Methane Pyrolysis over Carbon Catalysts for Hydrogen Production: Impact of Carbon Deposition on Electrical Resistivity and Polyaromatic Hydrocarbon Formation

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4th November 2025

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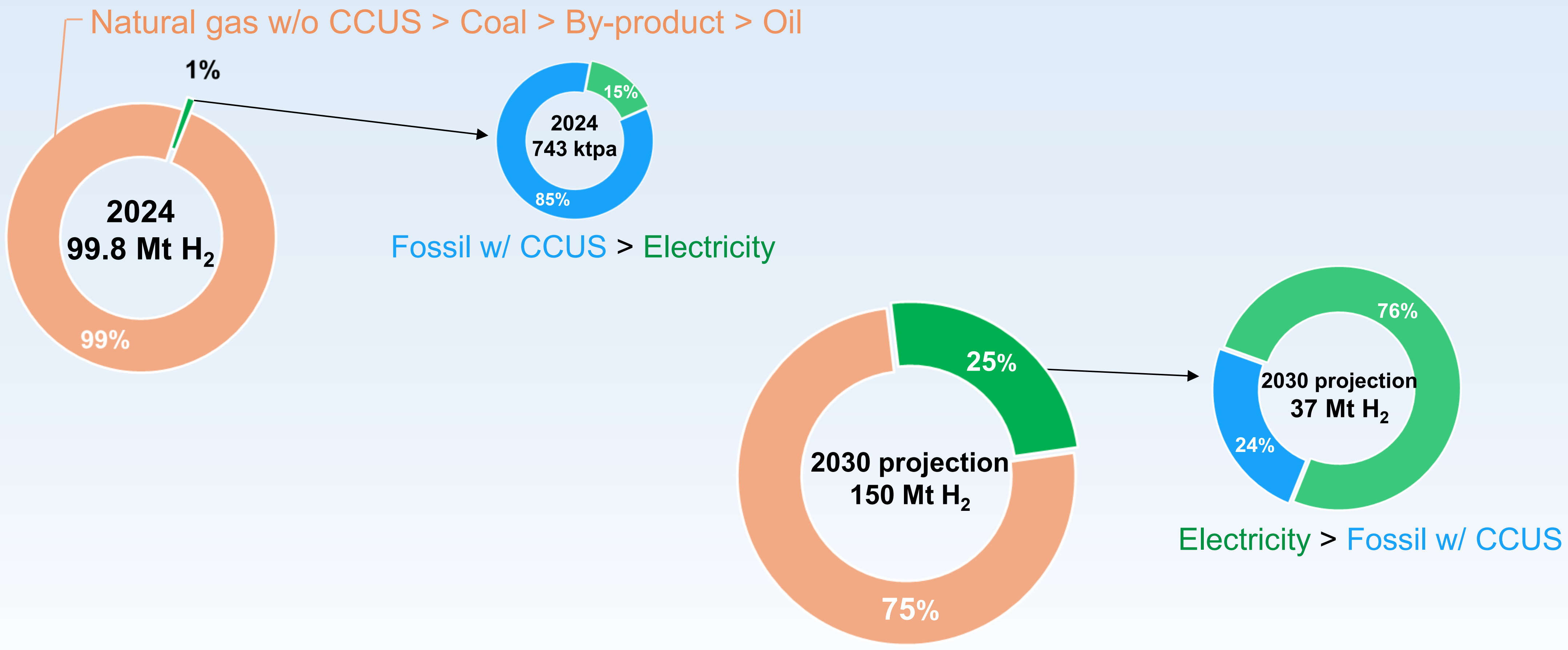
Hydrogen Economy

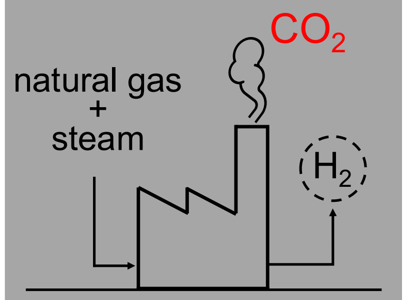


Low-emission H_2 can avoid **950 Mtpa** CO_2 emission in industry and refining

Hydrogen Production

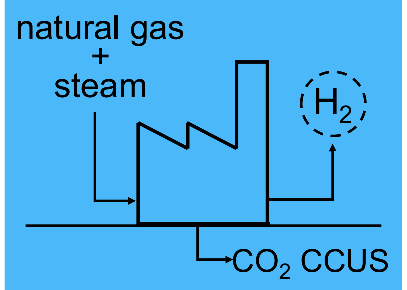
(N. Sánchez-Bastardo et al., Ind. Eng. Chem. Res. 2021, 60)
(A.O. Oni et al., Energy Convers. Manag. 2022, 254)
85% onsite emissions captured
(IEA (2025), Global Hydrogen Review 2025)

GREY HYDROGEN



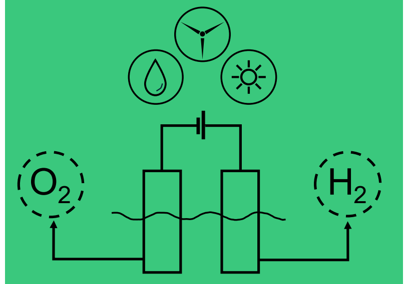
Steam methane reforming or ATR

BLUE HYDROGEN

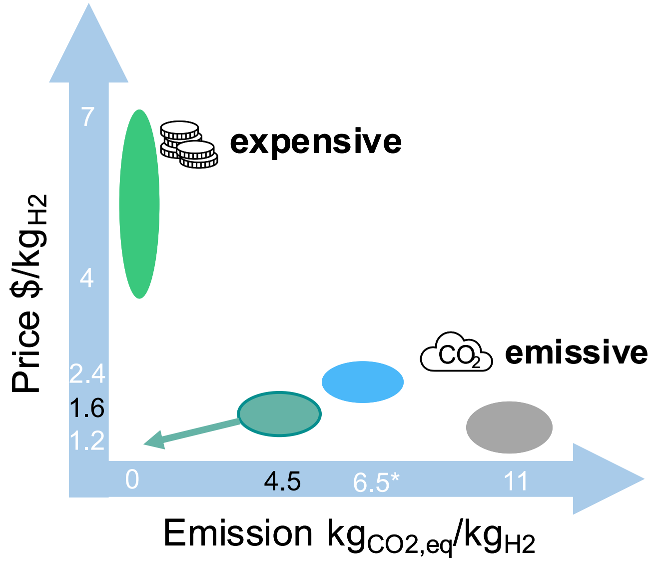


Steam methane reforming or ATR + CCUS

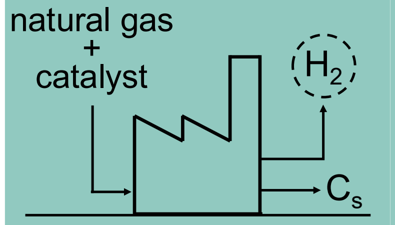
GREEN HYDROGEN



Water electrolysis (AWE, PEM or SOEC)



TURQUOISE HYDROGEN



Methane pyrolysis

$$CH_4 \rightleftharpoons 2H_2 + C_{solid}$$

$$\Delta H_{298K} = 37.7\ kJ/mol_{H_2}$$

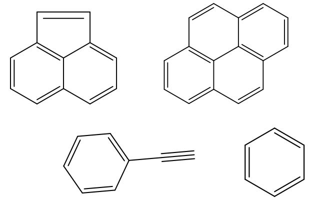
carbon ↔ metal catalyst

Cost reduction

- hydrogen yield ↑
- cokes valorization → graphite anodes

→ **Catalyst Design**

1 Aromatics?



2 Electrification?

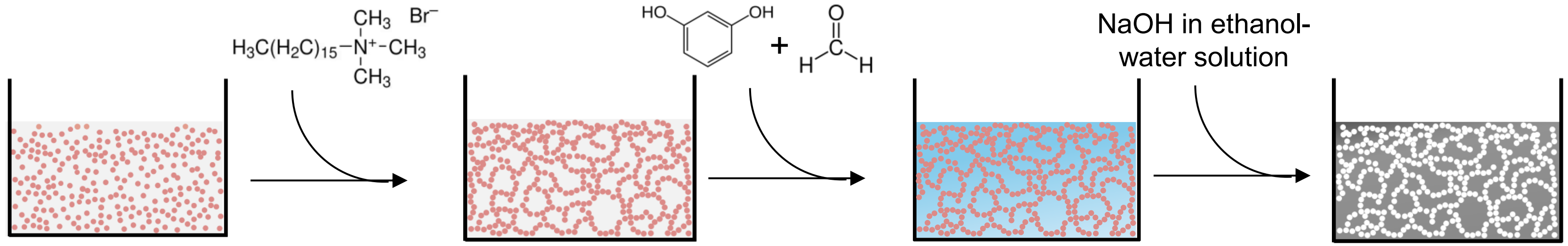
Outline

- Introduction methane pyrolysis for turquoise H_2
- Carbon catalyst synthesis and reactor setup
- Activity tests and polyarmotic hydrocarbons
- Electrical impedance spectroscopy
- Key takeaways

Carbon Catalysts

SMC2

colloidal silica (Ludox HS-40)	stabilized silica	silica-polymer composite	carbon



1. stabilization silica particles with CTAB surfactant (30 minutes at 50°C in mixer)
2. addition resorcinol and formaldehyde under mild suction
3. polymerization: 3 days 85°C with Na_2CO_3 catalyst
4. carbonization
5. leaching silica template
6. filtration + washing

properties

BET-surface (m²/g)	micro/ mesopore surface ratio	pore volume (cm³/g)
1234.3	0.08	2.64

CB Pearls 2000

hydrocarbon feedstock	primary particles	carbon black

gas

aromatics

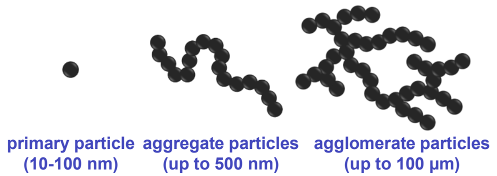
oil

O=O

1. partial comustion of hydrocarbons (1200 à 1900 °C)

conventional CB consisting of concentric regions of graphite

2. pelletization
3. densification



CABOT

properties

BET-surface (m²/g)	micro/ mesopore surface ratio	pore volume (cm³/g)
1425	0.69	1.27

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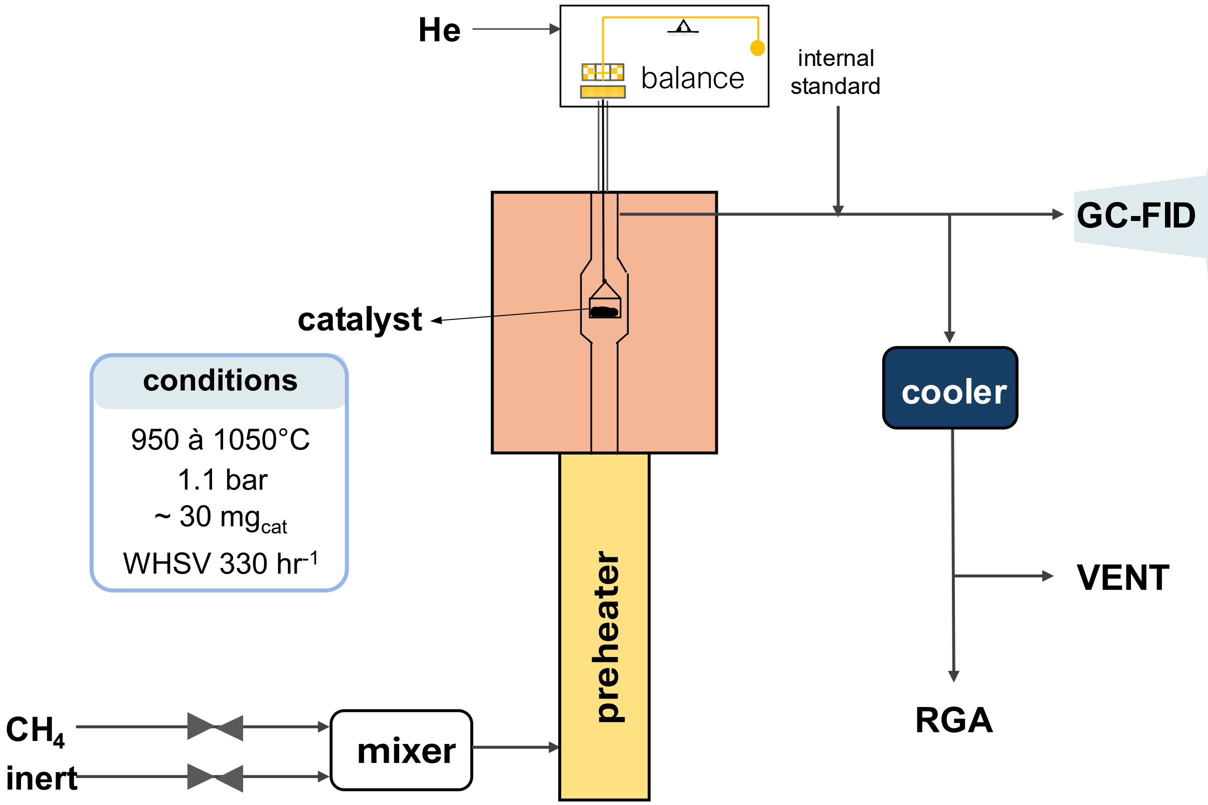
Catalyst Activity Tests - Methodology



IDENTIFICATION OF POLYAROMATIC HYDROCARBONS

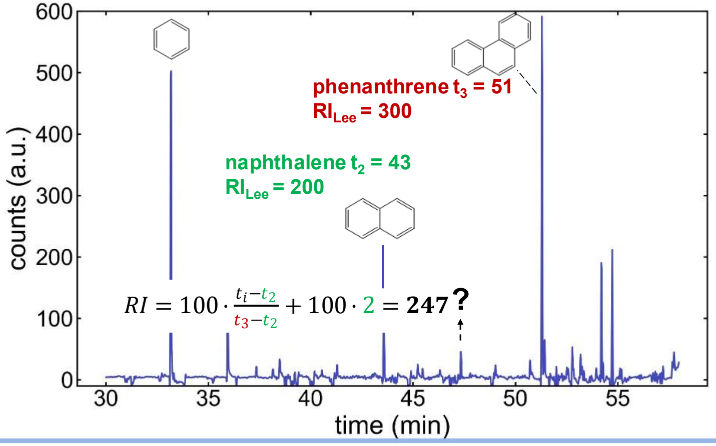
1. Kovats – Van Dool retention indices
   → ex-situ injection n-alkane mixture

pentane: 500
hexane: 600
…
dodecane: 1200
→ n is the number of carbons

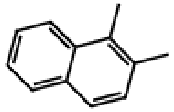
2. Lee retention indices
   → ex-situ injection benzene, naphthalene, phenanthrene and chrysene

benzene: 100
naphthalene: 200
phenanthrene: 300
chrysene: 400
→ n is the number of aromatic rings

$$RI = 100 \cdot \frac{t_i - t_n}{t_{n+1} - t_n} + 100 \cdot n$$

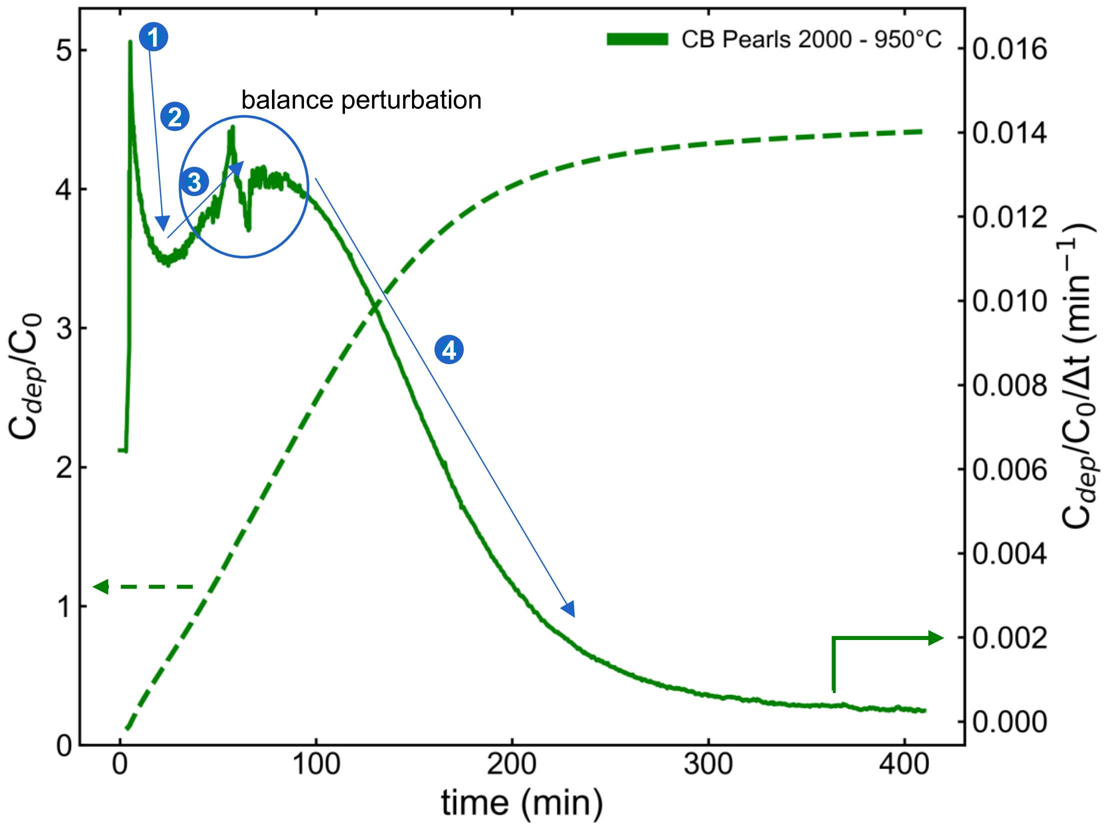


comparison with
- literature
- Nist

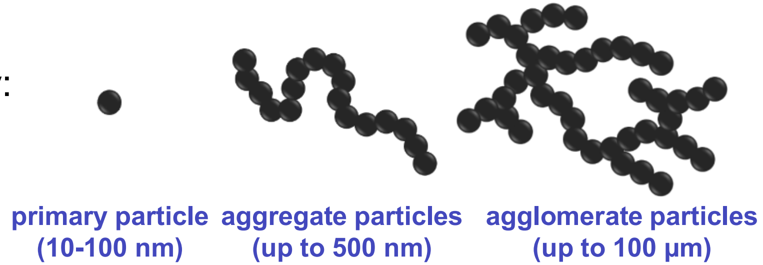
→ 

Catalyst Activity Tests – Results CB Pearls 2000

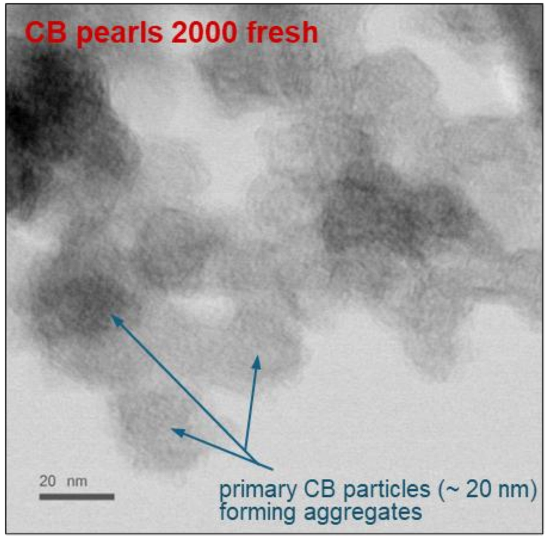
CB Pearls 2000 – 950°C – 1.1 bar – WHSV 330 hr-1

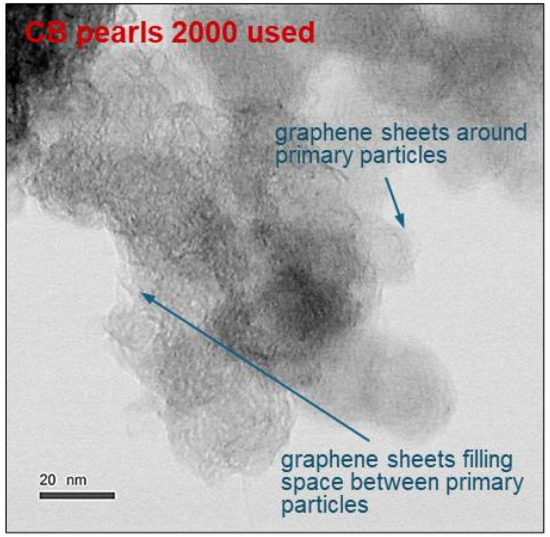


1. high initial activity: → microporosity



2. Primary deactivation: loss of active surface area due to **micro**pore filling/blockage
3. Increase activity: graphene sheets around particles → higher surface area counteracting the pore blocking/filling
4. Secondary deactivation: loss of active surface area due to **meso**pore filling/blockage





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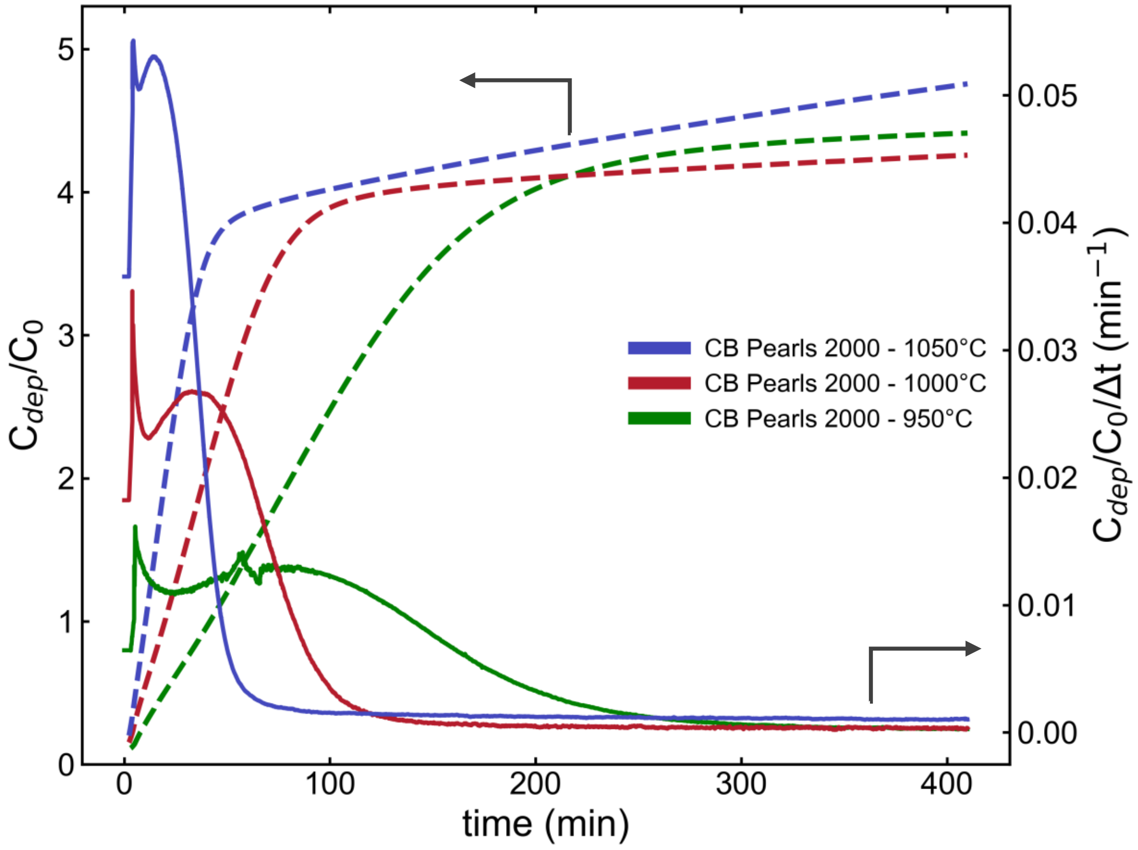
(A. Khrabry et al., Int. J. Hydrogen Energy 2024, 56)

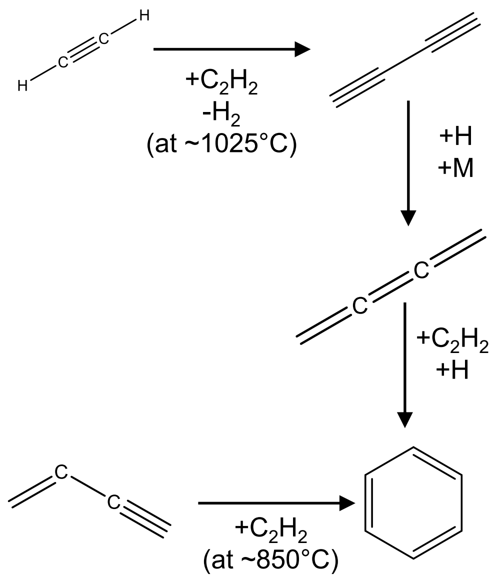
Catalyst Activity Tests – Results CB Pearls 2000

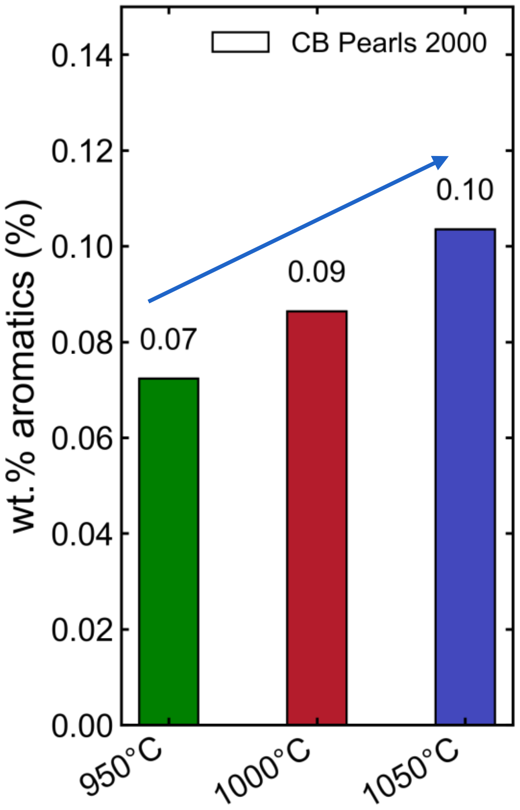
CB Pearls 2000 – 950 à 1050°C – 1.1 bar – WHSV 330 hr^{-1}



POLYAROMATIC HYDROCARBONS

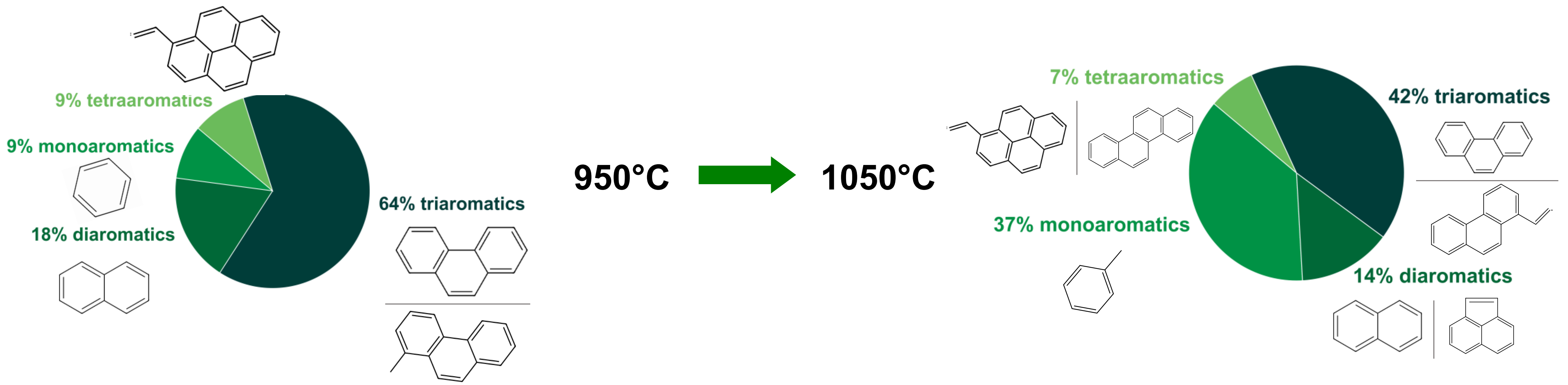
Increase of Polyaromatic Hydrocarbons concentration in product stream along with increase in acetylene outlet concentration



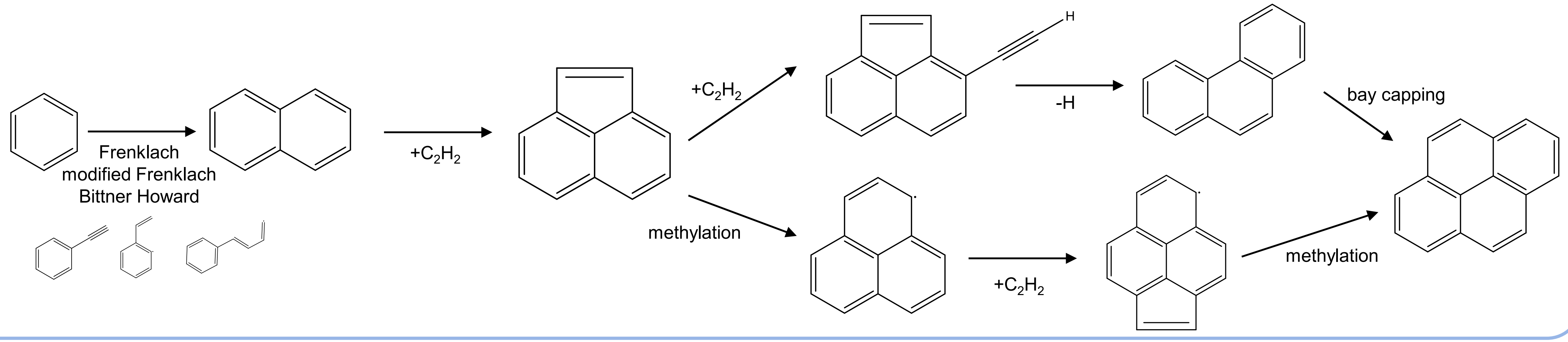


Catalyst Activity Tests – Results CB Pearls 2000

EXPERIMENTS



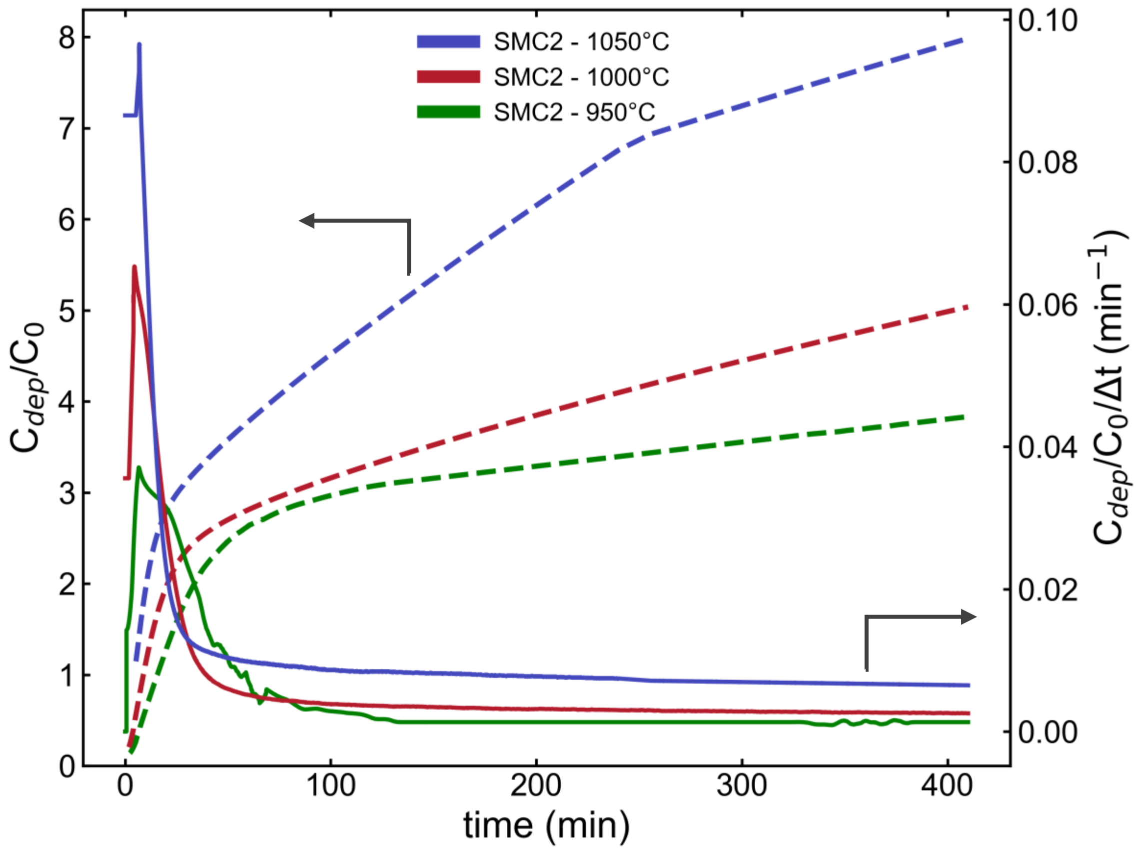
KINETICS THEORY

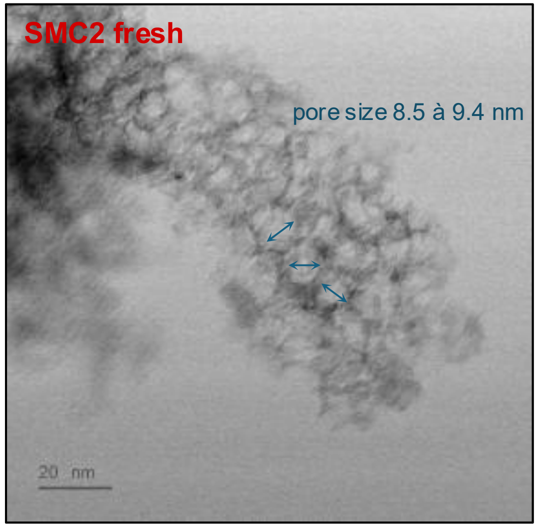


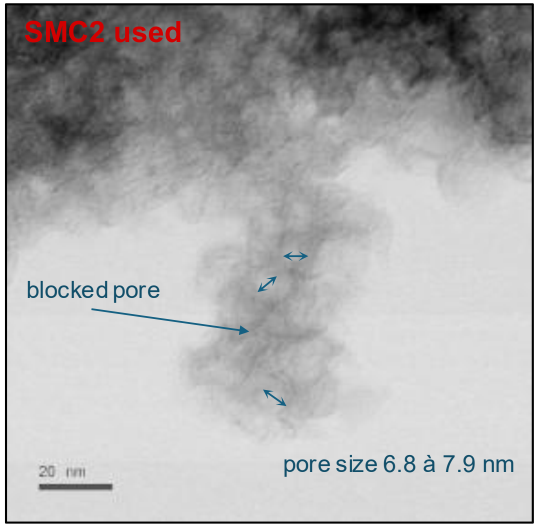
(T. Chu et al., Phys. Chem. Chem. Phys. 2019, 21)
(M. Frenklach et al., Proc. Combust. Inst. 2019, 37)
(M. Frenklach et al., Phys. Chem. Chem. Phys. 2024, 26)

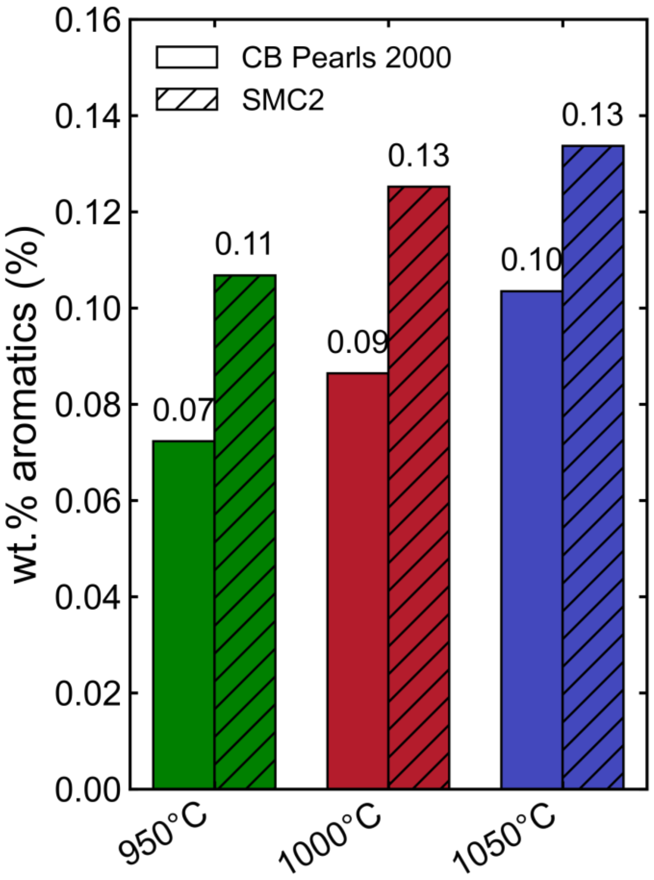
Catalyst Activity Tests – Results SMC2

SMC2 – 950 à 1050°C – 1.1 bar – WHSV 330 hr^{-1}









Larger concentration of polyaromatic hydrocarbons for SMC2 compared to CB Pearls 2000

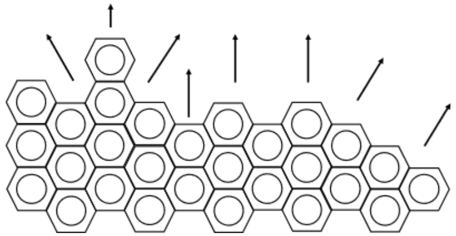
Catalyst Structural Changes

CARBON PRODUCT?

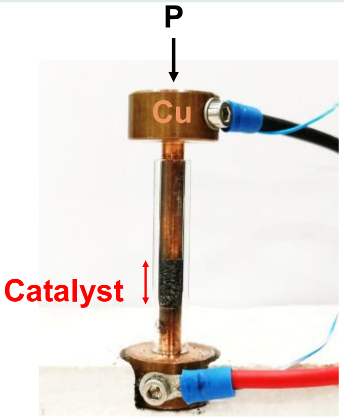
$CH_4 \rightleftharpoons 2H_2 + C_{solid}$ → **graphite-like**

Characterization

- XRD
- XPS (dislocations and heterogeneities ↓)
- STEM (graphene layer formation)
- Raman (I_D/I_G ↑)



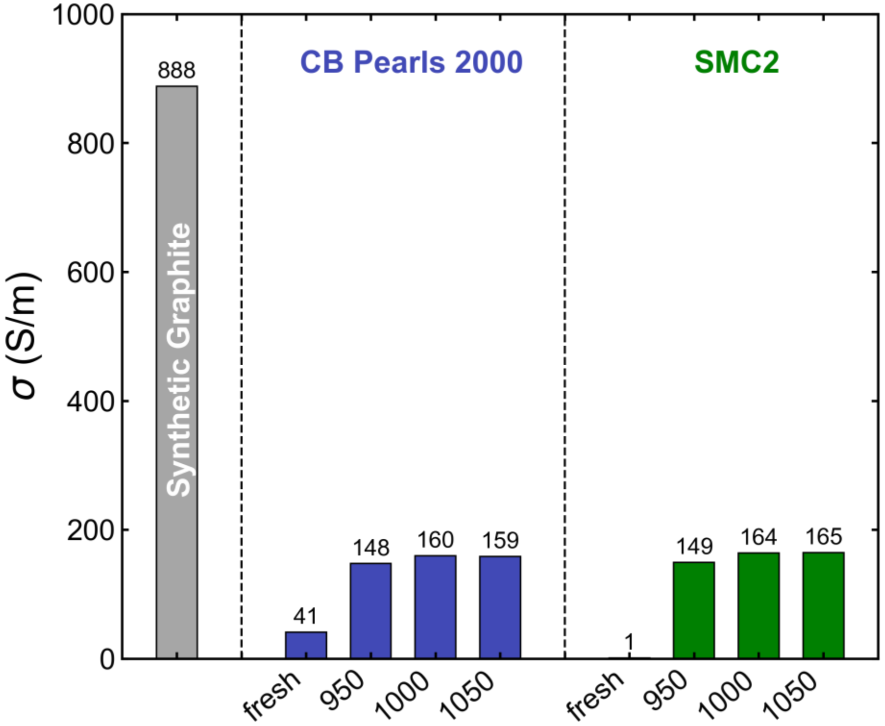
ELECTRICAL IMPEDANCE SPECTROSCOPY



- voltage = 2 V
- 40 Hz – 40 kHz AC
- quasi Ohmic behaviour
- P = 0.3 MPa

$$\sigma = \frac{l}{RA}$$

ELECTRICAL CONDUCTIVITY CATALYST



graphitic carbon deposition → higher σ

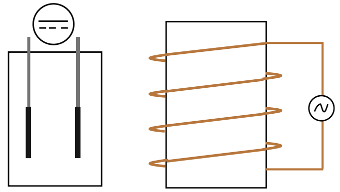
CB Pearls 2000

- higher σ than SMC2
- 41 S/m fresh
- ~160 S/m after 7 hours of reaction

SMC2

- 1 S/m fresh
- ~165 S/m after 7 hours of reaction

electrification

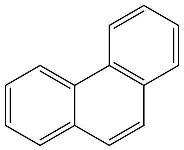


Key takeaways

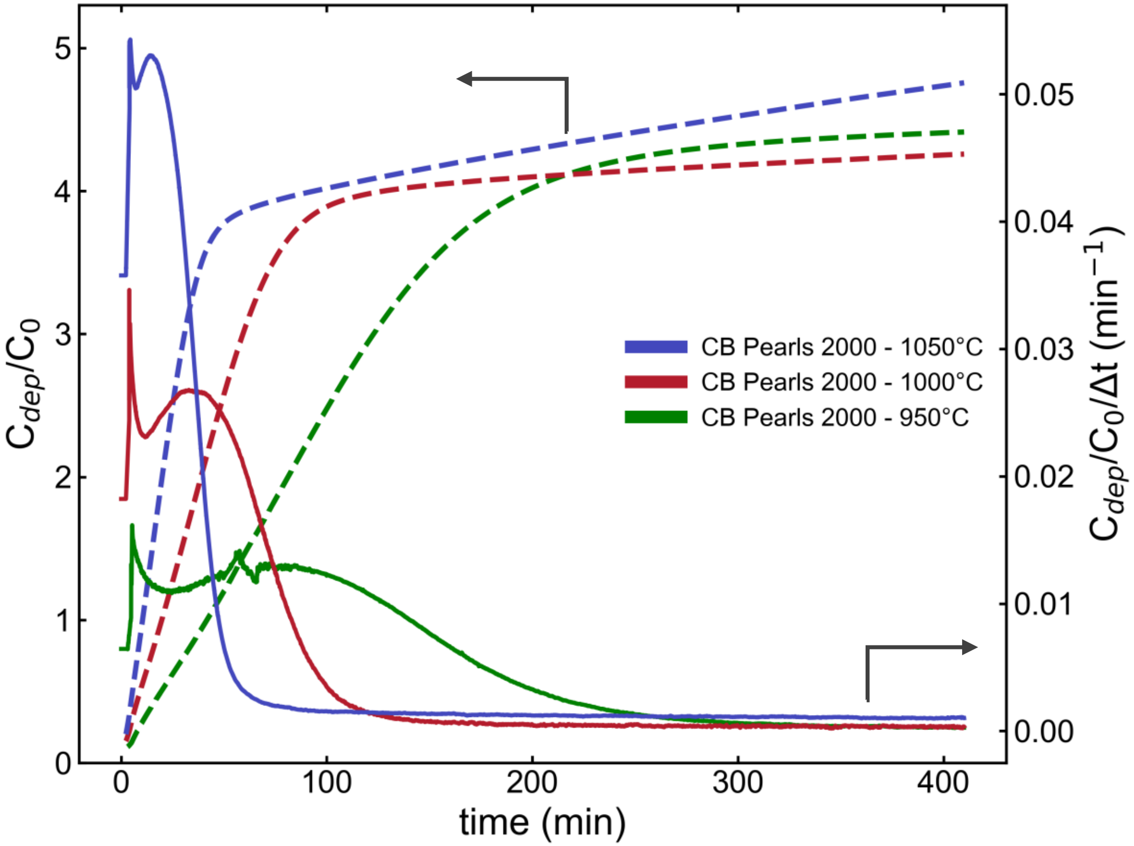
1. Methane pyrolysis for reduced emissions

2. SMC2 highest carbon yield
→ also more aromatics

3. Higher T → higher fraction of aromatics
→ largest fraction triaromatics



4. graphitic carbon → higher σ
→ potential for electrified reactors



Acknowledgments

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FWOSPB2024003001

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European Research Council

Established by the European Commission

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