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Direct synthesis of hydrogen peroxide in a catalytic membrane contactor

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Abstract

Asymmetric porous alumina membranes with palladium nanoparticles deposited into the thin surface layer are used as a structured catalyst to perform the direct synthesis of hydrogen peroxide with separate supply of the reactants in a catalytic membrane contactor. Parameters such as mode of supply of the gaseous species, type of liquid medium used, as well as differential and liquid side pressure, have been investigated and their influence on the productivity and selectivity of the reaction is discussed. The presented concept, which targets local hydrogen peroxide production, offers improved safety of the process compared to conventional methods for direct synthesis described in the literature. By optimization of the reactant supply, high productivity (up to 16.8 mol h^{-1} m^{-2} in methanol) and high selectivity (between 80% and 90%) to hydrogen peroxide could be demonstrated in this reaction for the first time with catalytic membranes.

Keywords: Catalytic membrane; Direct synthesis; Hydrogen peroxide; Membrane contactor; Palladium

1. Introduction

As an environmentally friendly oxidant H_2O_2 finds application in many industrial areas. Today it is mainly consumed for bleaching of paper and textiles and for detoxification of wastewater [1–3]. Of growing interest is the use of H_2O_2 as selective oxidant, e.g. for the manufacture of fine chemicals. Limitation, however, comes from its high price resulting from the complicated industrial production of H_2O_2 according to the dominating "anthraquinone method" [1,2] which uses an expensive and complex solvent system and is economically viable only for large-scale production units (>40 kt $year^{-1}$). The direct synthesis of H_2O_2 from O_2 and H_2 is an attractive alternative, which has been investigated for decades already [4–11]. However, due to problems related to safety and selectivity, this process as yet is not used on a commercial scale, although this might change in the near future [12].

The safety issue in the direct synthesis of H_2O_2 comes from the fact that H_2/O_2 mixtures are explosive over a very wide range of hydrogen concentrations (4–75 mol% in air, 4–94 mol% in oxygen at 1 atm pressure), which makes the task of designing a safe process a challenge. The second problem, i.e. low selectivity, is caused by the fact that materials catalyzing the formation of hydrogen peroxide (Fig. 1, reaction 1) in general are also active for its decomposition (Fig. 1, reactions 3 and 4) and for the parallel formation of water (Fig. 1, reaction 2).

A large number of studies on direct synthesis of H_2O_2 in recent years addressed these problems [13–29]. One possible process design relies on liquid phase oxidation of H_2 over supported catalysts [13,15–19,21–24,28,29]. Pd qualifies as the best catalytic material so far [15,17,19–21,23,24,28]. Au-catalysts [16,18] and bimetallic Pd/X-catalysts (X = Au, Pt, Ag, Ir) [13,14,16,22,24,29] were also investigated. Apart from the size of the metal particles, the oxidation state of the active material was identified as one of the crucial factors determining the performance. Some authors [19,21] reported that the reduced form Pd^0 is required for an effective production of hydrogen peroxide, whereas in other works [15,23,24,28] the oxidized form PdO was shown to offer higher activity and selectivity to H_2O_2. The combination of Pd with Au [13,16,22,29], Ir [13], and Pt [24,29] to bimetallic catalysts improves the catalytic performance, as does the addition of promoters (halide anions, sulfate anions) either to the reaction medium [17,19,21,28] or to the support [15,28]. The support itself also influences the performance of the catalyst. Some of the materials evaluated (CeO_2, Ga_2O_3, ThO_2, Y_2O_3, Fe_2O_3) were found to accelerate the decomposition of H_2O_2 [15,19,24]. The most commonly used supports are alumina, zirconia, and silica [15,19,21,23,24]. Furthermore, the reaction medium plays a significant role. Since the reaction takes place in the liquid phase, the solubility of the gaseous reactants is

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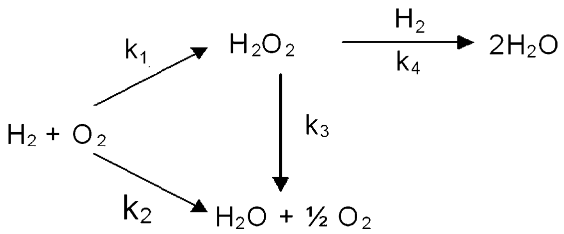

Fig. 1. Simplified reaction scheme of direct synthesis of H_2O_2.

a decisive factor for the overall reaction rate. Therefore, organic solvents or additives to the liquid phase (e.g. methanol [19,23]), in which hydrogen and oxygen show improved solubility, are preferred [19]. High pressure is also used to enhance the solubility, the formation rate, and the ultimate yield of H_2O_2 [17] affecting, however, the safety of the process. Recently, Degussa announced the start of a demonstration plant for direct synthesis of H_2O_2 based on supported catalysts [12], but as yet the safety issue stands against a wider use of this approach in industry.

To avoid direct contact of hydrogen and oxygen in the gas phase, the introduction of one of the reactants through a membrane has been suggested [14,20,25–27]. This process design was first described in the work of Choudhary at al. [14], who proposed a composite multi-layered catalyst. A tubular membrane support from Al_2O_3 was coated with a dense Pd/Ag alloy film permeable to hydrogen only. This film was further coated with a thin layer of Pd which was surface-oxidized to PdO, as it was found that this leads to higher selectivity to H_2O_2. Finally, the PdO catalyst was coated with a thin hydrophobic polymer layer to prevent decomposition of already formed H_2O_2 by subsequent contact with the active surface. Gaseous H_2 (pressure 2.4 bar) was fed to the catalyst from the support side of the Al_2O_3 membrane while O_2 (pressure 1 bar) was supplied dissolved in the aqueous reaction medium in contact with the hydrophobic polymer layer. The hydrogen atoms diffusing through the Pd alloy membrane react with the oxygen on the surface of the oxidized Pd film to form H_2O_2, which is then absorbed by the liquid reaction medium. A well-known problem observed with pure Pd membranes instead of a Pd/Ag alloy is the loss of permselectivity for H_2 due to the formation of the brittle β-Pd hydride phase in presence of H_2 at temperatures below 300 °C.

A major drawback of this catalyst design, however, comes from the slow diffusion of hydrogen through the dense Pd/Ag and Pd layer limiting the overall rate of the process and leading to low productivity. Within the range of experimental conditions covered, the maximum productivity per unit membrane area reached 62 $\text{mmol h}^{-1}\text{ m}^{-2}$, the productivity per gram of Pd 1.5 $\text{mmol h}^{-1}\text{ g}^{-1}$. The selectivity varied between 40% and 70%. Even if one considers the low pressure applied in this study, the performance of this membrane catalyst is rather poor compared to the typical H_2O_2 productivity obtained with conventional supported catalysts, e.g. 8.5 $\text{mol h}^{-1}\text{ g}^{-1}$ for a Pd/Al_2O_3 catalyst at 80 bar and 25 °C [19]. The poor utilization of the Pd is a consequence of the fact that only a minor part of it participates in the reaction while most of the Pd is used as a membrane for dosing of hydrogen.

2. The concept

The concept of a porous catalytic membrane contactor ("catalytic diffuser" [20,30–32]) was applied in this work to direct synthesis of hydrogen peroxide, offering a solution to the problem of poor Pd utilization while keeping the safety benefit of separation of the two gaseous reactants (Fig. 2). It relies on an asymmetric porous ceramic membrane. For our studies, tubular membranes with the fine-porous layer on the outside of the tubes were used. The catalyst is deposited only into the pores of the fine-porous surface layer. The gaseous reactants hydrogen and oxygen are supplied separately: one is fed from the coarse-porous support side, the other, dissolved in the liquid, from the side of the fine-porous layer. The liquid reaction medium wets the membrane, i.e. it penetrates into the pores. By applying overpressure on the gas side, the gas/liquid phase boundary is established inside the membrane close to the transition from the coarse-porous support to the fine-porous catalytic layer.

This concept was first proposed for direct synthesis of H_2O_2 in a research project funded by the European Commission [20]. Some of the results of this project were already reported [25–27]. For example, Abate et al. [25,26] and Melada et al. [27] describe a catalytic membrane with a multi-layered structure similar to that used by Choudhary et al. [14], but with the important difference that the Pd layer was porous. They confirmed the limitations discussed above, i.e. instability of a pure Pd catalytic membrane layer in presence of H_2 due to the formation of Pd hydride, and poor productivity per gram of Pd caused mainly by the high Pd loading and also by the limited diffusion rate of H_2 through the Pd layer [25,26]. Other parameters investigated to improve the performance of the catalytic membranes include the use of bimetallic catalysts (Pd/X, X = Ag, Pt) [25–27], the modification of the ceramic support by coating of a porous carbon layer on the membrane surface or inside the pores [26,27], the use of

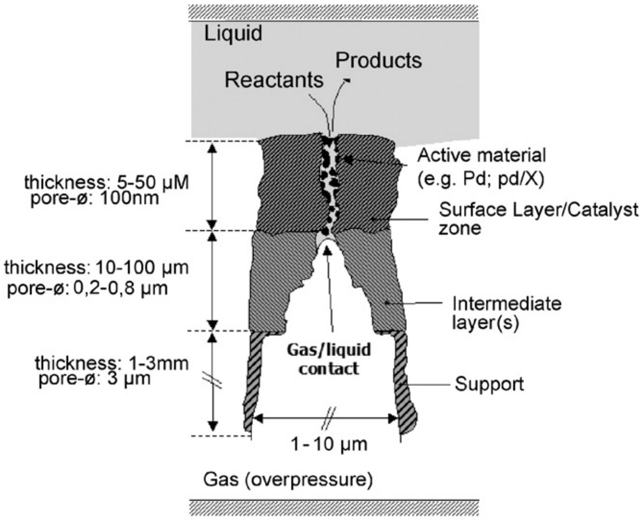

Fig. 2. Schematic representation of the catalytic diffuser concept [31] relying on the asymmetric structure of the membrane—a coarse-porous support, one or more intermediate layers with decreasing pore diameter and a thin fine-porous surface layer with the catalyst incorporated in highly dispersed form.

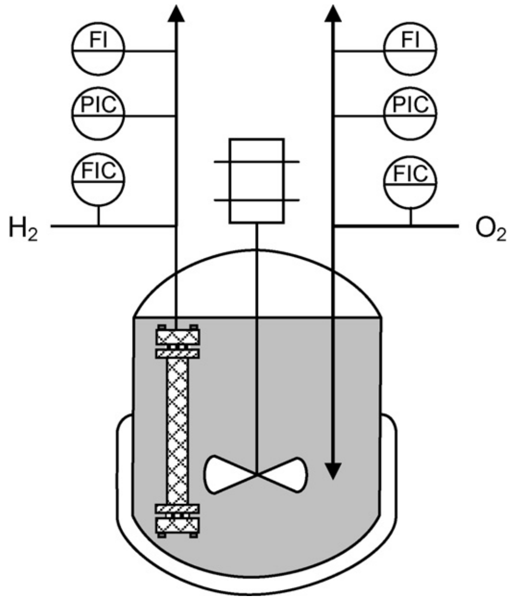

Fig. 3. Schematic representation of the experimental set-up for direct synthesis of H_2O_2 in a catalytic membrane contactor.

methanol as reaction medium [27], and the presence of Br^- as promoter [27].

However, all experiments using catalytic membranes for direct synthesis of H_2O_2 so far reported were performed at atmospheric or slightly increased liquid pressure (O_2 supply side) [25–27] and up to 8 bar H_2 gas side pressure at most [14,20].

We present here an overview of the results of our investigations at liquid pressures up to 69 bar and with different configurations for the supply of the reactants, aiming at high selectivity and high productivity for H_2O_2 as required for a practical implementation of the new technology.

3. Experimental

The direct synthesis of H_2O_2 from H_2 and O_2 was performed in a lab-scale autoclave (Parr Instruments, 5100 Series, capacity, 1.5 L, designed for up to 70 bar) operated in semi-batch mode (Fig. 3) with tubular asymmetric membranes ($d_{out} = 10$ mm, $d_{in} = 7$ mm, $l = 100$ mm) with a fine-porous α-Al_2O_3 ($d_{pore} = 100$ nm) layer on the outside. Table 1 provides details on the mean pore size and the thickness of the various layers of the ceramic membranes.

Dispersed monometallic Pd served as the active material. It was deposited specifically in the fine-porous layer on the outside of the membrane tube by means of wax-assisted metal organic chemical vapor deposition (MOCVD) [32,33]. Through the use of an organic wax acting as a solubilizing agent, this method reaches high Pd loadings also on inert materials such as low-surface-area α-alumina.

Table 1
Details of the asymmetric structure of the membrane tubes

Layer	Pore diameter [μm]	Thickness [μm]	Material
Support	3	ca. 1600	α-Al_2O_3
Intermediate	0.8–0.2	ca. 30	α-Al_2O_3
Surface	0.1	ca. 20	α-Al_2O_3

By controlling the amount of the wax applied to the membrane surface prior to the MOCVD, the deposition depth of the Pd into the porous structure can be controlled. The method yields uniform Pd loading over the whole surface of the tube. The size of the Pd nanoparticles has been determined by TEM, XRD, and CO chemisorption in the range of 5–15 nm. The particles are firmly anchored on the support. No leaching could be detected by analysis of the reaction mixture for dissolved Pd with atomic absorption spectroscopy.

The prepared catalytic membranes were immersed in the liquid reaction mixture in the autoclave through a holder, connecting the membrane to the gas supply line. Details on the mixture composition are as follows—volume of the liquid phase: 1.2 L; stabilizer (H_2SO_4): 1×10^{-2} mol L^{-1}; promoter (NaBr): 8 mg L^{-1}; stirring frequency: 800 rpm; solvent: H_2O, MeOH and mixtures thereof. The stabilizer and the promoter as well as its concentrations were chosen based on information from the literature [17,19,21].

To perform the process one of the gaseous reactants (hydrogen or oxygen) was fed through the membrane compartment, maintaining its desired pressure with a backpressure controller installed in the exit line. Its overpressure was set above the bubble point of the membrane support and below the bubble point of the fine-porous layer to avoid excess of reactant being introduced into the liquid in the form of gas bubbles. The other reactant was saturated in the liquid medium by continuously feeding it through the reactor headspace while stirring the liquid with an impeller. Its pressure was controlled by a second backpressure controller installed in the reactor exit line.

During the course of the reaction liquid samples were withdrawn from the reactor through a bottom valve in regular time intervals for product analysis. H_2O_2 concentrations were measured by volumetric permanganate titration. In case of pure methanol as solvent, H_2O was determined by Karl-Fischer titration.

The selectivity to H_2O_2 was calculated from the measured concentrations according to Eq. (1).

$$S(t) = \frac{c_{H_2O_2}(t)}{c_{H_2O_2}(t) + c_{H_2O}(t)} \tag{1}$$

For experiments with water or mixtures of methanol and water as solvent, the amount of H_2O formed by the reaction could not be measured accurately. Therefore, the selectivity to H_2O_2 was determined from the concentration of H_2O_2 and the consumption rate of hydrogen, which was integrated over time—Eq. (2) (V_L denotes the liquid volume in the reactor). The H_2 consumption rate was derived from the H_2 flow rates recorded by mass flow meters installed in the H_2 supply and membrane compartment exit lines, respectively.

$$S(t) = \frac{V_L c_{H_2O_2}(t)}{\int_0^t (\dot{n}_{H_2}^{in}(t) - \dot{n}_{H_2}^{out}(t))dt} \tag{2}$$

4. Results and discussion

The first experiments for direct synthesis of H_2O_2 were performed by saturating the liquid medium with O_2 and dosing H_2 from the gas phase directly into the catalytic layer. This way of supplying the reactants was chosen to render H_2 the limiting reactant. In that case high selectivity to H_2O_2 is expected from the simplified reaction scheme shown in Fig. 1. For this way of reactant supply all important process parameters were varied.

For constant differential pressure of 5 bar the influence of the liquid pressure on the H_2O_2 formation rate is shown in Fig. 4 by example of a series of experiments carried out at 10, 20, and 30 bar with a membrane having a Pd loading of ca. 5.5 mg (determined from the weight increase after Pd deposition), solvent water and temperature, 20 °C. The increase of the liquid pressure leads to a distinct increase of the H_2O_2 formation rate as a consequence of the increased concentration of the gaseous reactants in the liquid phase. Moreover, the H_2O_2 concentration profiles tend to become more linear at higher pressure, which indicates a decrease of the relative rate of decomposition of H_2O_2 as compared to its formation rate. In turn, the maximum attainable concentration of H_2O_2 becomes higher. If one assumes that the reaction rate is first order with respect to both hydrogen and oxygen, doubling of the liquid pressure should theoretically lead to a fourfold increase of the H_2O_2 formation rate. The experimentally observed increase is less pronounced, which could be explained either by mass transfer limitation of the gaseous reactants in the catalytic layer or by adsorption phenomena (i.e. saturation of the active surface with H_2 or O_2 at higher pressure) producing a more complex concentration dependency of the rate equation.

Experiments at constant gas pressure of 69 bar and varying differential pressure from 4 to 12 bar did not show a pronounced effect on the H_2O_2 formation rate. This is attributed to a compensation of various controversial effects: an increase of the H_2 mass transfer rate is expected for higher differential pressure whereas the decrease of the liquid pressure leads to a reduction of the concentration of dissolved O_2. Mass transfer experiments in which water filled in the autoclave was saturated either with H_2 or O_2 by gas diffusion through the membrane allowed to estimate the thickness of the liquid-filled region as a function of the differential pressure. The relationship between the thickness of the liquid-filled region and the differential pressure is depicted in Fig. 5. The film thickness decreases with increasing pressure from ca. 37 µm at 5 bar to ca. 22 µm at 12 bar. The pore sizes obtained from the Laplace equation for a contact angle of $\alpha = 0°$ (complete wetting) and the surface tension for water at 25 °C ($\sigma_L = 0.072\,\mathrm{Nm^{-1}}$) are also indicated in Fig. 5. By electron probe microanalysis (EPMA) of the Pd distribution over the membrane cross-section it was found that the region where Pd is deposited extends over ca. 40 µm from the external surface of the membrane inwards. One can therefore conclude that with increasing differential pressure less and less Pd participates in the reaction, and consequently the effective reaction rate does not benefit from the increased driving force for hydrogen mass transfer.

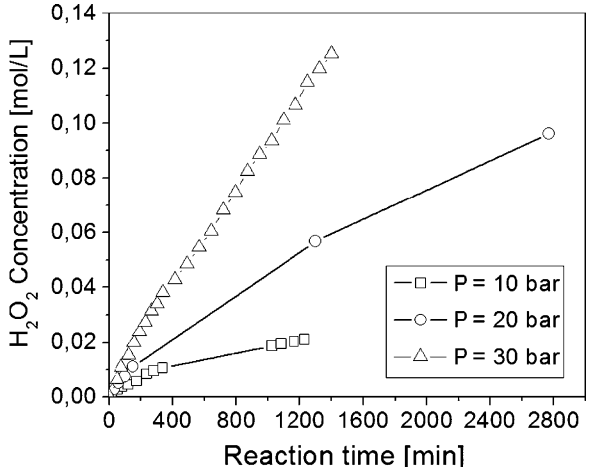

Fig. 4. Influence of the liquid pressure on direct synthesis of H_2O_2. Conditions: $P_{gas} = P_{liquid} + \Delta p$; $\Delta p = 5$ bar; $T = 20\,°C$; H_2O as solvent, Pd loading 5.5 mg.

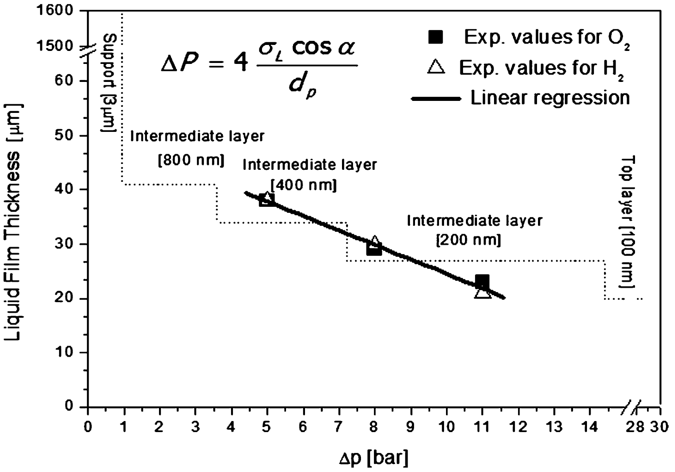

Fig. 5. Thickness of the liquid-filled region inside the membrane vs. the differential pressure. Derived from mass transfer measurements with H_2 and O_2 with different membranes at $T = 20\,°C$.

The effect of the solvent was also studied. Fig. 6 shows a comparison of results obtained with similar membranes for water and methanol as the solvent. Clearly, methanol is the preferred solvent as it leads to much higher H_2O_2 productivity (Fig. 6a). Two factors are responsible for the increased performance: the solubility of hydrogen and oxygen is about 6–10 times higher in methanol than in water, and the diffusivity of the gases in methanol is higher by a factor of ca. 5 compared to water. Both lead to an increased concentration of the gaseous reactants within the catalytic layer. Unfortunately, not only the formation of H_2O_2 is accelerated, but also the formation of the undesired by-product water as evident from Fig. 6b.

Table 2 lists the H_2O_2 concentrations obtained after a reaction time of 1000 min in a series of experiments with mixtures of methanol and water as solvent. The productivity of H_2O_2 per unit membrane area is given as well. The experiments were performed at 69 bar and 20 °C with a membrane containing 23.6 mg of Pd (determined by atomic absorption spectroscopy after dissolution of the Pd with concentrated hydrochloric acid). With pure methanol the highest productivity was reached, i.e.

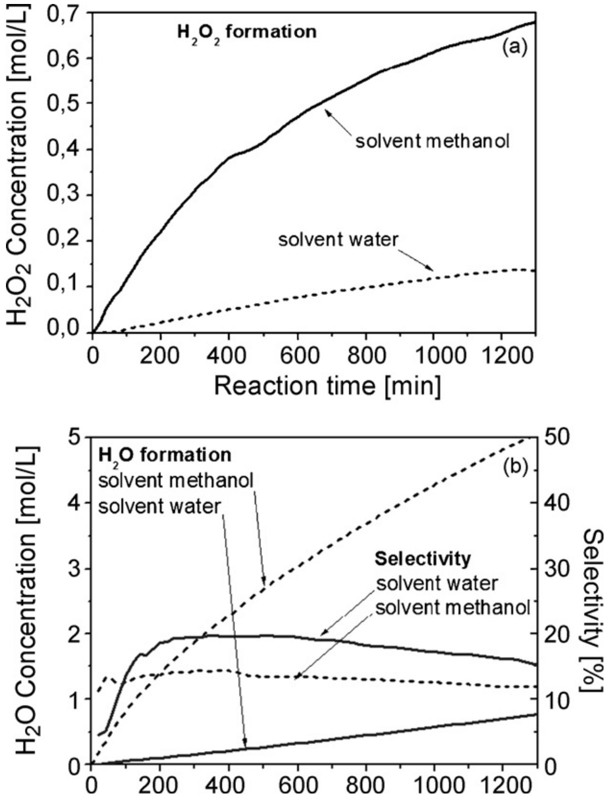

Fig. 6. Influence of the solvent (water and methanol): (a) on H_2O_2-formation and (b) on H_2O-formation (left y-axis) and on the selectivity to H_2O_2 (right y-axis). $T = 20\,°C$; $P_{gas} = 69$ bar; $P_{liquid} = 63$ bar (water) or 66 bar (methanol); Pd loading 23.6 mg.

$16.8\,mol\,h^{-1}\,m^{-2}$. Compared to the results for pure water, i.e. $2.0\,mol\,h^{-1}\,m^{-2}$, this corresponds to an eightfold increase. The productivity per gram of Pd reached $1.65\,mol\,h^{-1}\,g^{-1}$ for the case of pure methanol.

In order to understand the unexpectedly low selectivity to H_2O_2 (Fig. 6b), the concentration profiles of the reactants in the catalytic layer were analyzed in detail through mathematical modeling of mass transfer and reaction in this region based on the reaction kinetics derived from the experimental data. The general shape of the concentration profiles for H_2 and O_2 expected for the experimental conditions applied (i.e. undiluted H_2 and O_2) is shown in Fig. 7. H_2 reaches the highest concentration at the phase boundary, where we assume equilibrium between the H_2 pressure in the gas inside the membrane and the concentration of dissolved H_2 ($c^*_{H_2}$) in the liquid according to Henry's law. O_2 is introduced via the liquid phase, which is continuously re-saturated with O_2 in the autoclave. We can therefore expect equilibrium between the O_2 pressure in the headspace and the concentration of dissolved O_2 ($c_{O_2,L}$) in the solvent. The highest concentration of O_2 in the catalytic layer prevails at the side opposing the gas/liquid phase boundary, i.e. at the external surface of the tube. Hence, due to the consumption of the reactants inside the catalytic layer, opposing concentration profiles for the reactants are observed. From literature it is known that the selectivity depends on the concentration ratio of O_2 versus H_2. More specifically, for the conventional process with slurry catalysts it is reported that a molar ratio of O_2 versus H_2 of 2 or higher is required for high selectivity to H_2O_2 [21,23,27]. Fig. 7 shows, that this is not the case within the shaded area. Contrary to a conventional slurry reactor where the O_2 to H_2 concentration ratio inside the catalyst particles is always equal or higher than the value at the external surface due to the stoichiometry of the reaction, in the catalytic diffuser operated with undiluted reactants we face a severe change of this ratio over the reaction zone. Consequently, we must assume that the catalytic properties will also change over the reaction zone, i.e. low selectivity to H_2O_2 is expected within the shaded area.

Table 2
Comparison of the productivities of H_2O_2 obtained with mixtures of water and methanol as solvent

Solvent	H_2O_2 concentration after 1000 min [$mol\,l^{-1}$]	H_2O_2 Productivity per membrane area [$mol\,m^{-2}\,h^{-1}$]
MeOH	0.690	16.8
MeOH/H_2O (80/20)	0.402	9.7
MeOH/H_2O (70/30)	0.186	4.5
MeOH/H_2O (50/50)	0.139	3.4
Water	0.0817	2.0

$T = 20\,°C$; $P_{gas} = 69$ bar; $P_{liquid} = 64$–67 bar; Pd loading 23.6 mg.

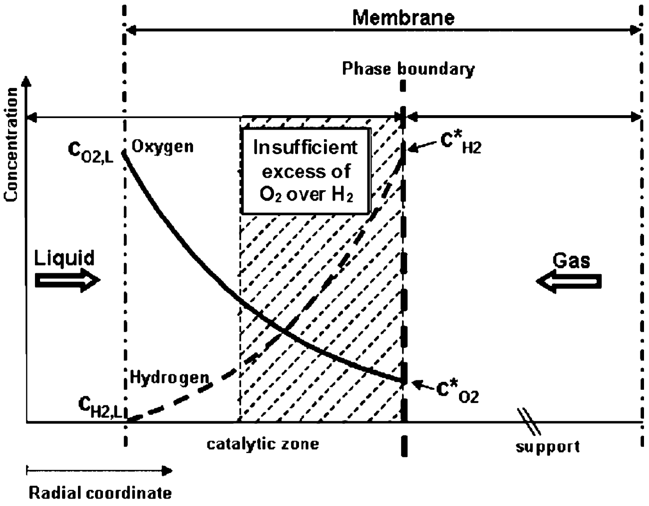

Fig. 7. Concentration profiles of H_2 (dashed line) and O_2 (solid line) within the catalytic zone: $c_{O_2,L}$ and $c_{H_2,L}$ denote the concentrations in the liquid bulk; $c^*_{O_2}$ and $c^*_{H_2}$ denote the concentrations at the phase boundary.

A second problem is associated with the particular mode of operation chosen: the target for catalyst preparation is to deposit the Pd exclusively within the fine-porous top layer of the asymmetric membrane. However, the preparation technique is not absolutely perfect. In practice a minor amount of Pd is always found deeper inside the support. If the O_2 in the liquid is not completely consumed within the catalytic layer, there will be a finite concentration of O_2 ($c^*_{O_2}$) at the gas/liquid phase boundary. This means that a certain amount of O_2 escapes to the gas phase inside the membrane where it will react with H_2 to water if Pd is present in the dry part of the membrane. This further decreases the selectivity.

However, the problems discussed above can be overcome by a smarter reactant supply ("reversed mode"): O_2 is supplied from

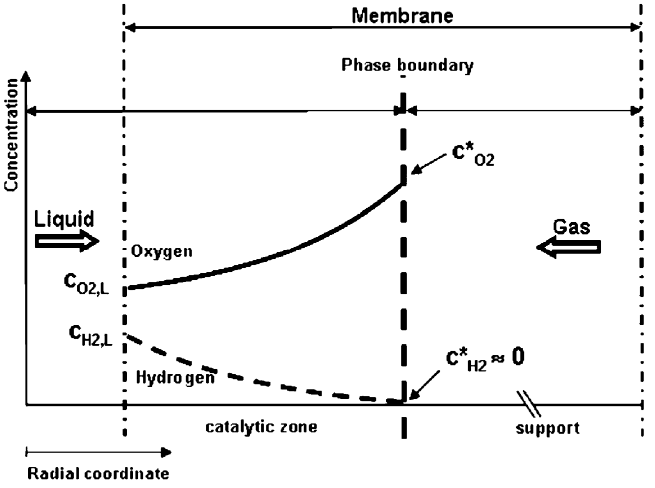

Fig. 8. Concentration profiles of H_2 and O_2 within the catalytic zone for the "reversed mode". $c_{O_2,L}$ and $c_{H_2,L}$ denote the concentrations in the liquid bulk, $c^*_{O_2}$ and $c^*_{H_2}$ those at the phase boundary.

the dry part of the membrane, i.e. from the support side, while diluted H_2 is introduced to the liquid phase. The general shape of the concentration profiles within the catalytic zone for these conditions is shown in Fig. 8. By dilution with N_2 the partial pressure of H_2 in the reactor headspace is set approximately to one third of the equilibrium concentration of dissolved O_2 corresponding to the O_2 pressure inside the membrane. Due to the stoichiometry of the reaction, which consumes at most 1 mole of O_2 per mole of H_2, this guarantees that the molar ratio of O_2 versus H_2 remains above the critical value of 2 everywhere in the reaction zone. Simulation shows that for the typical Pd loadings applied, the reaction is fast enough to completely convert the hydrogen within the catalytic layer, so that no H_2 escapes to the dry part of the membrane.

An experimental proof of the results of the theoretical analysis is provided in Fig. 9. In this experiment a membrane with a Pd loading of ca. 8 mg was used in the "reversed mode" with supply of pure O_2 through the membrane and partial saturation of the liquid with H_2. Pure methanol served as the solvent. The O_2 pressure inside the membrane was set to 67.2 bar, the H_2 partial pressure in the reactor headspace was 5.8 bar and the differential pressure over the membrane 3 bar. The selectivity to H_2O_2 decreased slowly from approximately 90% in the beginning of the reaction to about 82% after 20 h, when the H_2O_2 concentration in the liquid was 0.27 mol L^{-1}. The productivity per unit membrane area was 4.4 mol h^{-1} m^{-2}, and the productivity per gram of Pd reached 1.96 mol h^{-1} g^{-1}.

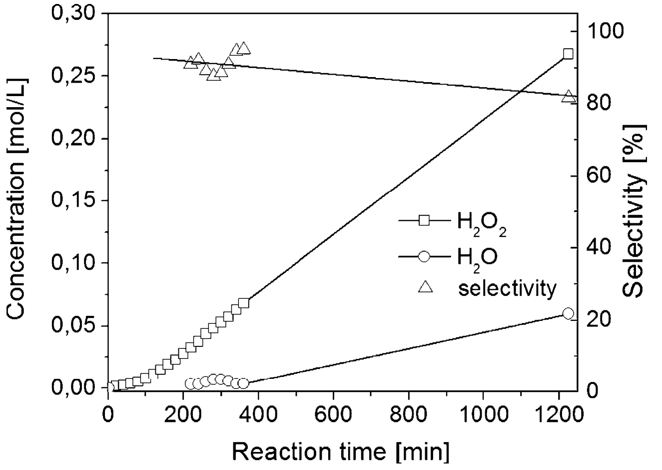

Fig. 9. Direct synthesis of H_2O_2 with supply of pure O_2 through the membrane and partial saturation of the liquid with H_2 ("reversed mode"). Experimental conditions: P_{gas} = 67.2 bar O_2; P_{liquid} = 64.2 bar H_2/N_2 (9/91); T = 20 °C; pure methanol as solvent; Pd loading ca. 8 mg.

For comparison, experiments were performed with 100 mg of a commercial powder catalyst (Heraeus K-0219, 5 wt.% Pd on Al_2O_3, particle size 10–20 μm) dispersed in the liquid phase in the autoclave instead of the immersed catalytic membrane. The conditions were chosen similar to those for the experiment with the catalytic membrane. At 20 °C, a pressure of 69 bar, pure methanol as solvent, and a gas composition of 78% N_2, 15% O_2, and 7% H_2, this catalyst reached a selectivity to H_2O_2 of 82–85% and a productivity per gram of Pd of 6.5 mol h^{-1} g^{-1}.

This higher activity of the slurry catalyst per gram of Pd may be explained mainly as a consequence of its smaller particle size compared to the thickness of the fine-porous catalytic layer in the membrane. This is associated with a lower catalyst efficiency for the membrane due to a longer diffusion path (limitation by pore diffusion). The external surface area per unit volume of the catalyst is also significantly larger for the powder catalyst than for the membrane. For a spherical particle with 15 μm diameter one obtains a value of 4000 cm^{-1}, whereas for a 40 μm thick layer with reactant supply through one side only, the specific surface area is just 250 cm^{-1}. Moreover, due to the different reactant supply, i.e. both reactants together through the external surface in case of dispersed particles versus each reactant separately from opposing sides in case of the membrane, the concentration profiles show different characteristics that influence the effective reaction rate. And finally, the commercial catalyst could have a lower Pd cluster size than the catalytic membrane.

However, it should be emphasized here that fine powder catalysts are much more difficult to operate industrially due to the need to retain the catalyst in the reactor. In that light the observed performance of the catalytic membrane contactor appears very promising.

5. Conclusions

We may summarize that the "catalytic diffuser" concept offers several benefits over traditional supported catalysts for direct synthesis of H_2O_2. It guarantees safe operation of the reaction due to the separate supply of the gaseous reactants. Compared to dense Pd alloy membranes, the H_2 mass transfer limitation is greatly reduced and much higher productivities for H_2O_2 were obtained (up to 16.8 mol h^{-1} m^{-2} in methanol). Through an optimized configuration for the reactant supply, high selectivity to H_2O_2 between 80% and 90% could also be demonstrated. It is expected that the performance of the catalytic membrane contactor can be further improved through optimization of the membrane properties, the nature of the active phase, the catalyst loading and dispersion, as well as the process conditions. These issues are dealt with in a current research project targeted at the development of a continuous process for local H_2O_2 production based on the new technology.

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