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Tubular Inorganic catalytic membrane reactors: advantages and performance in multiphase hydrogenation reactions

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Abstract

The tubular inorganic catalytic membrane (TICM) reactor is a novel multiphase solution for advanced chemical or environmental technologies. The advantages of the use of this technology are discussed with reference to two types of applications: (i) water remediation technologies by catalytic hydrogenation (nitrate removal and chlorinated hydrocarbon dehalogenation) and (ii) H_2O_2 synthesis by $H_2 + O_2$ reaction, both occurring over Pd-type catalysts supported over porous inorganic membranes. Some examples of the behaviour of these catalytic membranes are given in long-term tests in nitrate reduction, in chloroform dehalogenation and in H_2O_2 synthesis.

Keywords: Catalytic membrane; Hydrogenation; Structured reactor; Nitrate; H_2O_2; Chlorinated hydrocarbon

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1. Introduction

The interest on catalytic membrane-type reactors (CMR) is continuously increasing due to the broad range of possible applications from refinery to environment protection, but attention has been mainly focused on their application to catalytic reactions where the continuous selective removal of one or more products in equilibrium limited reactions allows the increase of the yield beyond the corresponding equilibrium value [1–4]. Although examples are still limited, the application of CMR has been extended in the last decade to its use to supply selectively a reactant to the reaction zone and realise an optimal concentration profile which can maximise the selectivity (see discussion on the reviews reported in [1,4,5]). This concept was applied to enhance yield and selectivity in propane direct oxidation to acrolein by dosing oxygen along the axial direction of a catalyst bed [6] and in ethene epoxidation by dosing the hydrocarbon through the walls of a ceramic membrane [7].

Porous membranes are typically used in these applications, because they offer a higher permeability than dense membranes, but the membrane itself is inert with respect to the catalytic reaction and the catalyst is physically separated from the membrane. Although this configuration highly promising for a technical development [4] (conventional fixed-bed catalyst pellets may be used), the dispersion of the catalyst component inside the porous membrane layer offer potential advantages especially when the catalytic behaviour is depending on the diffusion of the reactants. If the catalyst is inside the pores of the membrane, the combination of the open pore path and transmembrane pressure provide easier access of the reactants to

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the catalyst. For multiphase reactions such a type of membrane configuration is often preferable [4,5].

A relevant example of these concepts is given by hydrogenation reactions in liquid phase, where the reaction rate is often controlled by the kinetics of hydrogen mass transfer. Liquid-phase hydrogenations are carried out at high pressure due to the poor solubility of hydrogen in most organic liquids. Using catalytic membranes (i.e. membranes on which the catalyst is supported or having the membrane itself an inherently catalytic activity) high-pressure operation could be avoided, because a better three-phase contact may be realised. The selectivity of triphasic alkene hydrogenation reactions considerably improves when both the alkene and H_2 are forced to pass through a micro-porous catalytic membrane, because back mixing of the initial products is prevented [8] and the volatile reactant does not have to diffuse through a liquid film, as far as a gas/liquid interface is created inside the pores, in direct contact with the catalyst [9,10].

There might be interesting applications of this concept in the fine chemicals area and environmental protection technologies, but limited literature data are available. In addition, the use of catalytic membranes for multiphase hydrogenation reactions offer a series of additional advantages for the development of commercial technologies which are often not considered in discussing prospects for application of catalytic membrane-type reactors. The aim of this contribution is to discuss the features and possible advantages and/or limitations in using catalytic membranes in two interesting cases of multiphase hydrogenation reactions:

(i) Water remediation by catalytic hydrogenation (nitrate, nitrite and/or pesticide removal from contaminated water). Contamination of underground water by nitrate and pesticide is becoming a critical problem in Europe [11,12], where about a quarter of the wells in intensive agriculture areas show levels of contamination above the EU limits. Water remediation by catalytic hydrogenation could be an interesting solution in some cases.

(ii) H_2O_2 synthesis by $H_2 + O_2$ reaction in solution. H_2O_2 is a clean and versatile reactant in a range of selective oxidation reactions of interest of both petrochemical industry and fine chemical synthesis (alkene epoxidation, aromatic or alkane hydroxylation, etc.) as well as in various applications for depuration of wastewater, but its application has been inhibited by its high cost. The direct synthesis from a $H_2{+}O_2$ mixture allows potentially to considerably reduce the cost of H_2O_2 production, making thus possible to commercially develop a large range of applications and a considerable reduction of their impact on the environment.

The catalytic membrane can decouple catalytic (optimal catalyst performances) from engineering (mass and/or heat transfer, multiphase contact and fluidodynamics) aspects and thus are a good opportunity to optimise overall performances. The cases discussed here will be some examples on above aspects in order to give a contribution to evidence the opportunities and/or limitation in using catalytic membranes as an advanced type of structured reactors. However, the aim is not an in-deep discussion of each of the single reactions analysed.

Pd supported on porous inorganic membranes is used in all the previously mentioned reactions, although there are some differences in terms of the presence of a second co-catalyst and/or the nature and/or structure of the porous membrane. It is out of the scope and limits of this contribution to give a detailed discussion of the relationship between nature and composition of the catalytic membrane and performances, as well as of the role of the preparation methodology in determining the characteristics and reactivity of the catalytic membrane. Some aspects related to these question, mainly in relation to the reaction of nitrate or nitrite reduction, have been previously reported [5,13–16]. It should be remarked, however, that most of the cited results refer to tests using a slurry-type reactor (catalyst in the form of powder) or in the case of catalytic membrane to batch-type stirred-tank reactor experiments, while data reported here refer to flow type of experiments using a tubular continuous flow membrane reactor. In addition, differently from the previous results, long-term continuous experiments (up to 1000 h of time-on-stream) are reported here.

2. Experimental

2.1. *Catalytic membrane preparation*

Details of the synthesis procedure for Pd-based tubular catalytic membranes have been previously reported [5,13–16] and will thus only be briefly summarised here. In all cases tubular ceramic ultra- and micro-filtration membranes obtained from HITK (Hermsdorf, Germany) were used as support. These macroporous tubular membrane have an outer diameter of about 10 mm and an inner diameter of 7 mm. The support has an inner α-alumina layer necessary to have the right mechanical strength and two intermediate graded pore size layers also having α-alumina structure. The final micro-porous membrane layer (on the shell-side) was added by dip-coating (extracting in water-free atmosphere) using sol-type solutions of Ti- or Zr-isopropoxide. After ageing at room temperature and careful drying up to a temperature of 150 °C, the membrane was calcined at 500 °C. The estimated thickness of the membrane layer ranges in the 10–50 μm, depending on the porosity type of the final layer [5]. In the case of the catalytic membrane used for H_2O_2 synthesis the macroporous tubular membrane was instead coated with a carbon film [17] by applying a furfuryl alcohol resin on the alumina membrane followed by a controlled pyrolysis in oxygen-free atmosphere. The carbon layer is necessary for a better dispersion of Pd and to reduce the possibility of secondary decomposition of H_2O_2 by interaction with the oxide substrate [18].

Two different techniques were used to deposit the catalytically active components inside the pore-structure of the skin layer, i.e. surface impregnation (membrane is put on-centre on a rotating shaft and in contact with the surface of a bath containing the metal salts, usually an aqueous solution of Pd-nitrate or Sn- or Cu-chloride; after drying and calcination the membranes are reduced with H_2 at 300 °C and metallorganic chemical vapour deposition (MOCVD). The latter technique is based on the sequential deposition at 240–250 °C of metallorganic precursors of Pd and Sn such as Pd(II)(hfac)$_2$ and Sn(II)(hfac)$_2$ on the catalyst in an inert atmosphere. Although more expensive, the advantage of MOCVD is the possibility to obtain a more controlled surface deposition of the active components, while the surface impregnation method is closer to the possible method for preparing commercial catalytic membranes. The methods were previously discussed in details [5]. Pd and in some cases Cu or Sn were added as active components. Pd-only containing catalytic membranes are suitable for H_2O_2 synthesis, nitrite reduction and halogenated hydrocarbon conversion, while Pd/Cu or Pd/Sn are necessary in the case of nitrate reduction. In this case, the Pd/Me range was typically around 3–4, while the Pd loading typically was 5 wt.% based on the top layer. Typical Pd cluster size was in the 5–25 nm size range, being usually lower in the samples prepared by MOCVD [5]. The total amount of Pd loaded on a typical 10 cm long catalytic membrane was 20–25 mg.

2.2. Membrane reactor

Fig. 1a shows the general concept of the use of catalytic membranes in hydrogenation reactions in solution, while Fig. 1b and c shows some details of the chemistry occurring in the reduction of nitrates and synthesis of H_2O_2, respectively. The liquid phase is physically separated from the gas phase by using a tubular porous ceramic membrane. Hydrogen gas diffuses from the inner side of the tube through the porous wall to the catalyst which is deposited on the outer surface (in direct contact with the solution), where the reaction takes place. The gas flow through the membrane can be controlled by adjusting the differential pressure between the gas side and the liquid side. In the case of nitrate reduction, a $H_2 + CO_2$ mixture is fed through the membrane. CO_2 is added in order to have a local buffering effect which minimises the local increase of pH due to the generation of OH^- species in the nitrate reduction, as shown in Fig. 1b. In the case of H_2O_2 synthesis, pure H_2 is fed through the membrane. Small amounts of O_2 may be present in the gas phase in order to increase the productivity in H_2O_2 limited by the amount of O_2 dissolved in solution, but maintaining its concentration in the gas phase below the explosion limits (below about 1–2% O_2). Water is the solvent in the case of nitrate reduction, while a mixture of water and organic solvents such as methanol are used for H_2O_2 synthesis [18], in order to change the polarity of the solvent and increase the amount of O_2 dissolved in solution.

The performances of the catalytic membranes were studied either in a 1 l stirred-tank membrane reactor (the gas diffuses through the membrane immersed in the liquid vigorously stirred) or in a tubular continuous flow membrane reactor (the solution is not mixed and flows parallel to the axial direction of the membrane through which H_2 diffuses). Typical Liquid Hourly Space-Velocity (LHSV) through the membrane reactor

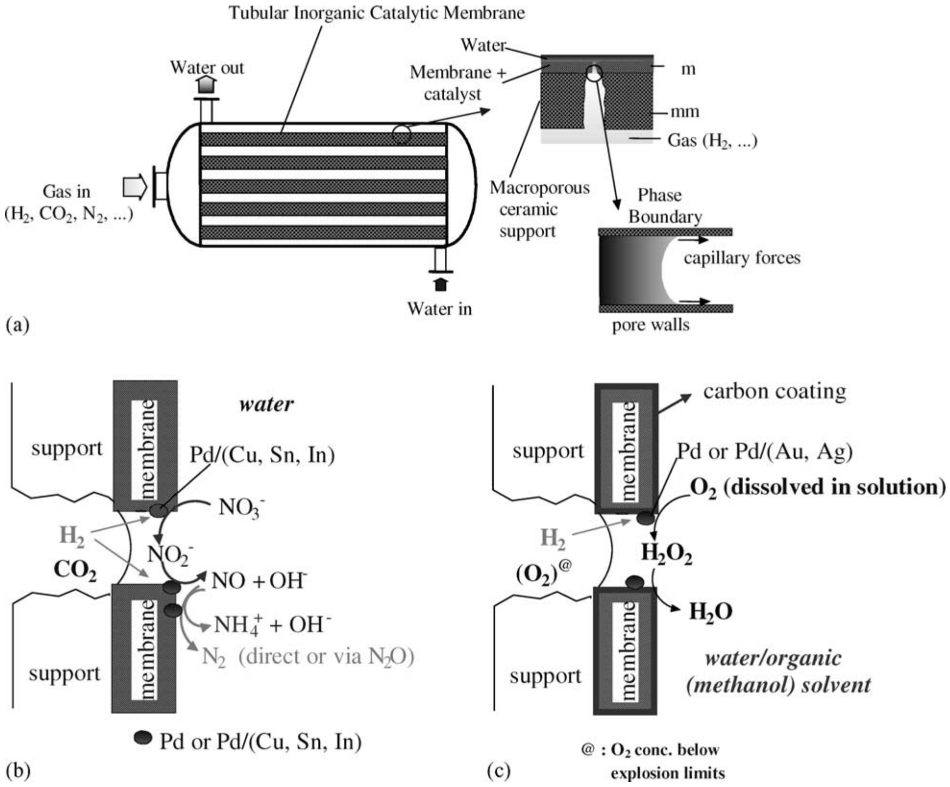

Fig. 1. Schematic diagram of a reactor module for catalytic membrane applications with the illustration of the working principle and arrangement of the active phase in the tubular inorganic catalytic membrane (a). Outline of the application of the concept to the nitrate reduction (b) and H_2O_2 synthesis (c).

in the second case is 60 h^{-1}, while residence time in the first case was 0.5 h. The stirred-tank membrane reactor is preferable for kinetic and screening studies, while the second type of reactor simulates conditions present in an effective membrane reactor modulus for this kind of applications (see Fig. 1a). Further details on the reactor and reaction apparatus as well as the analytical methodologies for analysis of the products of reactions were reported previously [5,13–16].

3. Results and discussion

3.1. Reduction of nitrates or nitrites in water

Excess intake of nitrate ions can be harmful, because nitrates can be easily reduced to nitrites in the intestines causing serious health problems. Several methods to eliminate nitrates in contaminated water are available at present. The two most used classes of methods are: (i) physicochemical processes (ion exchange and membrane techniques), and (ii) biological processes (heterotrophic or autotrophic techniques, the latter being the most widely used). While the first class of technologies do not eliminate the water contaminants, but rather concentrate them in waste solutions (brine), the biological denitrification effectively convert nitrate to non-toxic chemicals (N_2), but may be difficult to be installed for the purification of single wells in rural areas (it is suited only for medium–large applications). In these cases, as well as for some treatments of industrial wastewater (when phytotoxic chemicals are also present), catalytic reduction of nitrates is preferable, although slightly more expensive [16]. Another very relevant case is when together with nitrate halogenated hydrocarbons (pesticides, etc.) are present in significant amounts, an issue of increasing importance in several wells due to agriculture (mis)practice and the decrease capacity of soil to hold these contaminants especially in monoculture intensive areas. Due to the low biodegradability of halogenated hydrocarbons the chemical reduction is preferable against the biological reduction. Catalytic (chemical) reduction offers the additional important feature of being able to reduce both nitrate and halogenated hydrocarbons, as discussed later.

Nitrate ions are reduced on a supported Pd-Me catalysts, where Me is Cu, Sn or other transition metals, using H_2 as the reductant (Fig. 1b) [5,13–16,19–34]. H_2 may be generated in situ from formic acid decomposition [24,25], but the water contamination from the possible uncompleted formic acid decomposition and the higher cost of formic acid are severe drawbacks to this solution. The technology of catalytic nitrate reduction allows a virtually waste-free process, and can be scalable from small to large application. There is no noise production and the energy requirements are relatively low. However, conventional fixed-bed reactors with the catalyst in the form of pellets cannot be conveniently used, because the reaction of catalytic nitrate reduction is characterised by a series of features which prevent the use of conventional-type catalysts and have forced the researchers to find alternative innovative solutions, such as the following:

- The use of catalysts in the forms of cloths woven made from glass fibres on which Pd was deposited [26–29].
- The use of porous polymeric hollow fibre modules (made from polyetherimide, for example) containing the catalyst in the form of fine particles or the use of fine catalyst particles encapsulated in polyvinyl alcohol hydrogels [25,32,33].
- The use of inorganic catalytic membranes as supports [5,13,14,16,30,31].

In fact, the following features characterise the catalytic reduction of nitrates and determine the use of the previously cited new type of structured reactors [34].

1. There is a marked influence of the particle size. This is connected to the formation of hydroxyl anions as the reaction proceeds (see Fig. 1b). If the diffusion inside the catalyst particles is too slow compared to the reaction (hydrogenation is a quite fast reaction even at room temperature) the produced hydroxyl anions cannot diffuse out fast enough. The consequence is a local pH-increase which reduces the activity and favours the formation of ammonium, which formation must be minimised to below 0.5 ppm for drinking water production applications. This can be largely avoided by using extremely fine catalyst particles of a few micrometers [35]. The addition of CO_2 can have a beneficial role in buffering the pH increase, but again intra-particle diffusion may become the limiting factor.
2. The use of a catalyst in the form of suspended powder causes problems in catalyst recovery, and water contamination by suspended particles containing noble metals (limits for noble metals in drinking water are very low).
3. Incomplete deoxygenation of water prior contacting with the catalyst may cause the oxidation and passivation of Pd clusters, with a lowering of catalytic performances.
4. The growth of micro-organisms over the catalyst using tap water may cause the periodic need of regeneration of the catalyst.

While all the previous three cited technologies for structured reactors solve the first two basic questions which hinder the practical use of fixed-bed-, slurry- and fluidised-bed-type reactors in nitrate reduction for drinking water production, the catalytic membrane solution offer additional advantages regarding the two further questions and some other aspects, listed as follows:

- It is an intrinsically safe reactor technology, because there is a separate gas flow and solution flow. It is thus avoided that H_2 may come in contact with air (for example, in dead spaces) and may give rise to explosion mixtures.
- There is an improved three-phase contact (gaseous reactant/solution/solid catalyst), thus avoiding diffusion problems and providing a positive influence on the selectivity of the reaction. H_2 is fed directly near the catalytic active components, instead that being present only dissolved in solution as in the cases of glass and hollow fibres. This allows to have an uniform H_2 concentration at the catalyst surface along the entire reactor axial profile (clearly

difficult to achieve without a vigorous mixing of the solution which, however, this causes an increase in energy costs) with benefits in terms of both catalytic behaviour and reduced possibility of oxidation or passivation of Pd clusters.

- The gas flux through the membrane can be controlled by adjusting the pressure differential between the gas side and the liquid side. This provides a simple method for tuning the catalytic activity, which is a very important factor in environmental technologies such as water remediation where variable feed compositions in time should be handled.
- It is avoided by the formation of suspended particles in water, catalyst failure by attrition, etc. In hollow fibre there is always the possibility that some fine particles are not hold from the organic membrane and in glass fibre the metal–support bond is not very strong.
- It allows an easy scale-up of the technology due to the absence of agitated parts, etc. (see Fig. 1a). Furthermore, it is possible to develop easily small-size and transportable catalytic devices for on-site application, a relevant issue in water remediation of wells in rural areas.
- A membrane module is robust and may be regenerated easily by calcination and consecutive reduction, differently from polymer-type membranes which furthermore are much more sensitive to irreversible deactivation by micro-organisms growth.

The behaviour of catalytic membranes in nitrate reduction is considerably depending on the reaction conditions (although the dependence is similar to that of the analogous powder-type catalysts) and modality of preparation. These aspects were already discussed previously [5,13–16] and thus will be not further analysed. As mentioned also in Section 1, it should be remarked that previous results refer to batch-type stirred-tank reactor experiments and thus no or little attention was given to the stability performances of the catalytic ceramic membrane (long-term experiments) which instead is the featuring aspect discussed later on in tests made using a tubular continuous flow membrane reactor.

Reported in Fig. 2 is a complex sequence of experiments made in a tubular continuous flow membrane reactor which overview the features and stability of catalytic membrane for the reduction of nitrates in water. It should be highlighted that these tests are made in the absence of mixing and with the aqueous solution slowly flowing along the axial direction of the tubular catalytic membrane (laminar flow). This configuration enhances the problems related to diffusion of reagents and products, but it is more close to the possible practical application (see Fig. 1a) for which a fast mixing of the solution should be avoided to minimise energy costs. As a consequence of the absence of mixing, there is an increase of the pH from the inlet to outlet solution, even though CO_2 is also cofed through the membrane to minimise the pH increase. In the experiments reported in Fig. 2, the reactor inlet pH of the solution was decreased to about 3 using HCl, while the reactor outlet pH of the solution was found to be near 4.3. It should be also noted that the large majority of the other data reported in literature on the catalytic reduction of nitrate refer instead to conditions of well mixing of the solution. Another relevant difference is that in the experiments reported in a tubular continuous flow membrane reactor the feeding solution contains dissolved O_2, being in contact with air, while when the solution is presaturated with H_2 (again the large majority of literature data) dissolved oxygen is removed in this step.

The case A in Fig. 2 shows the time-on-stream behaviour of the fresh catalytic membrane (prereduced at 350 °C with hydrogen) in the reduction of nitrates in distilled water and at room temperature. After an initial short period of activation related to the in situ reduction of Pd (the catalytic membrane is prereduced ex situ, but then remains in contact with air and thus the Pd clusters become oxidised on the surface) the activity in nitrate reduction rapidly reaches a stationary condition, nearly corresponding to 85% of nitrate removal in the case A of Fig. 2. Activity remains quite stable for long time (about 180 h in the data in Fig. 2, but no deactivation was observed also for longer times). The rate of reaction is about 3–5 mg nitrate/(mg Pd h) (uncertainty in the value is related to the uncertainty in estimating the amount of Pd on the catalytic membrane), a value in good agreement with the previous reported data on the reduction of nitrate on similar catalytic membrane, but obtained in a well-mixed reactor [5]. Nitrite formation is negligible, while ammonium ion formation is initially high (about 8 ppm) and slowly decreases to a stable value below 2 ppm after more than 100 h of time-on-stream.

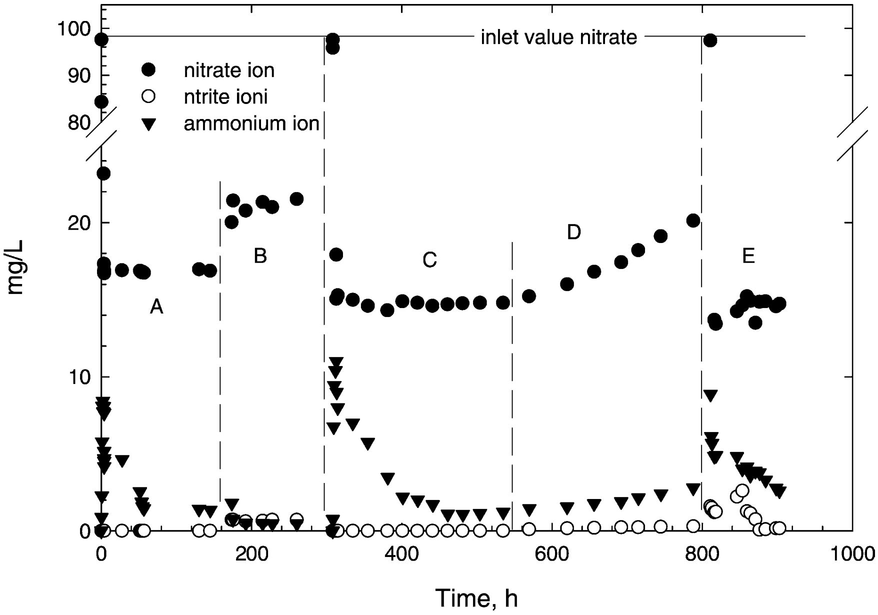

Fig. 2. Behaviour as a function of time-on-stream during a sequence of experiments in the reduction of nitrate in a tubular continuous flow membrane reactor (contact time: 52 min; laminar flow, no mixing). Pd-Cu (5:2)/TiO_2/Al_2O_3 catalytic membrane [16]. Reaction conditions: $CO_2/H_2 = 3$ feed (total pressure: 2 bar) sent through the membrane; inlet reactor pH value of the solution was 3 and outlet 4.3. Sequence of experiments are as follows. (A) Fresh catalytic membrane (prereduced at 350 °C with 20% H_2 in helium), temperature of the solution 22 °C. (B) Decrease of the inlet temperature of the solution to 15 °C. (C) The gaseous reducing feed is stopped for 48 h, but the catalytic membrane is left in contact with the aqueous solution; then the gaseous feed through the membrane ($CO_2/H_2 = 3$) started again; aqueous solution (inlet pH 3, temperature = 22 °C). (D) Use of tap water instead of distilled water; gaseous feed: $CO_2/H_2 = 3$, total pressure: 2 bar; liquid feed: inlet pH 3, temperature = 22 °C. (E) The catalytic membrane is removed from the reactor, calcined at 500 °C (after drying), prereduced at 350 °C with 20% H_2 in helium and then reintroduced in the membrane reactor. Other conditions as in the case A.

The final selectivity in nitrate reduction (selectivity to products other than nitrite and ammonium ions) is quite high (over 92%), although not enough for drinking water quality. However, by decreasing the temperature of the inlet water solution to 15 °C or less (case B), there is a minor decrease of the nitrate conversion (slightly less than 80%), but an increase of the selectivity to about 98% corresponding to an ammonium ion formation of less than 0.5 ppm (value necessary for drinking water quality). The time necessary to reach a constant formation of ammonium ion is over one order of magnitude higher than that necessary to reach a constant nitrate conversion (see case A in Fig. 2). Probably this is related to a slow in situ modification of the catalyst, tentatively due to the formation of Pd–Cu alloys as earlier suggested [21–23], although further study are necessary to clarify this question.

When the catalytic membrane is left in contact with the aqueous nitrate solution in the absence of the reducing gaseous feed, a modification of the catalyst is observed, due to both surface oxidation of Pd clusters and probably decomposition of the alloy, and adsorption of nitrate on the catalyst. When the reducing gaseous feed is added again (case C in Fig. 2), the change of the behaviour with time-on-stream is comparable to that discussed for the case A, although the time necessary to reach a stationary formation of ammonium ions is even longer. Final catalytic behaviour, however, is quite comparable in the cases A and C.

When tap water (not containing residual bacteriostatic chemicals) is used instead of fresh distilled water (case D), a progressive decline of the catalytic behaviour is observed as well as a slightly higher formation of nitrites. This is probably related to the growth of micro-organisms over the membrane and/or the effect of other ions/anions present in the tap water. It is possible, however, to regenerate the catalytic membrane by calcination followed by prereduction.

After reintroduction of the regenerated catalytic membrane in the reactor (case E in Fig. 2), the behaviour is quite comparable to that of the fresh catalytic membrane, although an initial higher formation of nitrite was observed. Their formation however decreases to negligible amounts in reaching a stationary activity.

3.2. Chlorinated hydrocarbon dehalogenation

As mentioned before, water wells are often contaminated both by nitrate and halogenated hydrocarbons and therefore the possibility of a water remediation technology which handles both contaminants is highly interesting. In order to check this possibility, being known the activity of palladium-based catalysts for treating groundwater contaminated with halogenated hydrocarbons by hydrodechlorination with dissolved hydrogen [36], the behaviour of the catalytic membrane in the reduction of chloroform was tested. Experiments were made in this case using a 1 l stirred-tank membrane reactor (batch-type operations with a reaction volume of 750 ml) as described in Section 2. The results obtained are reported in Fig. 3. The reduction of chloroform takes place according to the following reaction formula:

$$CHCl_3 + 3H_2 \rightarrow CH_4 + 3H^+ + 3Cl^- \qquad (1)$$

Although the conversion of the halogenated product is slower than the reduction of the nitrate, it is possible to arrive to complete dehalogenation of the chloroform with parallel formation of Cl^- and methane. The change of the conversion of chloroform indicates that there is no inhibition of the catalyst activity by the Cl^- ions formed during the reaction. The total amount of Cl^- formed suggests that no or negligible Cl_2 forms and that the amount of Cl^- ions which react with the catalyst (Pd) or the membrane is also negligible, although further studies are necessary to confirm this aspect. Further experiments using other chlorinated hydrocarbons (tetrachloromethane, trichloroethene and tetrachloroethene) in the presence of nitrate confirmed the applicability of the methodology and the simultaneous reduction of nitrate and dehalogenation of the hydrocarbon. Preliminary tests using pesticides (Atracine, Duron) evidence the applicability of the method also to this class of substances.

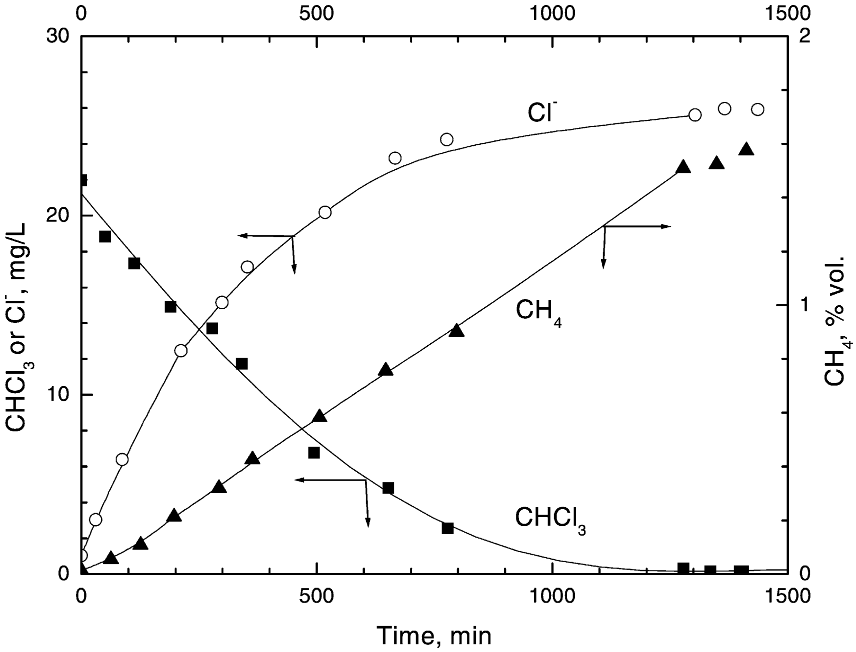

Fig. 3. Conversion of chloroform ($CHCl_3$) and formation of Cl^- ions and CH_4 during the catalytic reduction of $CHCl_3$ over a Pd/Alumina membrane (total amount Pd over the membrane, 15 mg). Batch 1 l stirred-tank reactor (750 ml reaction volume), pure H_2 flowing through the membrane, temperature of reaction 20 °C.

3.3. Synthesis of H_2O_2 from a $H_2 + O_2$ mixture

Pd-based membrane can be used also for the synthesis of H_2O_2 from H_2 and O_2, as outlined in Fig. 1c. The main advantages of the tubular inorganic catalytic membrane (TICM) reactor in the synthesis of H_2O_2 are the following:

- Intrinsically safe operation, because there is no direct contact between the oxidant (only O_2-presaturated-solution is fed to the reactor, avoiding thus the possibility to have zones in the reactor where gaseous mixtures inside the explosion limits can be formed) and the reductant (H_2). Small amounts of O_2 may be cofed with H_2 in order to increase productivity to hydrogen peroxide as indicated in Fig. 1c, but keeping O_2 concentration outside the explosion limits.
- The Pd surface is maintained in a reduced state. Due to the higher solubility of O_2 in water with respect to H_2, Pd tends to be oxidised with a considerably lowering of the catalytic performances. Instead in TICM reactor, the catalyst is at the interface between gas and liquid and it is thus possible to avoid oxidation of Pd.
- Minimal diffusion problems (negative for effectiveness of H_2O_2 synthesis) due to the presence of a thin film where the catalytically active element is deposited.
- Lower operation pressures, because there is an optimal contact between hydrogen (when the solution is saturated by both O_2 and H_2, the latter results to be less soluble and determines the overall effectiveness of the process; in the TICM reactor case, hydrogen diffuses at the H_2/water interface localised directly near the catalytic Pd particle surface and thus local pseudo-supersaturation conditions are possible), oxygen and the catalyst.
- The relatively simple process line-up should enable facile scaling of the process.

Reported in Fig. 4 are some preliminary results in the synthesis of H_2O_2 from $H_2 + O_2$ over a Pd/carbon/alumina membrane. As indicated before, the carbon coating of the ceramic membrane is useful to reduce H_2O_2 decomposition. The catalytic

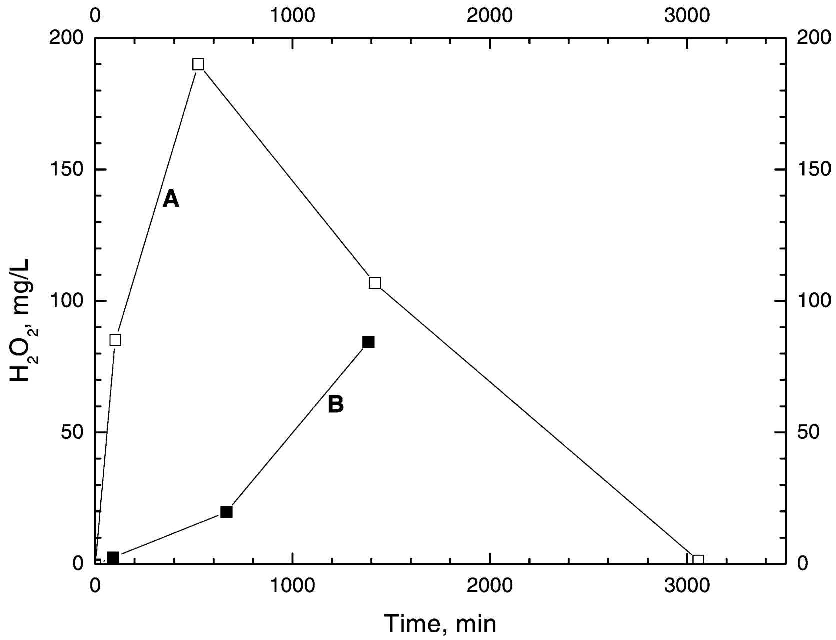

Fig. 4. Synthesis of H_2O_2 from $H_2 + O_2$ at room temperature over a Pd/carbon/alumina catalytic membrane (see text). (A) The solution is presaturated with oxygen at 5 bar and then (after stopping O_2 feed) H_2-only is fed into the catalytic membrane at 8 bar. (B) Both H_2 and O_2 (1:1) are cofed through the catalytic membrane (pressure: 5 bar).

membrane was prepared by coating of a α-alumina membrane (100 nm pores) with a carbon film by applying a furfuryl alcohol resin on the alumina membrane and by a further controlled pyrolisis. The active component (Pd) was deposited on this carbon film with the MOCVD method (see Section 2). Tests were made at room temperature in deionized water containing 2.8 g/l of 98% H_2SO_4 and 6 mg/l NaBr, according to example 1 of the patent [18b]. A 1 l batch-type stirred-tank membrane reactor was used; the H_2O_2 concentration was measured with $KMnO_4$-titration method.

Data in Fig. 4 refer to two types of experiments, both made at room temperature. The case A is when the solution is presaturated with oxygen at 5 bar and then (after stopping O_2 feed) only H_2 is fed into the catalytic membrane at 8 bar. The case B is instead when both H_2 and O_2 (1:1) are cofed through the catalytic membrane (pressure: 5 bar). The case B corresponds to the situation reported in the patents [18] where a mixture of $H_2 + O_2$ is send to the reactor containing the catalyst and the solvent, although for a better comparison with the case A, the feed is passed through the membrane. The case A corresponds instead to the situation of application of the catalytic membrane where O_2 is present only dissolved in solution and H_2 is fed through the membrane. As indicated before, this configuration is the preferable for safety reasons. However, as indicated in Fig. 4, this situation corresponds also to an about one order of magnitude increase in the reaction rate, due to the better multiphase contact between the reactants and the catalyst. For longer times, the formation of H_2O_2 decreases due to the full consumption of the O_2 dissolved in water and the consecutive decomposition of H_2O_2. Probably the optimisation of both the catalyst composition and of the solvent will allow minimising this decomposition reaction and thus enabling a further increase of the reaction rate.

4. Conclusions

Tubular inorganic catalytic membrane reactors are a novel multiphase solution for advanced chemical or environmental technologies which offer interesting prospects for the development of new catalytic technologies. Two types of applications were discussed: (i) water remediation technologies by catalytic hydrogenation (nitrate removal and chlorinated hydrocarbon dehalogenation) and (ii) H_2O_2 synthesis by $H_2 + O_2$ reaction, both occurring over Pd-type catalysts supported over porous inorganic membranes. Some examples were given of the behaviour of these catalytic membranes in long-term tests in nitrate reduction, in chloroform dehalogenation and in H_2O_2 synthesis. The results indicate the advantages of the use of this type of structured reactor and the good prospects for their application, although further studies are necessary to explore more systematically their advantages and limitations and determine general guidelines helping to identify when their use should be considered, even though the general higher cost of this solution with respect to conventional-type multiphase reactors.

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