Catalysis guidelines for membrane-driven industrial propylene production via non-oxidative dehydrogenation of propane

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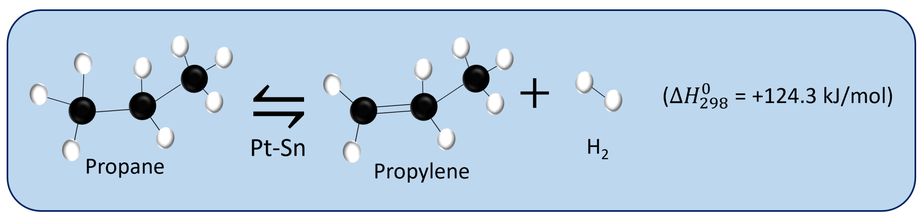
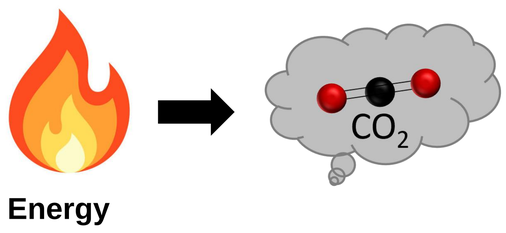
Motivation

- Ever-increasing global **propylene** demand
- Conventional propylene production: **steam cracking (SC)** and **fluid catalytic cracking (FCC)**, aimed at producing gasoline from crude oil
- **Climate crisis**: SC and FCC technologies cannot be expanded
  → **Development of alternative propylene production routes**

Non-oxidative dehydrogenation (NODH) of propane [1]:



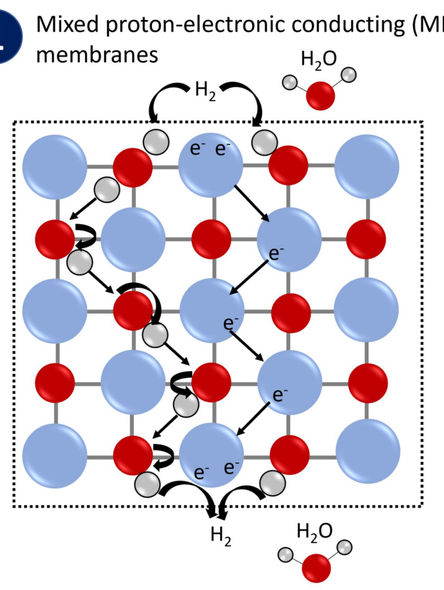
Challenges [1]:
- High *T*: 500-650 °C
- Equilibrium: 10-40% yield
- Coke formation



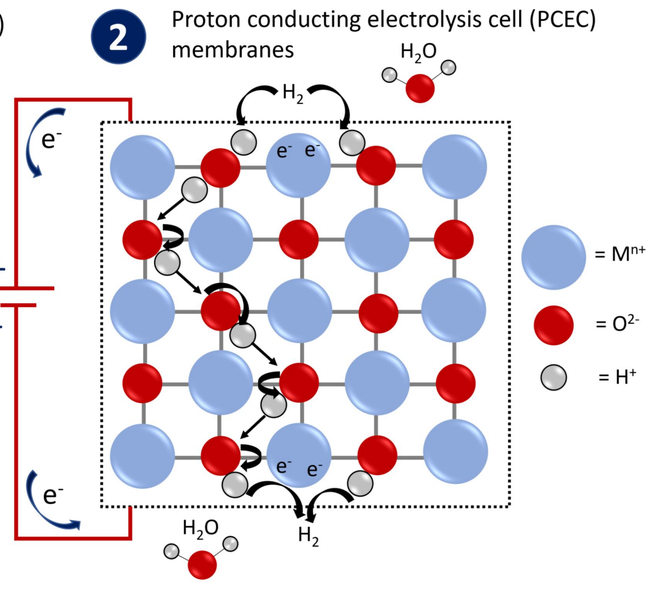
Scope of the project

How to make propane NODH more sustainable?
→ Shift equilibrium towards propylene by removing H_2 using dense ceramic membranes

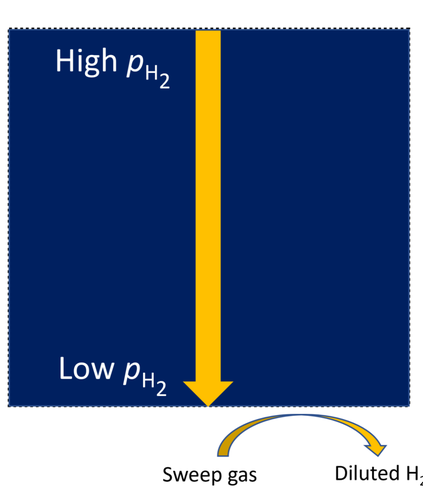
1 Mixed proton-electronic conducting (MPEC) membranes



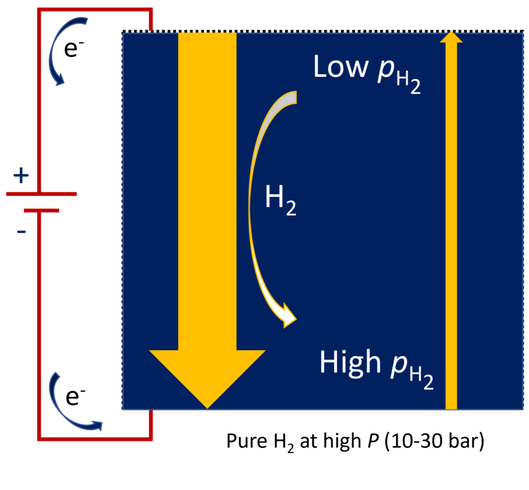
2 Proton conducting electrolysis cell (PCEC) membranes



1 Mixed proton-electronic conducting (MPEC) membranes → H_2 chemical potential



2 Proton conducting electrolysis cell (PCEC) membranes → electrochemical potential



Case study

Three different processes are simulated and compared:
1. UOP Oleflex process → conventional propane NODH process
2. MPEC-assisted propane NODH process
3. PCEC-assisted propane NODH process

Battery limits

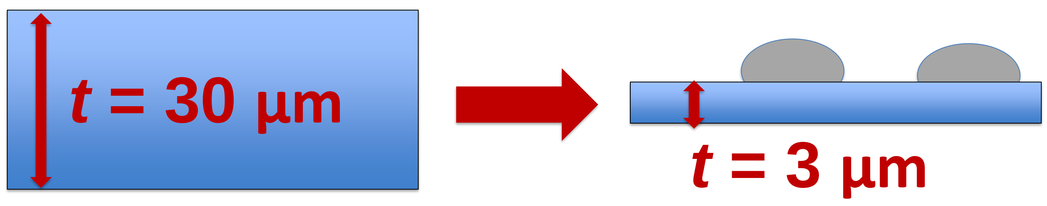
Fresh propane feed
Derived from natural gas processing plant
95 mol% propane, 2.5 mol% ethane, 2.5 mol% *n*-butane
Propylene product
Polymer grade: >99.5 mol% pure
Production capacity: 450 ktpa (8400 operating hours per year)
Hydrogen product
Fuel grade A: >98.0 mol% pure

Results and guidelines

Capital investment

	Capital cost (million USD, 2023)		
	Oleflex	**MPEC**	**PCEC**
Reactors	**40**	**5838**	**57**
Distillation columns	259	206	210
Fired heaters	20	9	9
Compressors + expanders	81	93	66
Heat exchangers	151	117	106
Total direct investment	**551**	**6263**	**448**

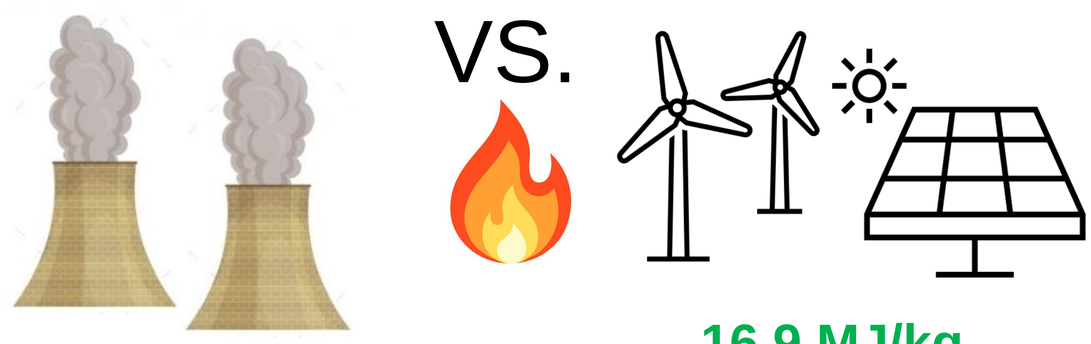
MPEC membranes reactors:



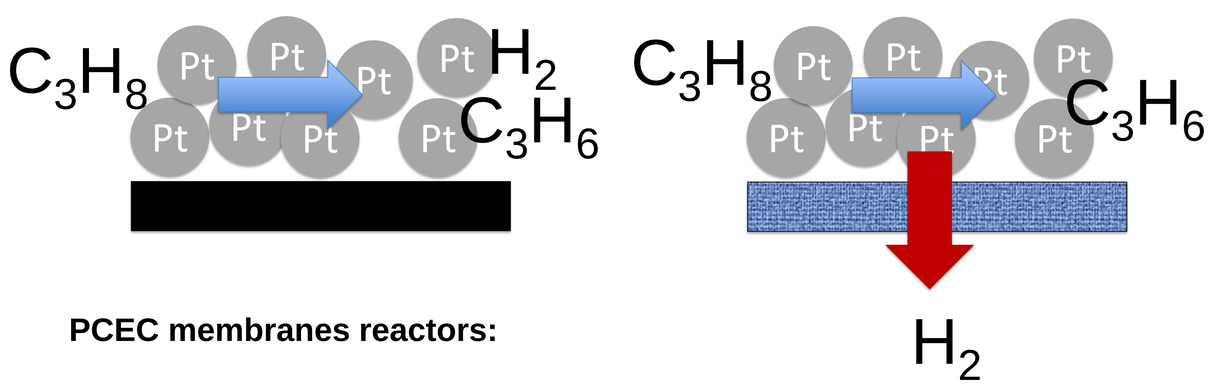
Requirements to make MPEC process financially attractive:
1. Much thinner membranes
2. Stable thin membranes
3. Efficient surface catalysts to match permeation and reaction rates

Energy usage

Conventional Oleflex process — **PCEC process**



22.7 MJ/kg → **-25%** → **16.9 MJ/kg**



PCEC membranes reactors:

Requirements:
Pt catalysts must be equally active, selective, and stable (i.e. coke resistant) under membrane reactor conditions (extremely low H_2 partial pressures) as under standard Oleflex conditions

Conclusion

Industrial perspective:
- MPEC process: can only be cost-competitive if extremely thin and stable membranes can be developed in combination with efficient surface catalysts
- PCEC process: is cost-competitive, can only be more sustainable if the used Pt catalyst is extremely stable under low H_2 partial pressures

References

[1] Sattler et al., *"Catalytic Dehydrogenation of Light Alkanes on Metals and Metal Oxides"*, Chem. Rev., **114**: p. 10613-10653, 2014

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