties and/or a low amount of active phase (Table 4). Conversely, tubes T1 and T2 display an appreciable catalytic activity although a decrease with respect to powders is evident at least as far as zirconia as support is concerned. The ammonia formed is in the same range as powders, while the maximum amount of intermediate nitrite is very low in the case of TiO_2 as the support.

Analysis in the continuous flow mode was carried out only on catalyst T2, because of its better catalytic performance with respect to the other membrane

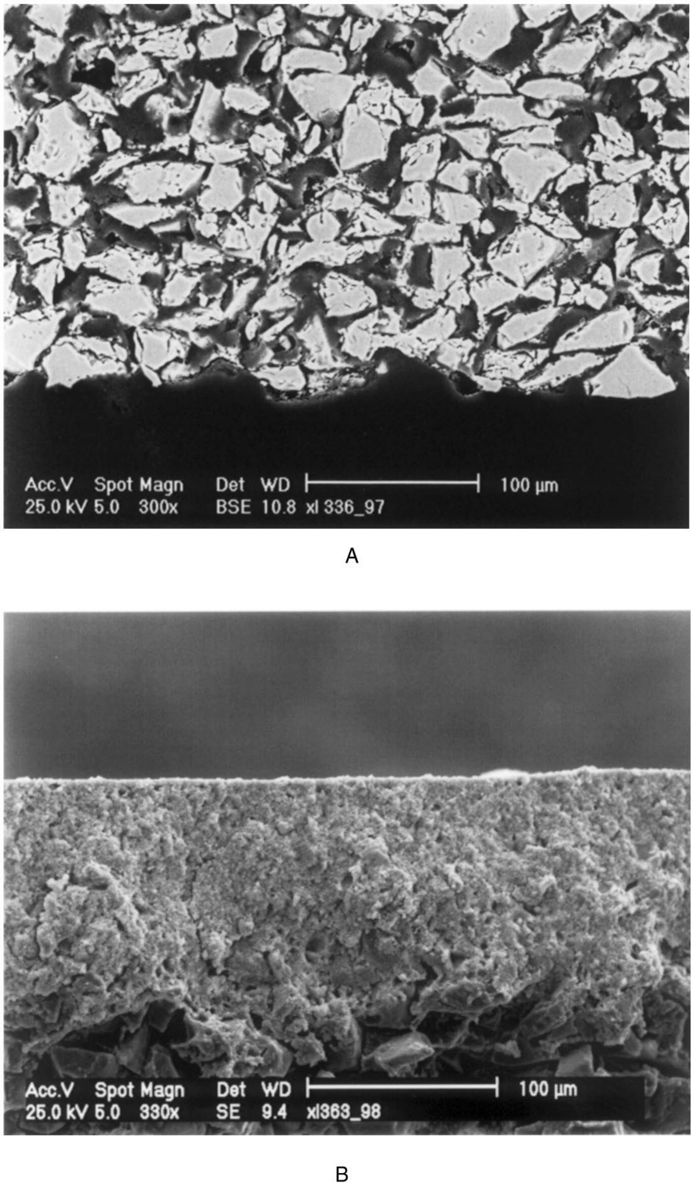

Fig. 6. SEM images of tubular membrane catalysts: **A** the bare alumina tube; **B** cross section of the intermediate alumina layer; **C** the final membrane deposited on the intermediate alumina layer; **D** the surface of T3 evidencing the presence of cracks.

catalysts tested. In this case, the effects of the initial pH, the residence time and the H_2 pressure inside the membrane were determined and they are reported in Figs. 8–10.

Increasing the pH of the initial solution (Fig. 8) in the range 2–6 results in a decrease of the ammonia formation, a slight increase in the amount of nitrite formed, while the residual nitrate remains at an acceptable level. These experiments have been made at a H_2 pressure of 0.38 bar that is below the bubbling point, in other words, only the hydrogen necessary for the reaction is consumed, at least in principle. It has to be

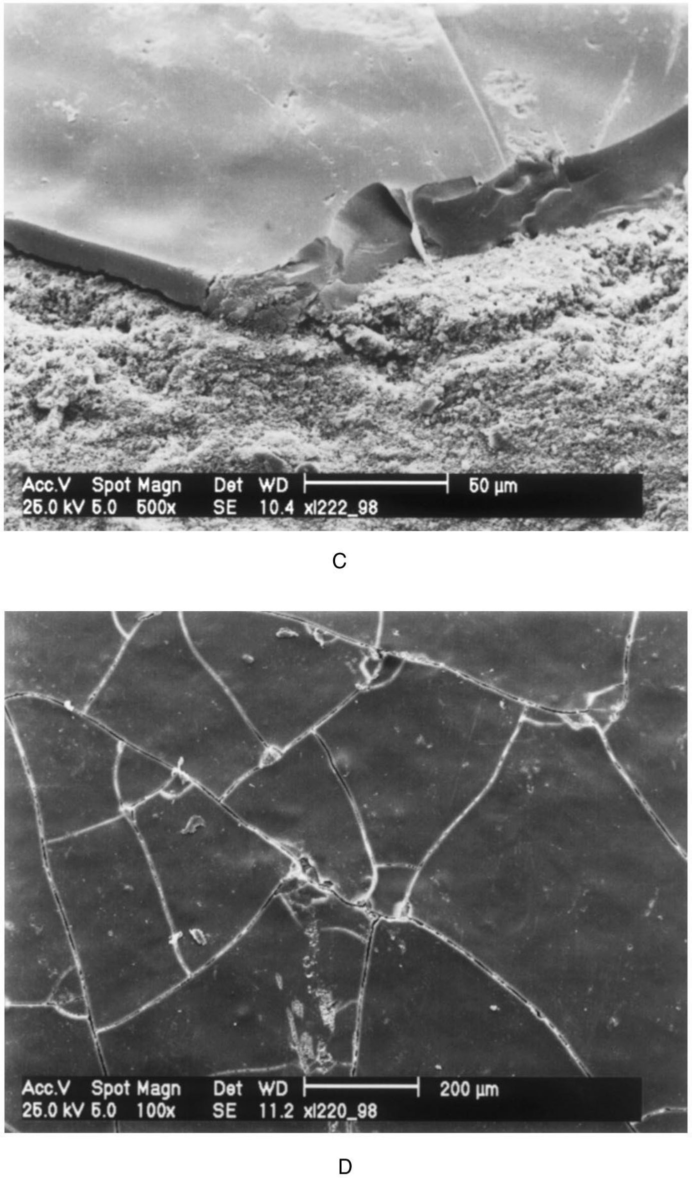

Fig. 6. (*Continued*)

pointed out that under these experimental conditions only the initial pH of the solution can be controlled, while the downstream pH value is about 11–12 as a consequence of the reaction. A pH gradient is therefore present as the solution flows over the tube in the reactor and this is not beneficial for the selectivity of the catalyst as ammonia formation is favored at high pH values.

As to the residence time (Fig. 9), in the range 12–52 min it seems to have a significant influence only on the residual amount of nitrate.

Finally the hydrogen pressure seems to exert a very similar effect (Fig. 10), as only the residual amount of nitrate is significantly affected. It has to be noticed that the two pressures chosen are either below the bubbling point or just above the bubbling point.

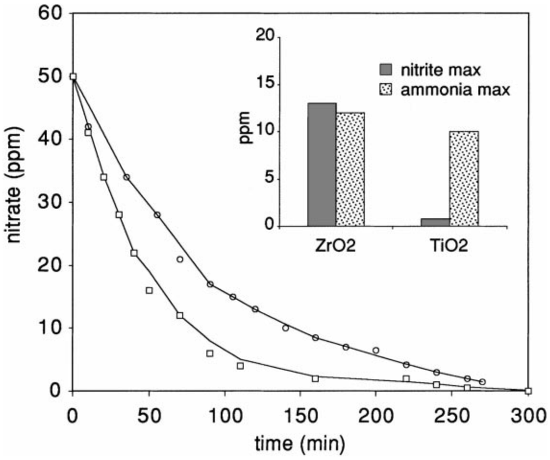

Fig. 7. Nitrate decay for T1 (squares) and T2 (circles) operating under recycling conditions. Insert: the corresponding maximum nitrite and ammonia formed.

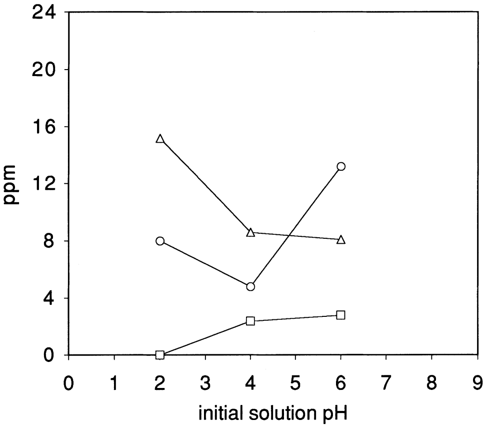

Fig. 8. Catalytic behavior of T2 under continuous flow operations: effect of the initial pH of solution; circles (nitrate), squares (nitrite), triangles (ammonia). Initial nitrate concentration 50 ppm, hydrogen pressure 0.38 bar, residence time 52 min.

4. Conclusions

The results reported in this work indicate that the conceptual solution here proposed for the problem of nitrate in drinking water, i.e. the development of tubular membrane catalysts for the removal of nitrate from drinking water, is indeed a viable one, as the reaction can be practiced at room temperature with an acceptable catalytic activity. At the same time, the use of hydrogen diffusion controlled conditions in the case of powder catalysts lead to an improvement in the minimization of the formation of ammonia. However, a comparison between the behavior of a catalyst in the form of a powder and a similar composition as a membrane is not straightforward and may lead to quite different results. In fact, although very comparable preparation methods have been used for the synthesis of powder and tubular membrane catalyst, the latter are significantly less active and slightly less selective in the reduction of nitrate to N_2. Thus, specific methods for the preparation of tubular membrane catalysts will have to be developed.

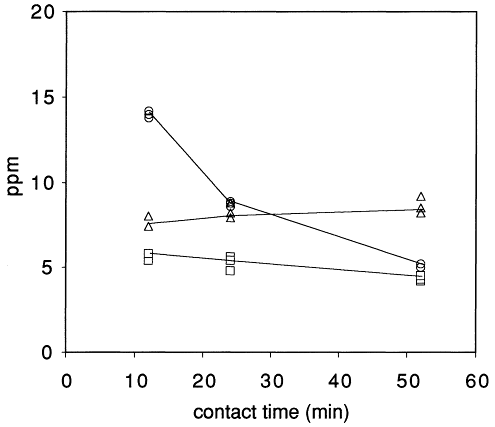

Fig. 9. Catalytic behavior of T2 under continuous flow operations: effect of the residence time; circles (nitrate), squares (nitrite), triangles (ammonia). Initial nitrate concentration 50 ppm, hydrogen pressure 0.60 bar, initial pH 6.

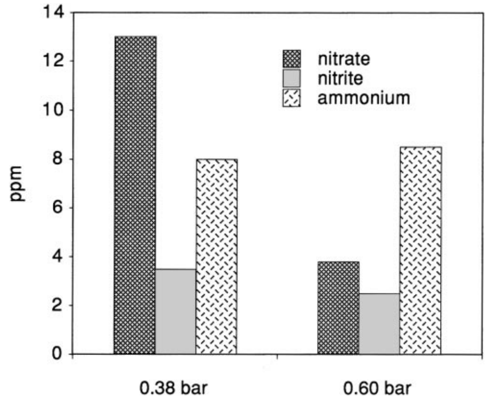

Fig. 10. Catalytic behavior of T2 under continuous flow operations: effect of the hydrogen pressure. Initial nitrate concentration 50 ppm, initial pH 6, residence time 52 min.

Another observation is that the use of zirconia as the support instead of alumina can improve the activity and modify significantly the selectivity of the catalysts, as shown by the behavior of Sn as a promoter that is opposite to what is known from the literature. This observation suggests that a systematic investigation of the effect of non conventional supports that has been neglected to date is necessary, as it might be an important parameter to control the activity and selectivity of the catalysts.

The control the selectivity of the active phase remains the key issue in the hydrogenation of nitrate. The design of an improved contact among the three phases (gas/liquid/solid) such as the use of the membrane type catalysts here reported is a viable solution to improve the performance, although specific improved preparation methodologies are necessary. However, in order to achieve the very low levels of ammonium ions presently allowed (<0.5 ppm), a further breakthrough is probably necessary, which can stem mainly from getting more insight into the mechanistic details of the reaction that are still far from being understood.

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