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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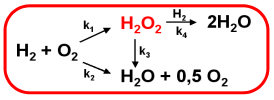
UMWELT STIFTUNG

Motivation

H_2O_2 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 most 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

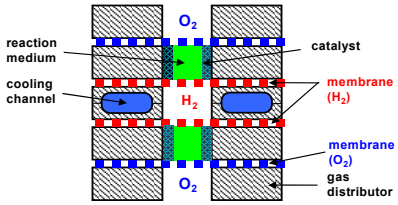
⇨ **Explore a novel process window**

Aims
- design a continuous hetero-geneous process
- use both liquid or supercritical CO_2 as solvent
- develop a new micro structured double membrane reactor

Partner
- Institut für Mikrotechnik Mainz, IMM GmbH
- Friedrich-Schiller-Universität Jena

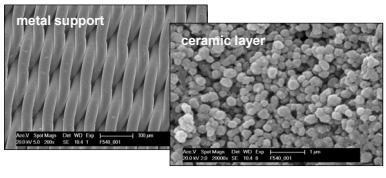
Double membrane micro reactor

Modular structure / cross section



- Reactor (l,w,h): ca. 600 x 60 x 60 mm
- Channel (l,w,h): 500 x 0.5 x 2 mm
- Volume: 2 x 10 mL
- Weight: ca 20 kg

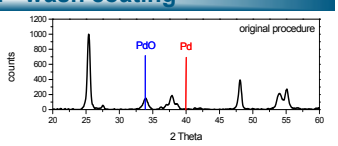
Planar metal ceramic membranes (Trumem®, ASPECT/Ru):

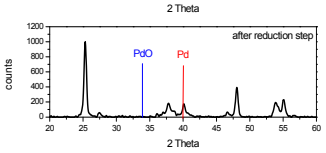


Support	ss mesh
Ceramic layer	mixed oxides
Pore sizes	30 nm
Dimensions	30 x 90 cm (w, l)
Total thickness	180 µm
Ceramic layer	ca. 15 µm

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})

Catalyst preparation - wash coating

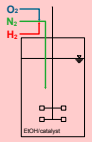




One test micro reactor = one catalyst type
20 Channels (l, w, h): 150 x 0.5 x 0.6 mm
- thickness of one coating layer is 50 – 60 µm
- can be varied through multiple coatings

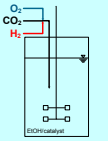
Type of experiments and conditions

Type A
Batch $H_2/O_2/N_2$/EtOH



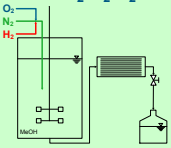
Conditions:
$H_2/O_2/N_2$ = 12/12/75 mol %
P_{sys} = 95 bar; T_{sys} = 23°C
O_2/H_2 = 1/1; m_{Pd} = 20 ÷ 23 mg
Solvent: EtOH + additives
Catalyst: powder

Type B
Batch $H_2/O_2/CO_2$/EtOH



Conditions:
$H_2/O_2/CO_2$ =5/10/85 mol %
P_{sys} = 110 bar; T_{sys} =44°C;
O_2/H_2 = 2/1; m_{Pd} = 25 ÷ 26 mg
Solvent: EtOH + additives
Catalyst: powder

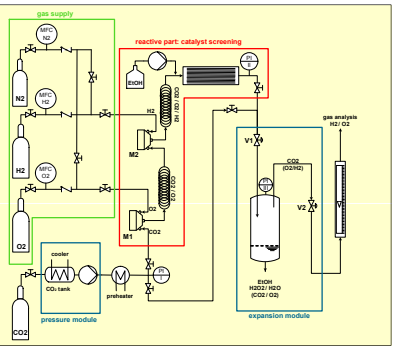
Type C
Continuous $H_2/O_2/N_2$/MeOH



Conditions:
$H_2/O_2/N_2$ = 5/32/63 mol%
P_{sys} = 60 bar; T_{sys} = 24°C
O_2/H_2 = 1/6; m_{Pd} = 0.8 ÷ 1 mg
F_{MeOH} = 3 ÷ 5 ml min^{-1}
Solvent: MeOH – additives
Catalyst: wall coating/test micro reactor

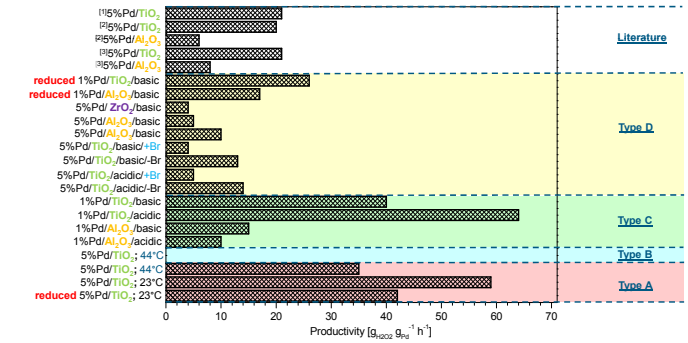
Type D
Continuous in CO_2 system
$H_2/O_2/CO_2$/EtOH

Conditions:
$H_2/O_2/CO_2$ = 4÷6/4÷6/78-92 mol%;
O_2/H_2 = 1/1;
P_{sys} = 80 ÷ 120 bar;
T_{sys} = 27°C or 40°C;
F_{CO2} = 4 ÷ 8 ml min^{-1};
F_{EtOH} = 3 ÷ 5 ml min^{-1}
Solvent: CO_2/EtOH + additives
Catalyst: wall coating/test micro reactor



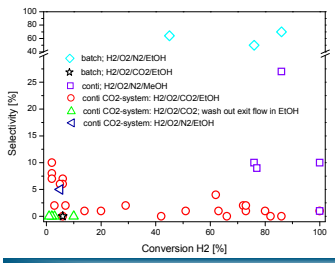
Results

Productivity

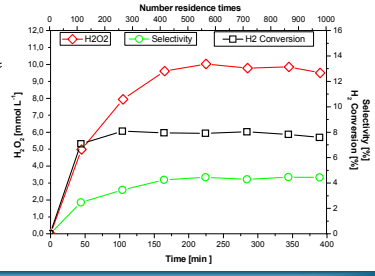


[1]Edwards and Hutschings, Angew. Chem. Int. Ed 47 (2008) 9192-9198; [2]Ntainjua, Green Chem. 10 (2008) 1162-1169; [3]Samantha, Appl. Catal. A 350 (2008) 133-149

Selectivity vs. conversion



Long therm stability / Experiment type D



Conclusions

Experimental set-up / CO_2 system
Very stable performance with both liquid and $scCO_2$.

Double membrane reactor
Completed and coated with 5%Pd/TiO_2 catalyst. Current work – characterisation of membrane permeation properties.

Catalyst screening
Best performance under batch conditions. For the CO_2 system: improved performance of reduced catalysts (readily comparable to literature data), however, with rather low selectivity. Further optimisation of catalyst performance at different experimental conditions is going on.

September 2011, Frankfurt