

Hydrocarbon dehydrogenation assisted by in situ hydrogen removal through Pd alloy composite membranes

R. Bergsträßer, R. Dittmeyer, Y.C. van Delft, A. de Groot
 Funded by: SenterNovem (Dutch Ministry of Economics)
 Period: 01. Feb. 2007 – 31. Jan. 2009
 Email: dittmeyer@dechema.de



Objective

Demonstration of the potential of hydrogen permselective palladium alloy membranes (manufactured by the energy research center of the Netherlands, ECN) for industrially important dehydrogenation reactions.

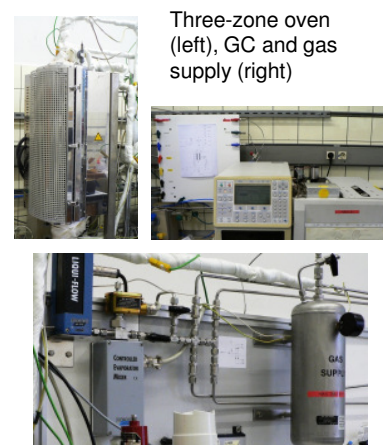
Background

Dehydrogenations are energy intensive reactions with conversion often being restricted by chemical equilibrium. In situ removal of hydrogen allows to lower the reaction temperature without reducing conversion and yield, thus improving the energy efficiency. Propane dehydrogenation was selected as an important large-scale industrial process and methylcyclohexane dehydrogenation as an interesting small-scale application connected to the chemical hydrogen storage in fuel cell vehicles.

- Propane → Propene
 - + High demand for on-purpose propene ("propylene gap")
 - + Conversion/yield limited to < 50% (large benefit of H₂ removal)
 - Challenging process: coke deposition on catalyst and membrane leads to performance degradation (periodic regeneration required)
- Methylcyclohexane → Toluene
 - + No degradation of membrane performance, less severe coking
 - Challenging system design: compactness, weight

Experimental Set-up

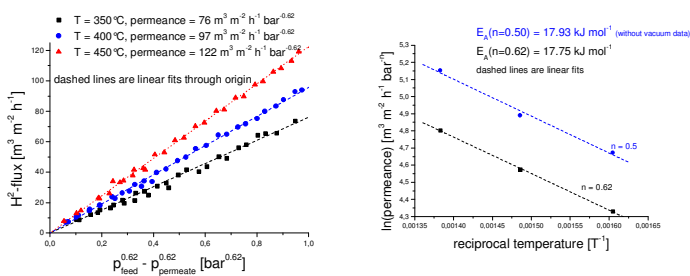
- Setup was designed for a wide range of experimental conditions (T = 350-600°C, P = 0.5-35 bar)
- High pressure operation is evaluated as conventional operating conditions are not necessarily the best for membrane-assisted dehydrogenation
- Product analysis via GC (two columns: molsieve 5Å, carboxen, 3 detectors: TCD, FID, methanizer-FID) and refractometer (TOL, MCH)



Controlled Evaporating & Mixing System

Hydrogen Permeance – Ideal Conditions

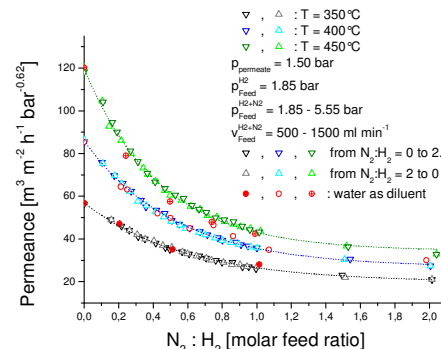
The best fit of the experimental data is obtained for a H₂ pressure exponent of 0.62. The activation energy of the Pd/Ag composite membranes is 17.8 kJ mol⁻¹.



Hydrogen Permeance – Concentration Polarisation

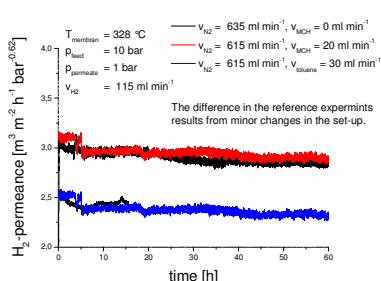
Influence of an inert diluent (N₂) at constant H₂ partial pressure.

- Permeance is limited by diffusion of H₂ to the membrane surface (transverse to the flow direction).
- Verified by simulations with COMSOL.



Methylcyclohexane Dehydrogenation

- No visible influence of MCH and TOL in the range of 2.5-80 vol.% on the H₂ permeance compared to nitrogen as diluent
- Preliminary experiments with imperfect membrane and diluted bed of a 0.5 wt.-% Pt/Al₂O₃ catalyst



Conditions: m_{cat} : 56.5 g, MCH feed: 84.8 g.h⁻¹, x_{MCH} : 0.78
 WHSV: 1.5 h⁻¹, T: 350 °C
 p_{ret} : 15 bar, p_{per} : 1 bar, A_M/V_{cat} : 110 m⁻¹

Results: MCH-Conversion: 0.72 (~ equilibrium)
 H₂-Flux: ca. 1 m³ m⁻² h⁻¹; H₂-Recovery: ca. 50%
 H₂-Separation factor: ca. 4
 H₂-Productivity: ca. 1.2 mol s⁻¹ m⁻³

⇒ ca. 5 L estimated reactor volume for 100 kW fuel cell ($\eta = 40\%$)

• Current work with improved membrane and catalyst aims at a compromise between conversion, H₂ recovery and productivity

Propane Dehydrogenation

- Coking of membrane starts at low C₃H₆ content and causes a marked loss of the H₂/C₃H₆ separation factor due to reduced H₂ flow

- No coking or reduction of the H₂ flow under C₃H₈ even after exposure for more than 72 hr

- Regeneration with H₂ is low and incomplete

- Use of synthetic air under conditions for catalyst regeneration leads to membrane damage, possibly due to membrane inhomogeneity (Ag content)

- Current work aims at membrane modification to reduce coking.

