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

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Commercially available ceramic ultra- and micro-filtration membranes made of different ceramic materials (Al₂O₃, ZrO₂, TiO₂, etc.) are used as starting material. In order to make these membranes catalytically active, different methods can be applied. A special MCCVD-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 tetraethylleads 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.

## Membrane Preparation

**Palladium-Chemical Vapor Deposition**

\[ \text{Pd} + 2 \text{H} \rightarrow \text{PdH} + \text{H}_2 \]

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

**Membrane coated with palladium**

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

## Experimental Results

### Nitrite Reduction - CO₂-Buffering vs. HCl-Dosing

If carbon dioxide is mixed to the hydrogen into the membrane, better H₂-selectivities are achieved, even though there is a lower pH in the bulk with HCl-dosing. The influence of the H₂:CO₂-Ratio on Activity and Selectivity:

1. **NH₄⁺ production** is further and further reduced with higher CO₂ concentration.
2. Activity increases initially with increasing CO₂ concentration, until H₂ concentration plateaus.

### Membrane Characterization

**Electron Probe Micro-Analysis**

- With a combination of the developed Pd-MCCVD- and CSM-technique it is possible to deposit palladium on membranes in the top membrane layer, coating of the support can be avoided.

## Forced Through Flow

**Forced Through Flow Concept**

- The catalytic reaction solution is pumped through a coated support; the catalytic metal (e.g. palladium) is deposited on the walls of the support.
- Advantages of the Forced Through Flow Concept:
  - Very short contact times at the catalyst can be achieved.
  - Diffusion and pore diffusion can be eliminated.
  - No concentration gradients in the pores of the catalyst.

**Results & Module Design**

**Membrane Characterization**

- **Technical Module Design for Catalytic Membranes**
- **Capillary Flow Porometry**

**Controlled Surface Reaction for bimetallic Pd-Sn active sites**

**Casting of membranes with a furfuryl alcohol resin**

Membrane coated with palladium at 5bar, reactor at 5 bar first, then H₂ fed into membrane at 15ml/min, reactor at ambient pressure, 25°C.

**Pd-Sn - 5% Sn**

**Heat treatment**

200°C in Reforming electrically conductive, high surface carbon (BET= 1400 m²/g C)

**Capillary Flow Pressure**

Pressure Drop \( \Delta P \) = \( \frac{F \cdot C \cdot L}{D \cdot 4 \cdot \rho \cdot v \cdot e} \)

**Flow direction for a normal filtration process in a ceramic membrane**

- For the Forced Through Flow concept a rotating filter disk setup might be favorable.

**Membrane Layer: ZrO₂**

- Diameters, thereby very high contact surface and it can be easily manufactured.

**Activity increases initially**

- Electrically conductive, carbon layer on the inside of the support is easily manufactured.

**Diameter**

- 10 cm

**Pressure**

- H₂O₂ -concentration determined by according to US-patent 4,772,458 (expl.1)

**Example:**

\[ 3 \text{NO}_3^- + 4 \text{H}^+ \rightarrow 2 \text{NO}_2^- + \text{NO} + 3 \text{H}_2\text{O} \]

**NH₄⁺ 15ml/min**

**Pd on ZrO₂-membrane layer**

- Palladium(II)-hexafluoroacetylacetonate

**Membrane Layer: ZrO₂**

- HCO₃⁻ + H₂O → CO₂ + 3 H₂

**NH₄⁺**

- 2 NO₃⁻ + 1.5 H₂ → 2 NO₂⁻ + NO + 3 H₂O

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