Karl-Winnacker-Institut — Technical Chemistry

Process development for small-scale direct synthesis of hydrogen peroxide in a catalytic membrane contactor

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Motivation

Hydrogen peroxide is an oxidizing agent widely used in many industrial areas:
- ✓Chemical industry - production of peroxy compounds
- ✓Textile and paper industry – bleaching agent
- ✓Environmental protection – detoxification of waste waters and exhaust gases

H_2O_2 advantages:
- ✓Environmentally harmless – the only by–product is water
- ✓Higher activity and selectivity than conventional oxidizing agents

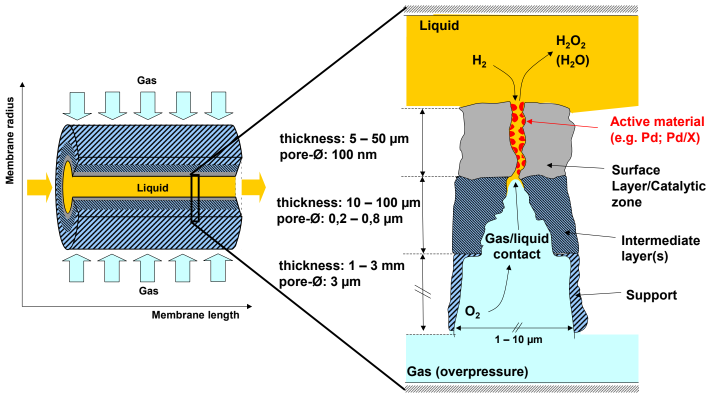
H_2O_2 disadvantages:
- ✓Expensive – manufacturing price 0.53-0.80 EUR/kg
- ✓Complicated synthesis – "Anthraquinone Process"

Limitations of the "Anthraquinone Process" :
- ✓Economically viable only for large scale production units (>40 kt/a)
- ✓Expensive and complex solvent system
- ✓Waste of alkyl-anthraquinone during the hydrogenating step due to side reactions

Objectives

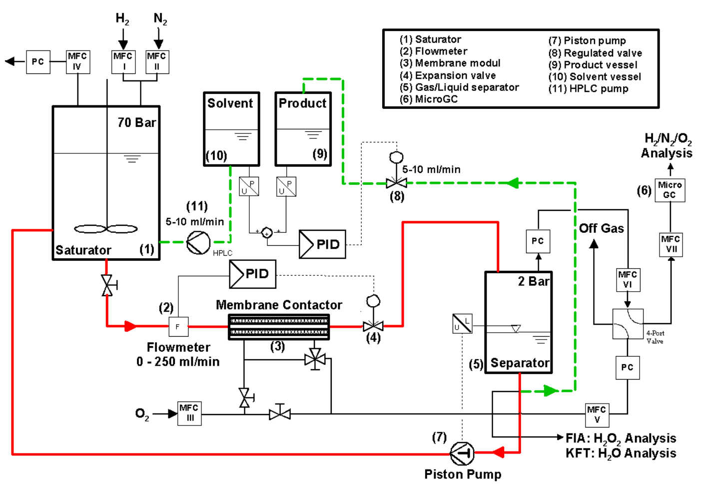
The aim of the project is to develop a compact system for on-site direct synthesis of hydrogen peroxide from O_2 and H_2 on small scale. An important issue is the safety of the continuous process, guaranteed by the use of a catalytic membrane contactor, operating based on the principle of the "catalytic diffuser".

"Catalytic diffuser" concept



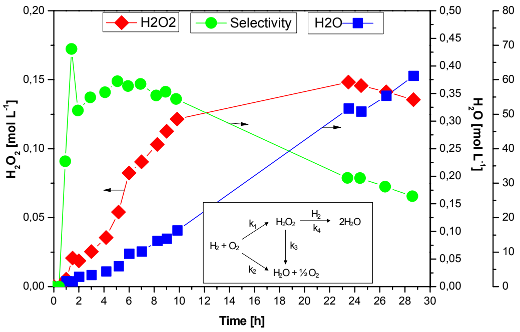
Promises of the approach:
- ✓Separated supply of H_2 and O_2 – safe operation
- ✓Highly dispersed active material, therefore high active surface area per m^2 of membrane area and per gram of catalyst – high productivity
- ✓Moderate limitation by mass transfer due to thin catalytic zone
- ✓Relatively easy scale-up by exploiting multi-channel tubes
- ✓Well suited for on-site production for direct use in small scale applications

Experimental set-up for continuous operation



Catalyst development

In order to verify that our catalyst coating method for ceramic membranes (Impregnation-Decomposition of Pd-Acetate) leads to active catalysts, several supported catalyst were prepared with this method and tested for the H_2O_2 direct synthesis. Different supports like Al_2O_3, TiO_2 , Carbon and C-infiltrated Al_2O_3 were used. The experiments were performed in semi-batch mode with methanol and in batch mode with water as solvent.



Concentration profiles of H_2O_2 and H_2O for a typical semi-batch experiment with a 2%Pd/TiO_2 catalyst.

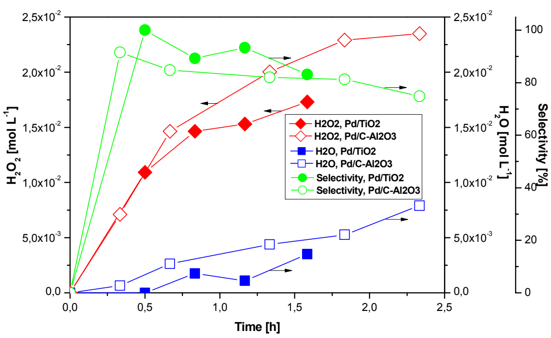
Conditions:
19,4 mg Pd;
1,2 LMeOH
0,03 mol/L H_2SO_4
14 mg/L NaBr;
P = 60 bar
T = 20°C
$H_2/O_2/N_2$ = 8/27/65

Catalyst	Conditions	Activity [gH_2O_2 gPd^{-1} h^{-1}]	Selectivity [%]
2%Pd/TiO_2-MJ	Semi-batch experiments Solvent methanol 0,03 mol/L H_2SO_4, 15 mg/L NaBr P = 60 bar; T = 20°C; $H_2/O_2/N_2$ = 8/27/65	**31,67**	**78,9**
2%Pd/α-Al_2O_3-MJ		0	0
2%Pd/C (StröhleinAK)		26,54	68,8
2%Au2%Pd/TiO_2-MJ		1,92	62,2
1%Pd/TiO_2-HITK	Batch experiments Solvent water/methanol 0,03 mol/L H_2SO_4, 15 mg/L NaBr P = 60 bar; T = 20°C; $H_2/O_2/N_2$ = 3/12/45	**30,65**	**69,2**
1%Pd/Al_2O_3-HITK		8,66	47,5
2%Pd/C(Hydraffin23)		2,48	19,4
0,5%Pd/1%C/Al_2O_3-HITK		**90,47**	**49,0**

H_2O_2 synthesis with catalytic membranes

Up to now only single channel catalytic membranes (d_{out}= 1 cm, d_{in} = 0,7 cm, l = 10 cm) from TiO_2, or C-infiltrated Al_2O_3 were tested. Work on multi channel tubes is in progress. The first experiments led to unexpectedly low H_2O_2 concentrations ($3 \cdot 10^{-4}$ mol L^{-1}) with low selectivity (9%).

In order to understand the reasons for the poor performance, a mathematical model, describing the combination of chemical reaction and mass transport within the membrane contactor, was set up. The simulations indicate highly limited H_2 transport from the center of the channel by diffusion to the catalytic zone in the conditions of laminar flow observed. Filling the membrane channel with innert glass beads to accelerate radial mixing led to much higher H_2O_2 concentrations and selectivity as visible from the graph below.



H_2O_2 direct synthesis with Pd/TiO_2-7 and Pd/C-Al_2O_3-442 membranes filled with 0,5 mm glass beads. Reaction performed in single loop.

Conditions:
MeOH
15 mg/L NaBr
0,03 mol/L H_2SO_4
P(H_2/N_2) = 50 bar
H_2/N_2 = 30/70
P(O_2) = 54 bar
F = 5 ml/min

Summary and outlook

Summary
- ✓Completed experimental set-up for continuous operation
- ✓Proved long-term operational stability of the continuous system with single channel membranes
- ✓Developed a reliable system and method for continuous H_2O_2 detection
- ✓Developed suitable catalyst coating procedure leading to active catalysts
- ✓Identified promising catalytic systems (Pd/C-Al_2O_3, Pd/TiO_2),

Outlook
- ✓Identification of suitable process conditions in order to achieve technically relevant H_2O_2 concentrations (ca. 3-5 % w/w) with the continuous system
- ✓Proof of the long-term operational stability of the system with multi-channel membranes for increased productivity