# Catalytic Reduction of Nitrate and Nitrite in Water with Porous, Catalytically Active Membranes

M. Reif, R. Dittmeyer
Contact: reif@dechema.de, dittmeyer@dechema.de

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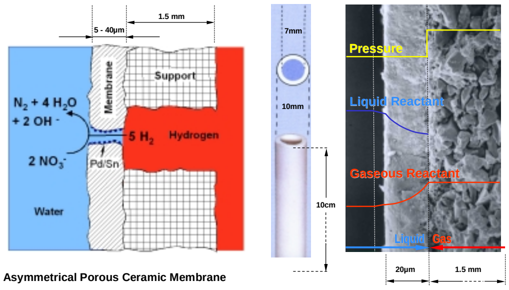
## Catalytic Diffuser




Asymmetrical Porous Ceramic Membrane

- material of membrane layer $\alpha$-$Al_2O_3$, $\gamma$-$Al_2O_3$, $ZrO_2$, $TiO_2$, C, etc.
- pore size of membrane layer: 5 - 400 nm
- pore size of support: 3 µm

Concentration Profile in Catalytic Membrane Layer for Gas-Liquid-Reactions

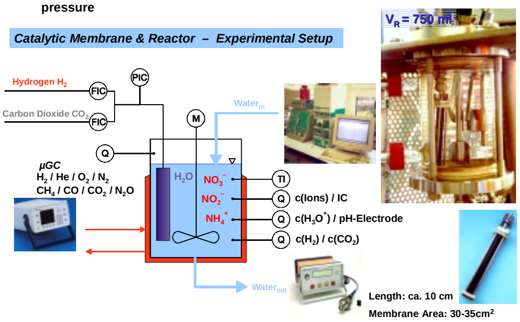
A (Liquid) + B (Gas) → C

Example: $2\ NO_3^- + 5\ H_2 \rightarrow N_2 + 2OH^- + 4\ H_2O$

### Advantages of the Catalytic Diffuser / Contactor Concept

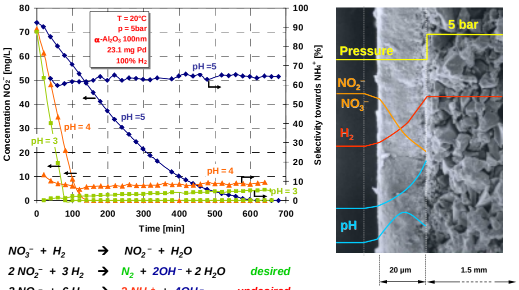
- specific dosing of gaseous reactant (e.g. $H_2$), effective contacting of reactants (gas, liquid) and catalyst; simplified process design
- catalyst fixation, no separation of the catalyst from the reaction solution necessary
- reduced limitation of mass transfer by thin catalytically active membrane layer
- control of reaction by adjustment of activity through the $H_2$-pressure in membrane
- high $H_2$-pressure (0-15bar) possible in membrane, reactor at atmospheric pressure

### Catalytic Membrane & Reactor – Experimental Setup




Length: ca. 10 cm
Membrane Area: 30-35cm²

## Forced Through Flow



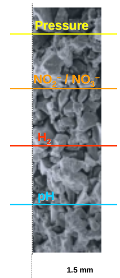

$NO_3^- + H_2 \rightarrow NO_2^- + H_2O$

$2\ NO_2^- + 3\ H_2 \rightarrow N_2 + 2OH^- + 2\ H_2O$ *desired*

$2\ NO_2^- + 6\ H_2 \rightarrow 2\ NH_4^+ + 4OH^-$ *undesired*

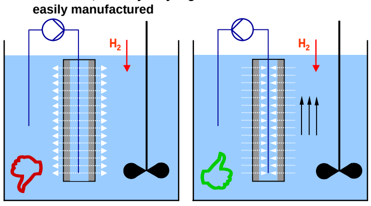
### Forced Through Flow Concept

*In the Forced Through Flow concept the reaction solution is pumped through a coated support; the catalytic metal (e.g. palladium) was deposited on the walls of the support*




### Advantages of the Forced Through Flow Concept

- very short contact times at the catalyst can be achieved
- film diffusion and pore diffusion can be eliminated ⇒ no concentration gradients in the pore system of the catalyst
- very effective contacting between reactants dissolved in reaction media and solid catalyst on pore walls
- with a catalytically active metal coated ceramic support behaves like a micro reactor with very small channel diameters, thereby very high contact surface and it can be easily manufactured




*If reaction mixture is pumped through the support from the inside to the outside, the support is easily plugged (see left). Is the water sucked from the outside to the inside of the membrane and is there a sufficient cross-flow on the retentate side, Forced Through Flow operation can be maintained over a long time.*

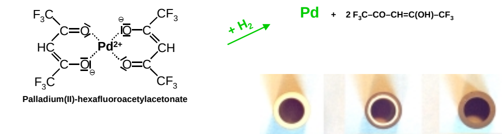
Plugged membrane supports

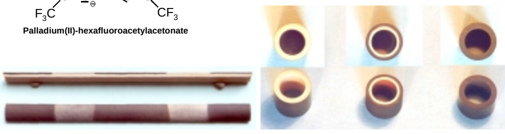
*Cross section of membrane support coated with Pd*

## Membrane Preparation

*Commercially available ceramic ultra- and micro-filtration membranes made of different ceramic materials ($Al_2O_3$, $ZrO_2$, $TiO_2$ etc.) are used as starting material. In order to make these membranes catalytically active, different methods can be applied. A special MOCVD-method was developed to coat only the membrane layer of the membranes with palladium and to avoid coating of the support. Small Pd-clusters can be deposited inside the porous membrane layer. A controlled surface reaction with tetrabutyltin is used to generate bimetallic Pd/Sn sites on the membrane. In order to produce a high surface, electrically conductive carbon layer in the porous skin layer of the membrane, the membranes are coated with a furfuryl alcohol resin with subsequent heat treatment.*

### Palladium-Chemical Vapor Deposition



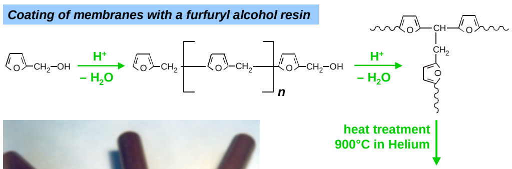



*Control of penetration depth and place of Pd-CVD-deposition into ceramic membrane*

### Controlled Surface Reaction for bimetallic Pd/Sn active sites

Pd—H + $Sn(C_4H_9)_4$ → $PdSn(C_4H_9)_3$ + $C_4H_{10}$ → (+ 1.5 $H_2$) Pd — Sn + $3C_4H_{10}$

### Coating of membranes with a furfuryl alcohol resin

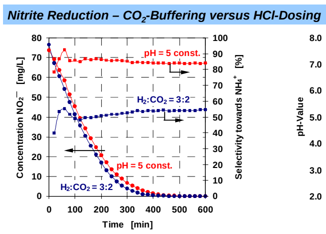



*electrically conductive, high surface carbon (BET≈ 1400 m² / g C)*

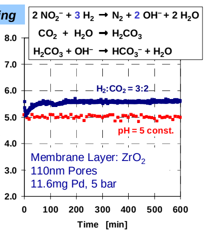
*Membranes coated with palladium*

## Experimental Results

### Nitrite Reduction – $CO_2$-Buffering versus HCl-Dosing

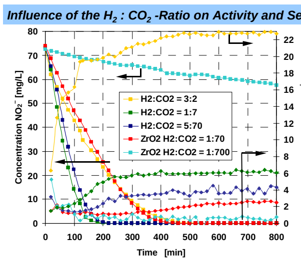



$2\ NO_2^- + 3\ H_2 \rightarrow N_2 + 2\ OH^- + 2\ H_2O$
$CO_2 + H_2O \rightarrow H_2CO_3$
$H_2CO_3 + OH^- \rightarrow HCO_3^- + H_2O$




*If carbon dioxide is mixed to the hydrogen into the membrane, better $N_2$-selectivities are achieved, even though there is a lower pH in the bulk with HCl-dosing*

### Influence of the $H_2$ : $CO_2$ -Ratio on Activity and Selectivity

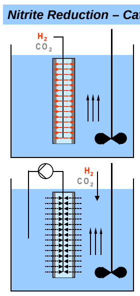



*$ZrO_2$ 110nm pores 18.6mg palladium 5bar, 20°C*

*$NH_4^+$ -production is further and further reduced with higher $CO_2$ -concentration*

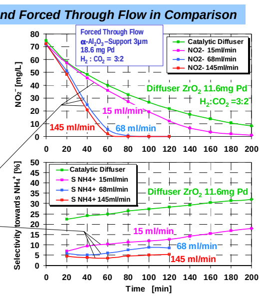
*Activity increases initially with increasing $CO_2$ -concentration, until $H_2$ -concentration gets limiting*

### Nitrite Reduction – Catalytic Diffuser and Forced Through Flow in Comparison



Catalytic Diffuser / Contactor Concept

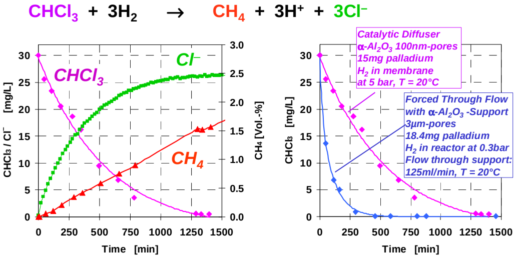
Forced Through Flow Concept



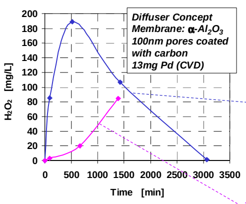

## Results & Module Design

### Dechlorination of Chlorinated Hydrocarbons – Chloroform-Reduction

$CHCl_3 + 3H_2 \rightarrow CH_4 + 3H^+ + 3Cl^-$




### $H_2O_2$-Synthesis from $H_2$ and $O_2$



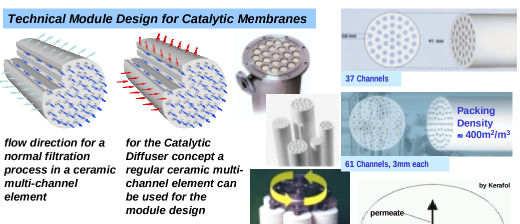

Reaction solution:
2.8 g of 98% $H_2SO_4$, 6mg NaBr in 1 liter of de-ionized water, no organic solvent according to US-patent 4,772,458 (expl.1)

$H_2O_2$-concentration determined by $KMnO_4$-titration

*Solution pre-saturated with $O_2$ at 5 bar first, then $H_2$ fed into membrane at 8bar, reactor at ambient pressure, T=20°C*

*$H_2$ and $O_2$ (1:1) fed into membrane at 5bar, reactor at ambient pressure, T=20°C*

### Technical Module Design for Catalytic Membranes

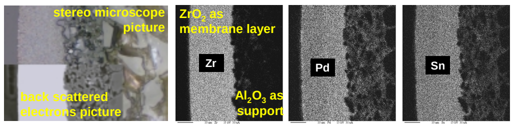



flow direction for a normal filtration process in a ceramic multi-channel element

for the Catalytic Diffuser concept a regular ceramic multi-channel element can be used for the module design

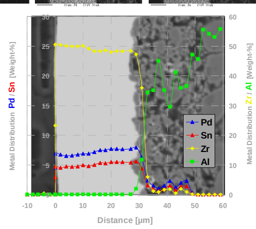
for the Forced Through Flow concept a rotating filter disk setup might be favorable

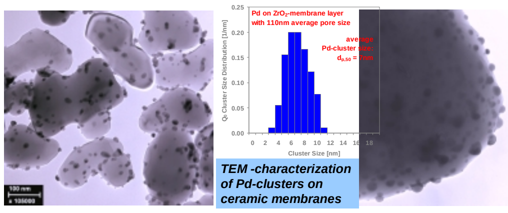
## Membrane Characterization




### Electron Probe Micro-Analysis

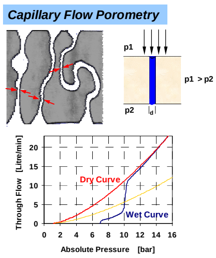
⇒ *With a combination of the developed Pd-MOCVD- and CSR-technique it is possible to deposit palladium and tin mainly in the top membrane layer, coating of the support can be avoided.*




TEM -characterization of Pd-clusters on ceramic membranes

### Capillary Flow Porometry




Pressure Forces = Capillary Forces

$\Delta p \cdot r^2 \cdot \pi = 2 \cdot \sigma \cdot \pi \cdot r \cdot \cos\alpha$

$\Rightarrow\ d = C \cdot 4 \cdot \sigma / \Delta p$