DECHEMA Karl-Winnacker-Institut

Chemical Technology

Direct synthesis of hydrogen peroxide with CO_2 as solvent in a double membrane micro reactor

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UMWELT STIFTUNG

Motivation

H_2O_2 annual global consumption is ca. $3{\cdot}10^6$ t/y
Expected growth (just for the HPPO-Process) is ca. $2{\cdot}10^5$ t/y

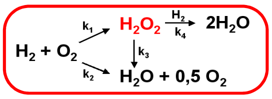
H_2O_2 advantages:

- Environmentally harmless
- Higher activity and selectivity than conventional oxygen

H_2O_2 "bottle-neck":

- Expensive – 0.53-0.80 € /kg
- Industrial synthesis: "Anthraquinone Process" - energy intensive and environmentally unfriendly

H_2O_2 direct synthesis: an attractive alternative



Challenges:

Safety
Wide explosion range of H_2/O_2 mixtures

Activity
Low reactant concentrations due to low solubility of H_2 and O_2 ⇒ ***high pressure; organic solvents; additives***

Selectivity
Water is thermo-dynamically more stable

Project idea and aims

Use of membranes

- enhanced process safety – separate supply of H_2 and O_2
- direct supply and even distribution of H_2 und O_2 along the micro channel

Micro reaction technology

- enhanced heat- and mass-transfer and reduced limitations on reaction kinetics
- improved process safety

CO_2 as medium

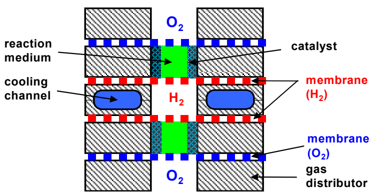
- non toxic, non flammable
- easy separable from the products by expansion of the reaction mixture
- enhanced mass transport of the reactants

Explore a novel process window

Project aims:

- design a continuous heterogeneous process for the H_2O_2 direct synthesis
- use both liquid or supercritical CO_2 as solvent
- develop a new type of micro structured double membrane reactor

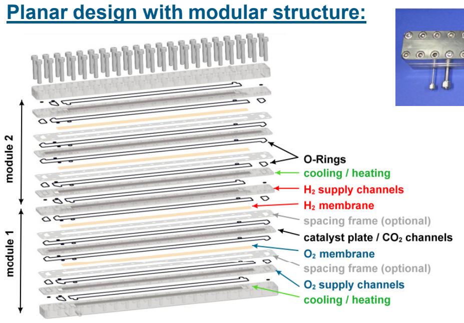
Possible reactor design:

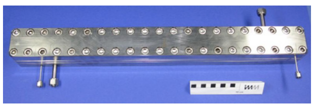


Project partner: IMM Institut für Mikrotechnik Mainz GmbH, Dipl.-Ing. Ulrich Krtschil, Dipl.-Ing. Christian Hofmann

Double membrane micro reactor

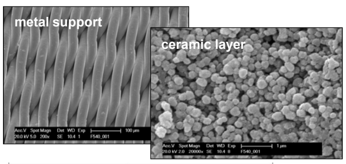
Planar design with modular structure:

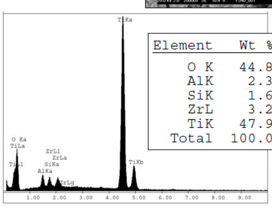




- Reactor (l,w,h): ca 600 x 60 x 60 mm
- Plates: 316 L ss
- O-Rings: Viton
- Channel (l,w,h): 500 x 0.5 x 2 mm
- Volume: 2 x 10 ml
- Weight: ca 20 kg

Planar metal ceramic membranes (Trumem®, ASPECT/Ru):





Element	Wt %	At %
O K	44.89	70.40
AlK	2.31	2.15
SiK	1.63	1.46
ZrL	3.27	0.90
TiK	47.90	25.09
Total	100.00	100.00

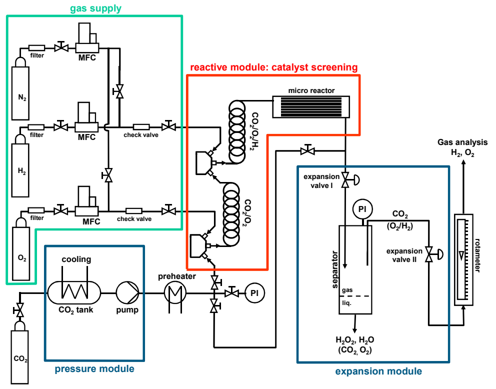
Support	ss mesh
Ceramic layer	mixed oxides
Pore sizes	30 nm
Dimensions	30 x 90 cm (w, l)
Total thickness	180 µm
Ceramic layer	ca. 15 µm

Permeation properties:

- **Dry membrane:** at 1 bar $F(H_2)$ = 34 L h^{-1}cm^{-2} for ΔP = 0.5 bar
- **Wetted membrane**: bubble point at 18 bar (Galden, σ = 16.9 dynes cm^{-1})

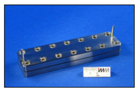
Experimental set-up

Designed with interchangeable reactive part: test micro reactors for catalyst screening experiments built in at first, replaced at a later project stage with the double membrane micro reactor.



- use both liquid and supercritical CO_2 as sol-vent
- P = 60 to 200 bar
- T = -10 to + 50°C
- $F(CO_2)$ = 50 to 350 NL h^{-1} = 100 to 700 g h^{-1}

Catalyst coating

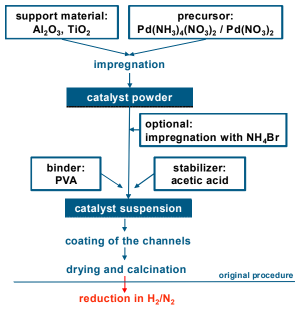


One test micro reactor = one catalyst type

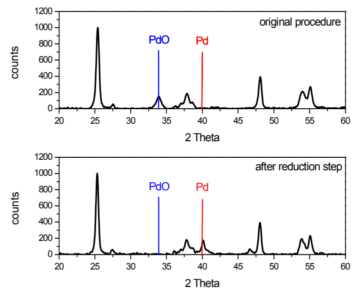
20 Channels (l, w, h): 150 x 0.5 x 0.6 mm

- thickness of one coating layer is 50 – 60 µm
- can be varied through multiple coatings

Wash coating procedure



XRD spectra of catalyst powder



Catalyst performance

Catalyst / Micro reactor		H_2/O_2 Ratio	H_2 Conv. [%]	H_2O_2 Sel. [%]	H_2O_2 Prod. [$g_{H2O2}\ g_{Pd}^{-1}\ h^{-1}$]
5% Pd/TiO_2 acidic precursor m(Pd) = 8 mg	Original coating procedure	1/2	71.8	1.5	13.6
		1/1	100.0	0.9	10.7
		1/3	73.3	0.9	8.4
5% Pd/TiO_2 acidic precursor and bromide, m(Pd) = 7.5 mg		1/2	5.9	6.65	4.9
		1/1	6.9	1.6	1.3
		1/3	14.1	0.4	0.7
5% Pd/TiO_2 basic precursor m(Pd) = 7.7 mg		1/1,5	79.6	1.1	10.5
5% Pd/TiO_2 basic precursor and bromide; m(Pd) = 7.2 mg		1/1	61.6	3.7	28.9
5% Pd/TiO_2 basic precursor m(Pd) = 7.7 mg	After reduction	1/1	30.6	5.1	17.9
1% Pd/Al_2O_3 basic precursor m(Pd) = 0.8 mg		1/1	2.2	20.7	50.1

Conditions: $T1(CO_2$ flow) = 40°C; P1(system) = 92 - 97 bar; T2(exp.valve I) = 50°C; P2(separator) = 18 bar; $F(CO_2$-rotameter) = 2.2 L min^{-1}; $F(CO_2$-sys) = 6.23 ml min^{-1}; F(EtOH) = 4.2 ml min^{-1} ; Solvent: $scCO_2$/ EtOH +15 mg L^{-1} Na Br + 0.04 mol L^{-1} H_2SO_4

Conclusions

Experimental set-up: successfully developed and put into operation. Very stable performance was observed with both liquid and supercritical CO_2.
Double membrane reactor: completed manufacturing after the choice of suitable planar metal/ceramic membranes. Extensive characterisation of membrane permeation properties for H_2 and O_2 is planned.
Catalyst screening: improved performance of reduced catalysts with productivities comparable to literature data, however, with rather low selectivity. Further optimisation of catalyst performance at different experimental conditions is planned.