Development of an inherently safe, cost-efficient and flexible process for direct synthesis of hydrogen peroxide from hydrogen and oxygen by means of catalytic membranes

Period: 01. 06. 2006 - 31. 03. 2009

Partner: Hermsdorfer Institut für Technische Keramik e.V. (HITK)

Funder: AiF e.V.

Project Manager: Aneta Pashkova

Research Group: Chemical Technology

1. Aim of the project

The aim of our project is to design a compact system for small-scale on-site hydrogen peroxide production. A continuous process has been developed where hydrogen peroxide is synthesised directly from gaseous hydrogen and oxygen over a Pd-based catalyst in a catalytic membrane contactor. The principle of the contactor and preliminary results for direct synthesis of hydrogen peroxide are described in Refs. [1, 2] moreover, experimental results from the related European research project NEOPS are presented in Ref. [3].

2. Motivation

Hydrogen peroxide is a widely used oxidizing agent in many industrial areas: as a bleaching agent in the textile and paper industry, for detoxification of waste waters and exhaust gases in environmental protection, and for production of peroxo compounds in the chemical industry. It is environmentally harmless (water is the only by-product) and has higher selectivity and activity than molecular oxygen.

Today, hydrogen peroxide is almost exclusively produced according to the so-called "anthraquinone method" (Figure 1). This enables the reaction of hydrogen with atmospheric oxygen to give hydrogen peroxide, with anthraquinone (Q) used as a hydrogen carrier, in four steps:
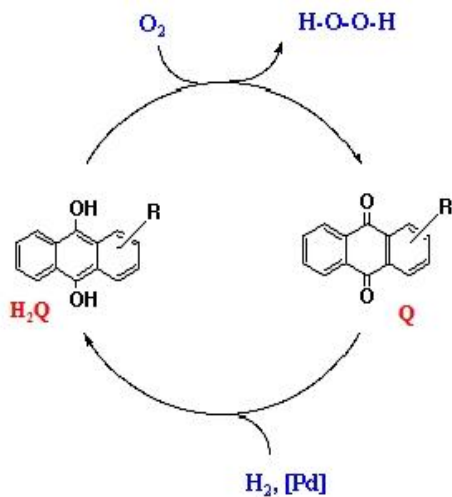
Figure 1: Schematic representation of the "anthraquinone process"

Step 1 Hydrogenation: $Q + H_2 \rightarrow H_2Q$ -.palladium catalyses the reaction between hydrogen and anthraquinone (Q) to form anthrahydroquinone (H_2Q):
Step 2 - Filtration: The palladium catalyst is filtered out of the solution.
Step 3 - Oxidation: $H_2Q + O_2 \rightarrow Q + H_2O_2$ - the solution is oxidised by blowing air through it, forming the hydrogen peroxide
Step 4 - Extraction: The synthesised peroxide is removed in a liquid-liquid extraction column and concentrated by vacuum distillation

This manufacturing method, however, is economically viable only for large-scale production units (ca. 40.000 - 60.000 $t \cdot a^{-1}$) and requires an expensive and complex solvent system. Therefore, the direct synthesis of H_2O_2 from O_2 and H_2 over Pd-catalysts (Figure 2) is an attractive alternative which has been investigated for decades already [4-9]. However, due to drawbacks related to the safety of the process (H_2/O_2 gas mixtures are explosive in a wide concentration range) and to the moderate selectivity (water is the thermodynamically stable product), this process, as yet, is not used on a commercial scale although this might change in the near future [10].
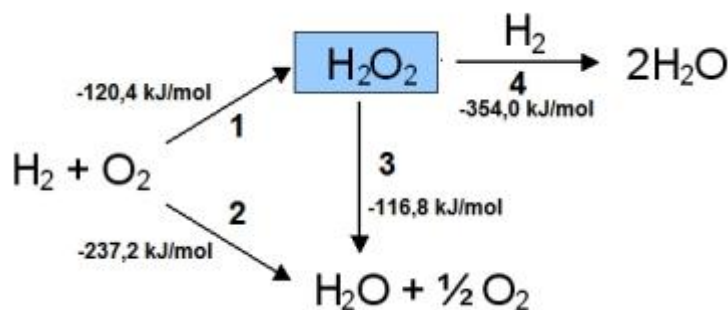

Figure 2: Reaction scheme for direct synthesis of H_2O_2 from H_2 and O_2 over Pd catalysts (reaction 1). The same catalytic material catalyses the formation of H_2O (reaction 2) as well as the decomposition of H_2O_2 to H_2O (reaction 3) or its further hydrogenation (reaction 4).

3. The concept

The direct synthesis of H_2O_2 is performed in a catalytic membrane contactor working based on the principle of a catalytic diffusor (Figure 3). The latter represents an asymmetric tubular ceramic membrane (e.g., from alumina) into which catalytically active material (Pd, Pd/Au, Pd/Ir) is incorporated in highly dispersed form only in the fine-porous surface layer. The reactants are supplied separately on opposite sides of the membrane, i.e., gaseous oxygen on the coarse-porous support side and hydrogen dissolved in a solvent wetting the membrane on the surface-layer side. By applying a controlled overpressure on the gas side, the gas/liquid contact plane is established inside the membrane close to the fine-porous layer with the active catalyst where the reaction takes place. This approach offers advantages over a conventional suspended catalyst in several ways: It guarantees safe operation of the process due to the separated supply of both reactants as well as reduced mass transfer limitations by maintaining a thin catalytic zone. In the same time it allows an efficient contact of the gaseous reactants on the surface of a wetted solid catalyst. It can be scaled up rather easily by employing multichannel tubes or capillary bundles, and it is well suited for small-scale on-site production of H_2O_2 .
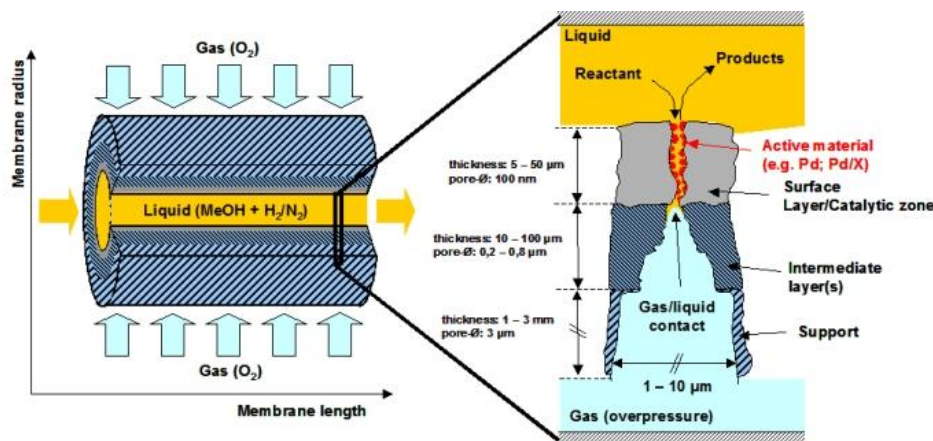

Figure 3: Operating principle of a catalytic diffusor for a solid-catalyzed gas/liquid reaction.

4. Ceramic membranes and coating procedure

The tubular ceramic membranes (TCMs) (Figure 4, Figure 5), which have to be coated on the inside with the active material (Pd, Pd/Au, Pd/Ir), are prepared by our project partner HITK (Hermsdorfer Institut für Technische Keramik e.V.). They represent asymmetric micro-filtration membranes with typical parameters summarized in Table 1. On the SEM picture (Figure 5), the separate layers of the membrane can be very well distinguished.

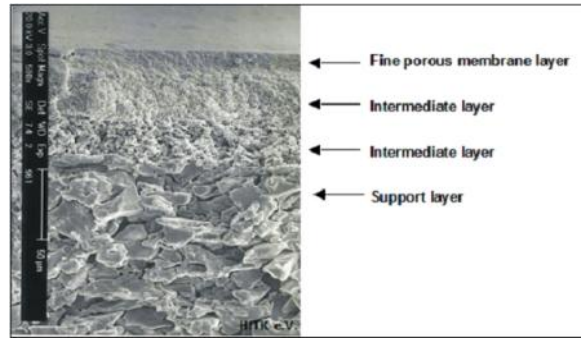**Figure 4: Tubular ceramic membranes (TCMs). Courtesy of HITK e.V.**

Figure 5: Scanning electron micrograph of an asymmetric membrane made of a-alumina. Courtesy of HITK e.V.

Table 1: Typical properties of the different layers of an asymmetric ceramic membrane.

Layer	Pore diameter [µm]	Thickness [µm]	Material
Support	3	~1600	$\alpha\text{-}Al_2O_3$
Intermediate	0.8 – 0.2	~30	$\alpha\text{-}Al_2O_3$
Fine porous	0.1	~20	$\alpha\text{-}Al_2O_3$ or ZrO_2

For deposition of the catalytically active metals into the fine-porous layer on the inside of the membrane tubes, a method based on impregnation/decomposition of Palladium-II-acetate is applied as this has shown advantages for Pd deposition on the inside of thin capillaries and multi-channel tubes.

Description of the method: The desired amount of Palladium-(II)-acetate is dissolved in acetone. The membrane (tube, capillary, multi-channel element) is placed in a stainless steel module (Figure 6), and its ends are sealed with suitable O-rings. The coating solution is charged into the module, wetting the membrane from the outside and gradually filling its pores. Due to the fact that the pore size changes with the membrane radius (asymmetric TCMs), first the bigger pores of the support are occupied and the solution gradually penetrates into the small fine pours membrane layer (pore diameter ca. 100 nm). The membrane is purged with a constant flow of air on the inside in order to evaporate the solvent and to obtain crystalline Pd-acetate, which is then decomposed by heating the membrane up to 250 °C under N_2 atmosphere. As a result, nanocrystals of pure metallic Pd remain on the pore walls.

Due to the described procedure, it is possible to concentrate the catalytic active Pd on purpose in the fine porous layer on the inside of the membrane tube (Figure 7)
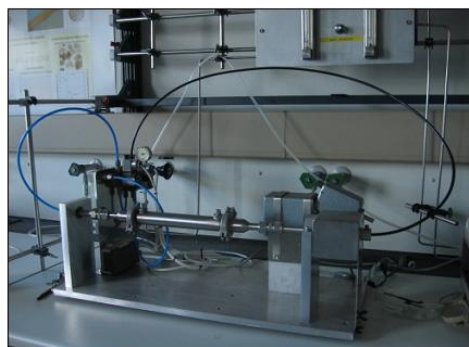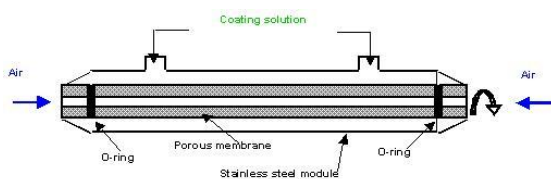
Figure 6: Schematic representation of the experimental set-up for the Pd-(II)-acetate coating method

Figure 7: Seven-channel (left) and single channel (right) membranes coated by impregnation/decomposition of Pd-(II)-acetate.

5. Experimental set-up

The experimental set-up for a continuous process is schematically represented in Figure 8. It consists of two different loops: The key part of the main loop (red straight line) is the membrane module (3) where the reaction takes place. The solvent (e.g., methanol) is saturated with H_2/N_2 in the saturation vessel (1) at up to 70 bars total pressure and then fed on the tube side through the membrane module (3) while wetting the fine porous layer with the catalyst. O_2 is supplied from the shell side of the membrane at a certain overpressure compared to the liquid in order to displace the liquid from the coarse porous support and to adjust the gas/liquid interface near to the thin catalytic zone. A key aspect guaranteeing the safe operation of the process is the adjustment of the flow through the membrane module in such a way that nearly the whole amount of dissolved H_2 is consumed along the length of the membrane due to the reaction. The flow is regulated with the help of a valve (4) and a flow meter (2). After leaving the membrane module (3), the reaction mixture containing dissolved O_2, N_2, eventually H_2, if not completely reacted, and H_2O_2 as well as H_2O as liquid products is expanded to atmospheric pressure with the expansion valve (4). The gas phase is separated from the liquid in the degassing unit (5) and analysed for H_2 / O_2 / N_2 with the help of a micro GC (6). The liquid phase is re-compressed with the help of the recycle pump (7) and sent back into the saturation vessel (1) to enable concentrations of hydrogen peroxide exceeding the limit imposed by the gas solubility.
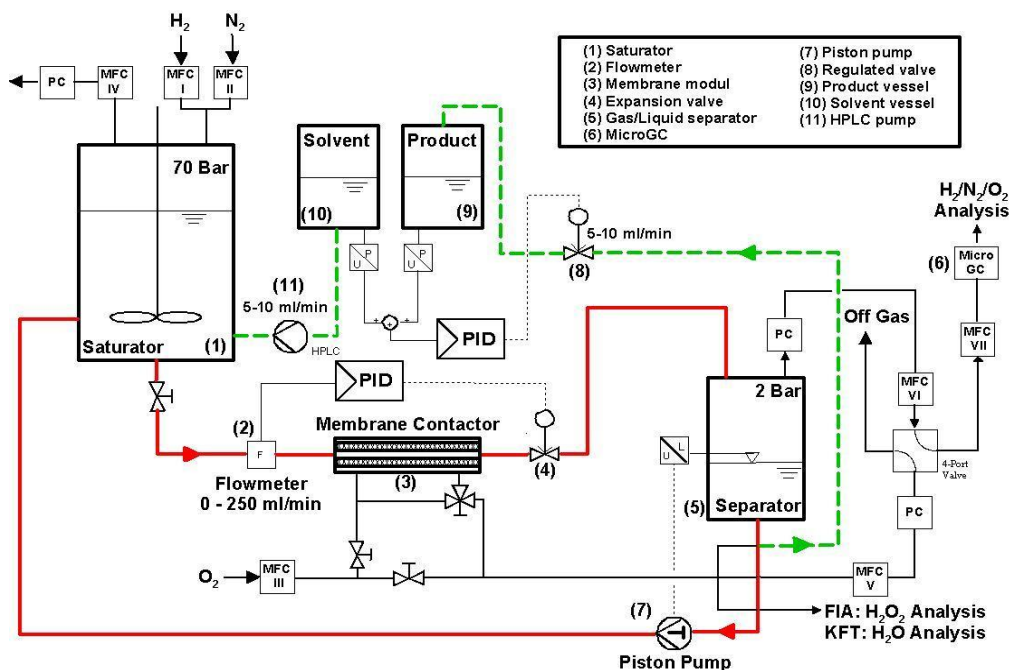
Figure 8: Experimental set-up of a continuously operating system for direct synthesis of H $_2$ O $_2$

The secondary loop (dotted green line) maintains continuous operation by compensating the amount of liquid withdrawn from the system: A certain amount of the liquid flow is taken from the main loop with the help of valve (8) and collected in the product reservoir (9). In order to operate the process continuously, i.e., to keep the liquid level in the saturation vessel (1) constant, from a second reservoir with fresh methanol (10) a corresponding amount of liquid is fed into the pressure vessel with the help of a HPLC pump (11).

6. Results

The experimental set-up for continuous operation has been successfully tested with single channel alumina membranes (dout = 1cm, l = 10 cm). A pressure difference up to 10 bar between the gas phase and the liquid phase in the membrane module was reached and kept stable over several hours of operation. However, the process conditions still have to be optimised in order to obtain technically relevant H2O2 concentrations up to several % w/w.

Parallel to the development of the continuous system different supported catalysts has been prepared, with the same catalytic coating procedure as for the ceramic membranes, and tested for the direct synthesis of hydrogen peroxide. Our aim was to verify if the developed from us coating procedure leads to active catalysts, and to investigate the role of the support on the catalyst performance as well as to identify the most suitable one for the H2O2 direct synthesis. Table 2 summarises the properties of the different catalysts and the type of experiments performed with them. Two different alumina and carbon supports as well as titania were used, coated with different amount of metal. A bimetallic catalyst (Pd/Au on titania) has also been prepared.

Table 2: Summary of the properties of the prepared supported catalysts and the type of experiment performed with them

Catalyst	Support size [μm]	Support BET [m²/g]	Pd particle size [nm]	Experiment type
2%Pd/TiO₂	< 1000	< 10	2,5	Semi-Batch Solvent MeOH
2%Pd/α-Al₂O₃-MJ	315 - 500	16	2,2	
2%Pd/C (StröhleinAK)	< 500	75	19,2	
2%Au2%Pd/TiO₂	< 1000	<10	22,9 (Pd+Au)	
1%Pd/TiO₂-HITK	160 - 250	10,5	1,8	Batch Solvent H₂O
1%Pd/Al₂O₃-HITK	160 - 250	7,8	1,4	
2%Pd/C (Hydraffin23e)	315 - 500	937	5,3	

All semi-batch measurements were performed in a 1,5 L laboratory pressure vessel, which was charged with the solvent (1,2 L methanol, with additives NaBr and H2SO4) and the catalyst, added while stirring the liquid to prevent its gatherng on the bottom of the reactor. The reactor was pressurised with N2 to the desired total pressure (60 to 64 bar). H2 and O2 were premixed in a stainless steel tubing and fed directly in the liquid in the desired ratio (normally H/O/N= 8/27/65). All three gases were constantly supplied through out the whole experiment (7 to 10 hours). The total pressure in the reactor was kept constant with a backpressure regulator mounted in the exit line. Liquid samples were withdrawn on regular time intervals and analysed for the products - water and hydrogen peroxide. With the help of a Matlab kinetic model developed for the H2O2 synthesis, the experimentally observed concentration profiles of the products were fitted in order to obtain the direct formation rate of H2O2 (k1), direct formation rate of H2O (k2) and catalyst activity and selectivity. The results are summarised in Table 3.

Table 3: Semi-batch experiments - results summary

Catalyst	K1,eff [mol L⁻¹ min⁻¹]	K2,eff [mol L⁻¹ min⁻¹]	Activity [gH₂O₂ gPd⁻¹ h⁻¹]	Selectivity to H₂O₂ [%]
2%Pd/TiO₂-HITK	2,51·10⁻⁴	6,69·10⁻⁵	31,67	78,9
2%Pd/α-Al₂O₃-MJ	0	1,15·10⁻⁴	0	0
2%Pd/C (StröhleinAK)	2,18·10⁻⁴	9,90·10⁻⁵	26,54	68,8
2%Au2%Pd/TiO₂	3,08·10⁻⁵	1,87·10⁻⁵	1,92	62,2

The batch experiments were performed in a smaller pressure vessel (600 ml volume), charged with 300 ml solvent (water + additives) and the desired amount of catalyst. The reactor was pressurised first with N2 then with O2 and afterwards with H2 to obtain the desired gas mixture (H/O/N = 3/12/75) at first without stirring the liquid. After reaching the desired total pressure (60 bar) the gas supply valve was closed and the stirrer was started, which marked the start of the reaction. During the experiment the total pressure drop due to the synthesis process was followed. After two hours the measurement was stopped, and the liquid analysed for hydrogen peroxide. Table 4 summarises the results from the batch experiments with solvent water.

Table 4: Batch experiments - results summary

Catalyst	Activity [gH_2O_2 gPd^{-1} h^{-1}]	Selectivity [%]
1% Pd/TiO$_2$-HITK	30,65	69,2
1% Pd/Al$_2$O$_3$-HITK	8,66	47,5
2% Pd/C (Hydraffin 23 e)	2,48	19,4

Comparing the results from both types of experiments we could identify the best catalyst for the reaction at our conditions: Pd dispersed on titania support. Surprisingly one of the alumina catalysts (2%Pd/a-Al2O3-MJ) was inactive to H2O2 and the other one showed a moderate performance. The bimetllic catalyst (2%Au2%Pd/TiO2) showed also low activity and selectivity towards H2O2 although in the literature Au is reported to enhance the effect of Pd and lead to higher H2O2 formation [11].

7.Outlook

Our current work is devoted to optimisation of the reaction conditions in the continuous system in order to achieve higher H2O2 concentrations. This includes preparation not only of alumina, but also of titania catalytic membranes. The stable performance of the system should be also verified with multi channel elements, in order to increase the amount of catalyst and to have higher surface to volume ratio leading to higher productivity.
Finally a techno economical analysis of the process should be performed.

8. References

[1] Centi, R. Dittmeyer, S. Perathoner, M. Reif, Catal. Today, 79-80, 2003, 139.
[2] Dittmeyer, K. Svajda and M. Reif, Top. Catal., 29, 2004, 3.
[3] A. Pashkova, K. Svajda and R. Dittmeyer, Chem. Eng. J., 139, 2008, 165-171.
[4] Y. Izumi, H. Miyazki, S. Kawahara (Tokuyama Soda Kabushiki Kaisha), US Patent 4,009,252, 1977.
[5] W. F. Brill (Halcon), US Patent 4,661,339, 1987.
[6] L. W. Gosser, J.-A. T. Schwarz (DuPont), US Patent 4,832,938, 1989.
[7] L. W. Gosser (DuPont), US Patent 4,889,705, 1989.
[8] B. Bertsch-Frank, I. Hemme, L. Van Hoppel, S. Katusic, J. Rollmann (Degussa-Hüls), US Patent 6,387,346, 2002.
[9] J. H. Lunsford, J. Catal., 216, 2003, 455.
[10] C. Basse, B. Jaeger, Elements, Degussa Science Newsletter, 17, 2006, 4-7.
[11] J. K. Edwards, A: Thomas, B. Solsona, Ph. Landon, A. Carley and G. Hutchings, Catal. Today, 122, 2007, 397-402.