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Catalytic Processes for Gas Conversion

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(New) catalytic processes for production at different scale

Large scale, integrated petrochemical complexes due to economy of scale

Exxon Mobil's largest integrated manufacturing complex located in Singapore

BASF's largest verbund site located in Ludwigshafen, Germany

Small scale, decentralized chemical plants closer to alternative feedstocks

Fulcrum bioFuels plant located in Nevada, USA
Strategically located adjacent to waste landfill

Vision and Strategies

1. Circular carbon feedstock
   (only viable with green H_2):
   CO_2, flue gas, biogas, municipal waste
   Includes natural gas (no green H_2)

2. Waste stream processing/ upgrading
- Impure/ mix streams = requires purification/ separation = higher costs
- Depends on scale of operation

Research themes in my sub-group: dynamic and intensified catalytic processes

1. 'drop-in' synthetic fuels via Fischer-Tropsch Synthesis (FTS)
2. new catalysts and processes for CO_2/CO to chemicals
3. 'drop-in' synthetic fuels and chemicals via plastics hydrogenolysis – together with Prof. Erik Heeres

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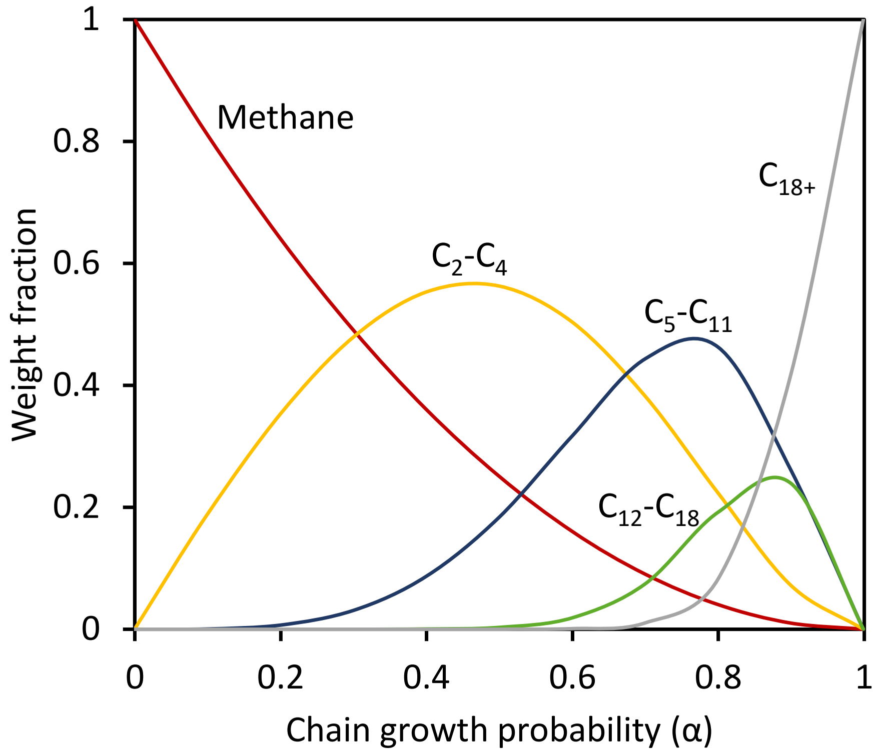
Fischer-Tropsch Synthesis

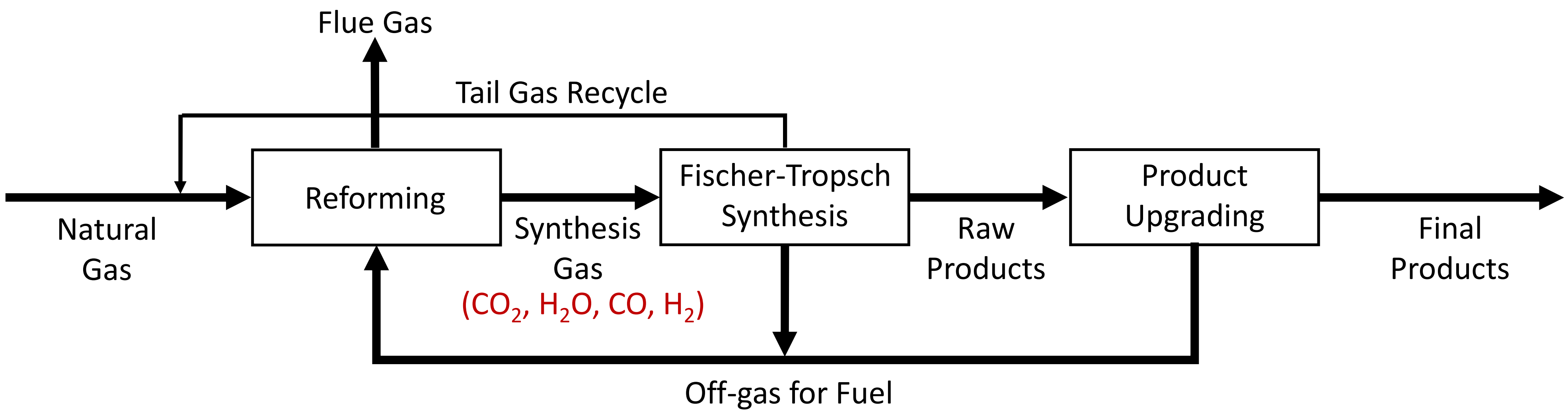
Fischer-Tropsch Synthesis: $n\,CO + (2n+1)\,H_2 \rightarrow C_nH_{2n+2} + n\,H_2O$ $\Delta H = -165$ kJ/mol



Fischer-Tropsch Synthesis

Steam methane reforming: $CH_4 + H_2O \rightleftharpoons CO + 3\ H_2$ $\Delta H = 206$ kJ/mol

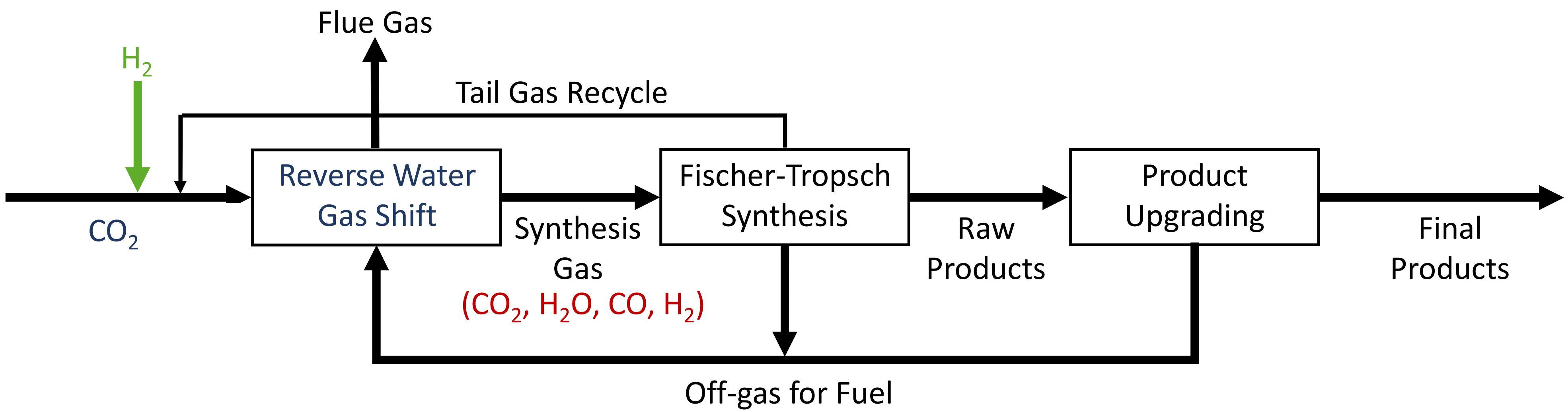
Fischer-Tropsch Synthesis: $n\ CO + (2n+1)\ H_2 \rightarrow C_nH_{2n+2} + n\ H_2O$ $\Delta H = -165$ kJ/mol



Fischer-Tropsch Synthesis

Reverse Water Gas Shift: $CO_2 + H_2 \rightleftharpoons CO + H_2O$ ΔH = 41 kJ/mol

Fischer-Tropsch Synthesis: $n\ CO + (2n+1)\ H_2 \rightarrow C_nH_{2n+2} + n\ H_2O$ ΔH = -165 kJ/mol



Reverse Water Gas Shift

Reverse Water Gas Shift: $CO_2 + H_2 \rightleftharpoons CO + H_2O$ $\Delta H = 41$ kJ/mol

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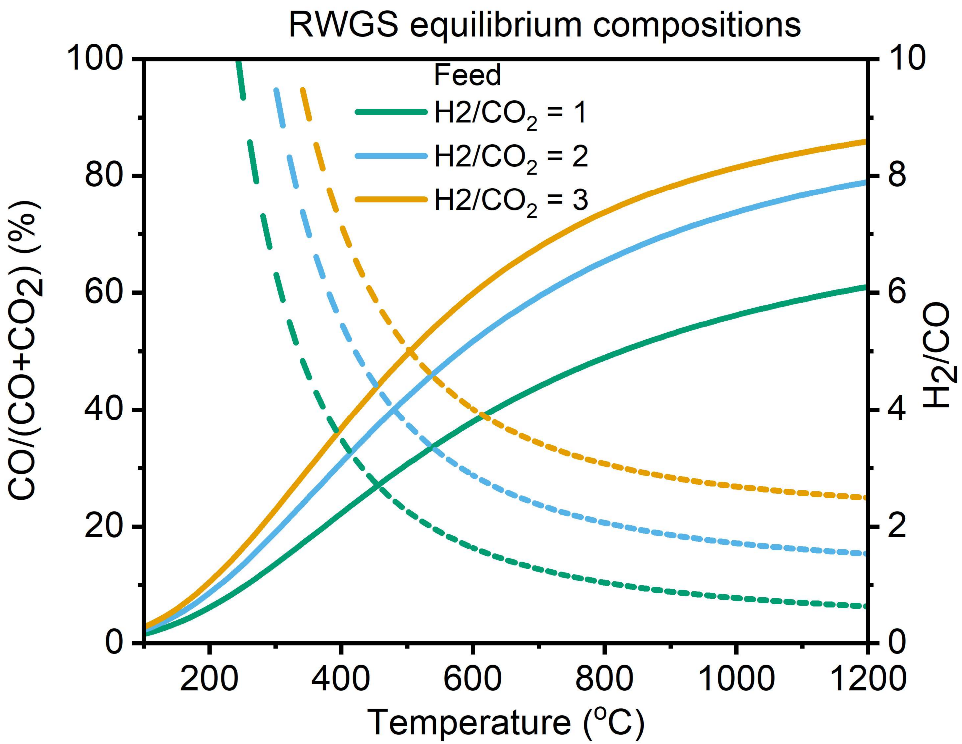
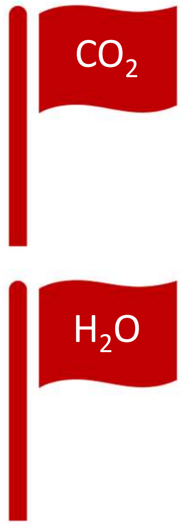
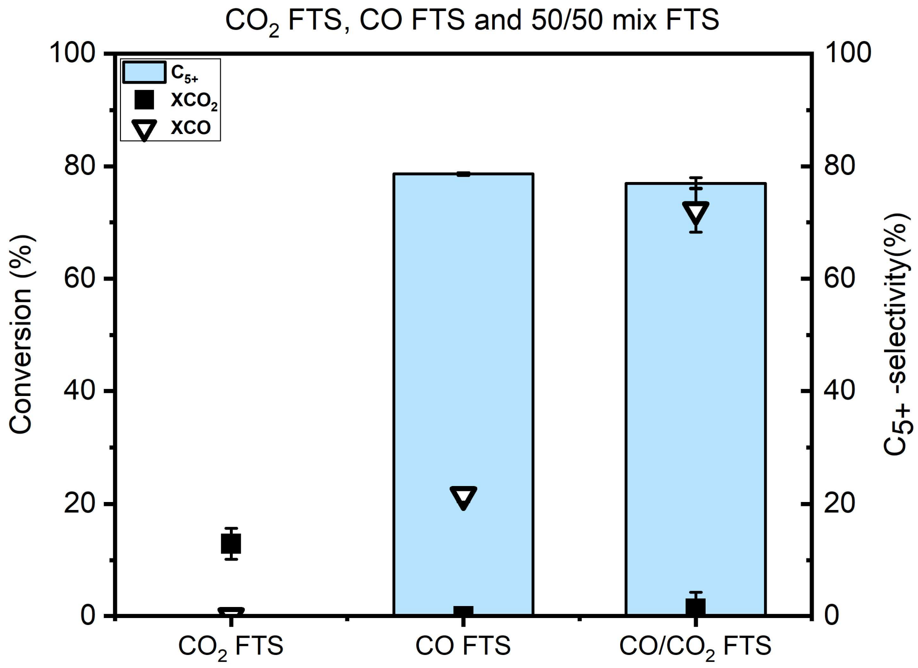


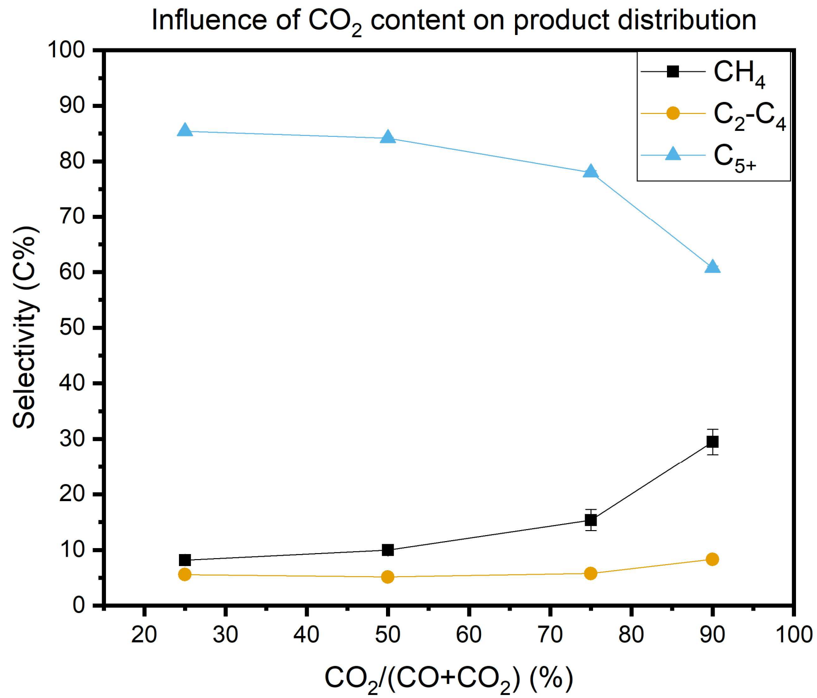


Influence of CO_2 in FTS

CO_2

Reverse Water Gas Shift:	$CO_2 + H_2 \rightleftharpoons CO + H_2O$	ΔH = 41 kJ/mol
Fischer-Tropsch Synthesis:	$n\ CO + (2n+1)\ H_2 \rightarrow C_nH_{2n+2} + n\ H_2O$	ΔH = -165 kJ/mol



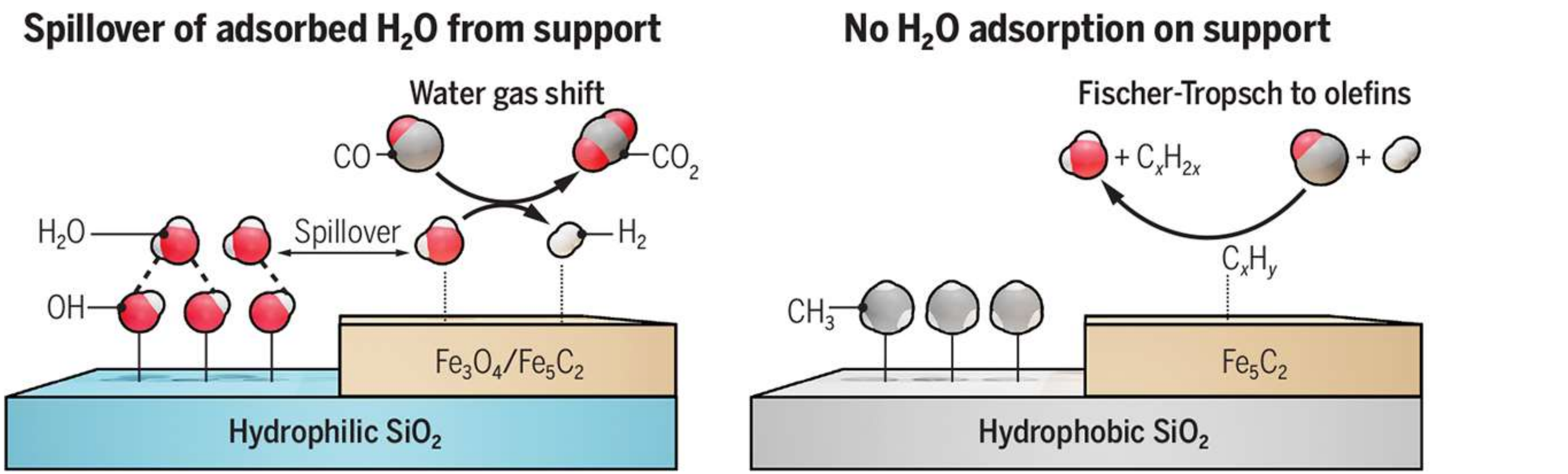


220 °C, 21 bar, CO_2 FTS with H_2/CO_2=3/1, FTS H_2/CO=2/1 and CO/CO_2 FTS with $H_2/CO_2/CO$=5/1/1

Influence of H_2O in FTS

Reverse Water Gas Shift: $CO_2 + H_2 \rightleftharpoons CO + H_2O$ $\Delta H = 41$ kJ/mol

Fischer-Tropsch Synthesis: $n\,CO + (2n+1)\,H_2 \rightarrow C_nH_{2n+2} + n\,H_2O$ $\Delta H = -165$ kJ/mol



H2O

J. Xie. *Science*. **2021**, 371, 577

Influence of H_2O in FTS

Reverse Water Gas Shift: $CO_2 + H_2 \rightleftharpoons CO + H_2O$ ΔH = 41 kJ/mol

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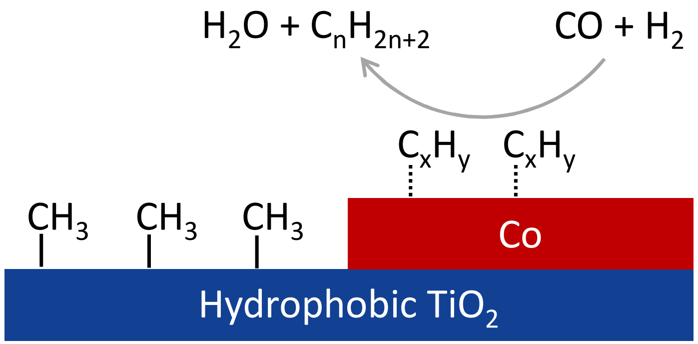
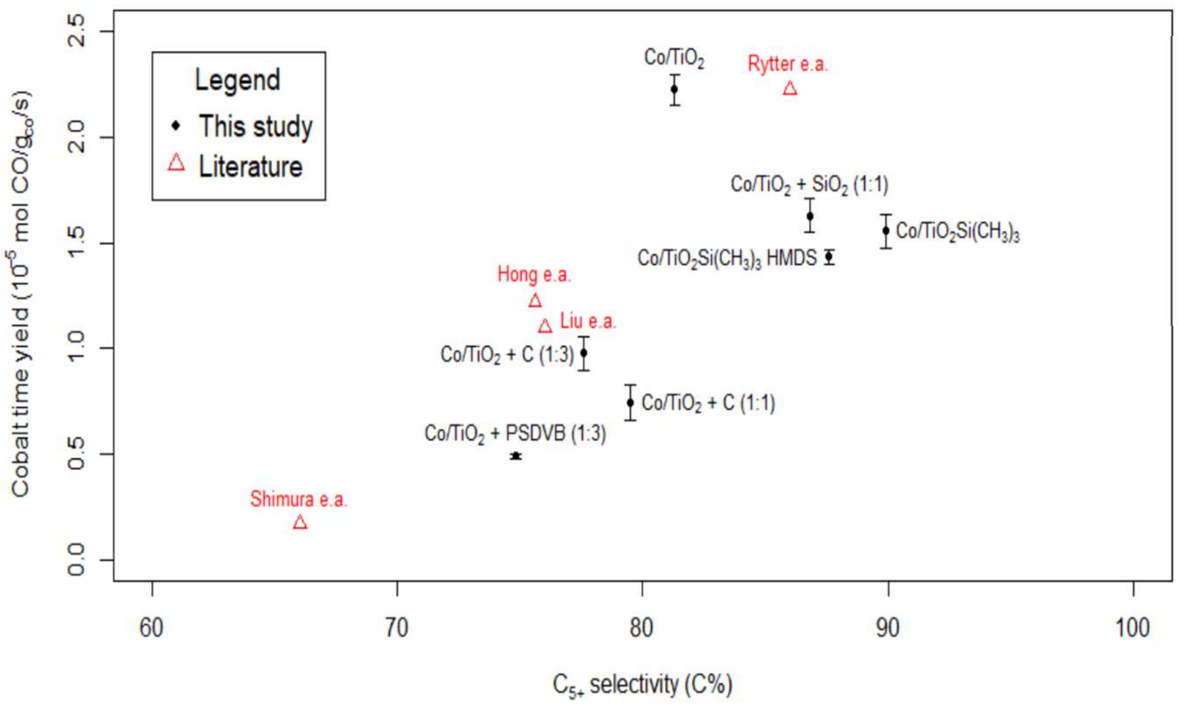
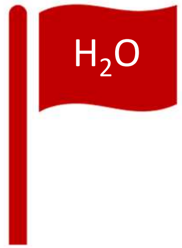


No H_2O adsorption on support



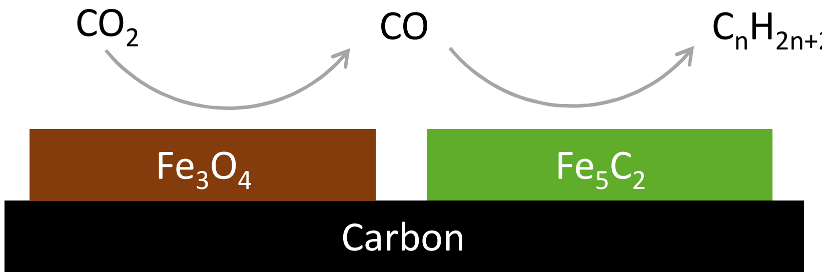


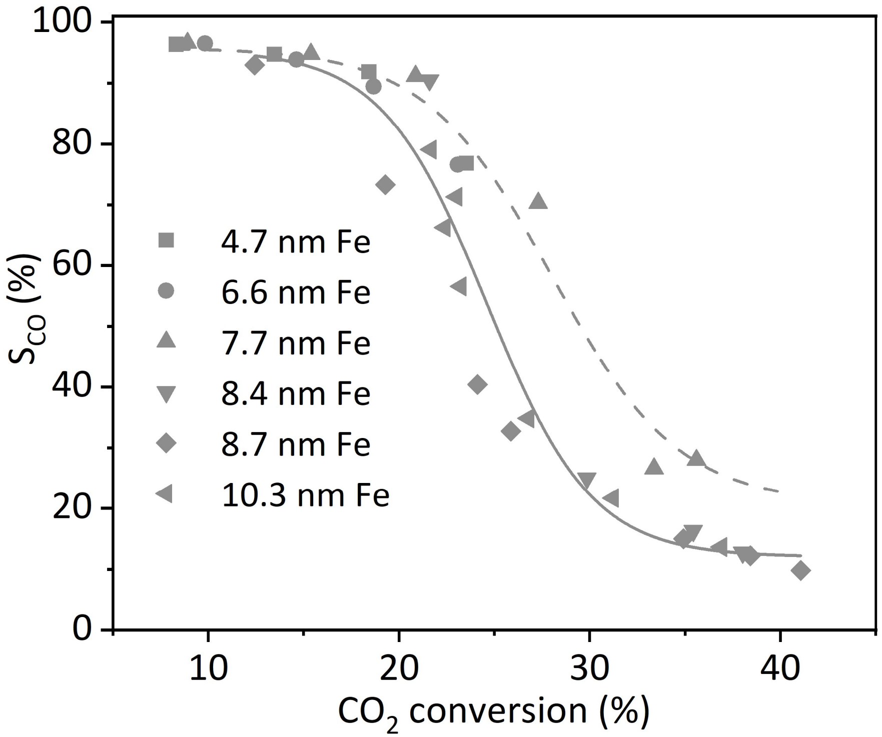
220 °C, 21 bar, $H_2/CO = 2$, CO conversion less than 10 %

CO_2-FTS

Reverse Water Gas Shift: $CO_2 + H_2 \rightleftharpoons CO + H_2O$ ΔH = 41 kJ/mol

Fischer-Tropsch Synthesis: $n\ CO + (2n+1)\ H_2 \rightarrow C_nH_{2n+2} + n\ H_2O$ ΔH = -165 kJ/mol





300 °C, 11 bar, H_2/CO_2 = 3, 600 - 72000 $mL \cdot g_{cat}^{-1} \cdot h^{-1}$

W. Meng, B.C.A. de Jong, J. Xie et al. *Chem. Eng. J.* **2024**

CO2-FTS

Reverse Water Gas Shift: $CO_2 + H_2 \rightleftharpoons CO + H_2O$ ΔH = 41 kJ/mol

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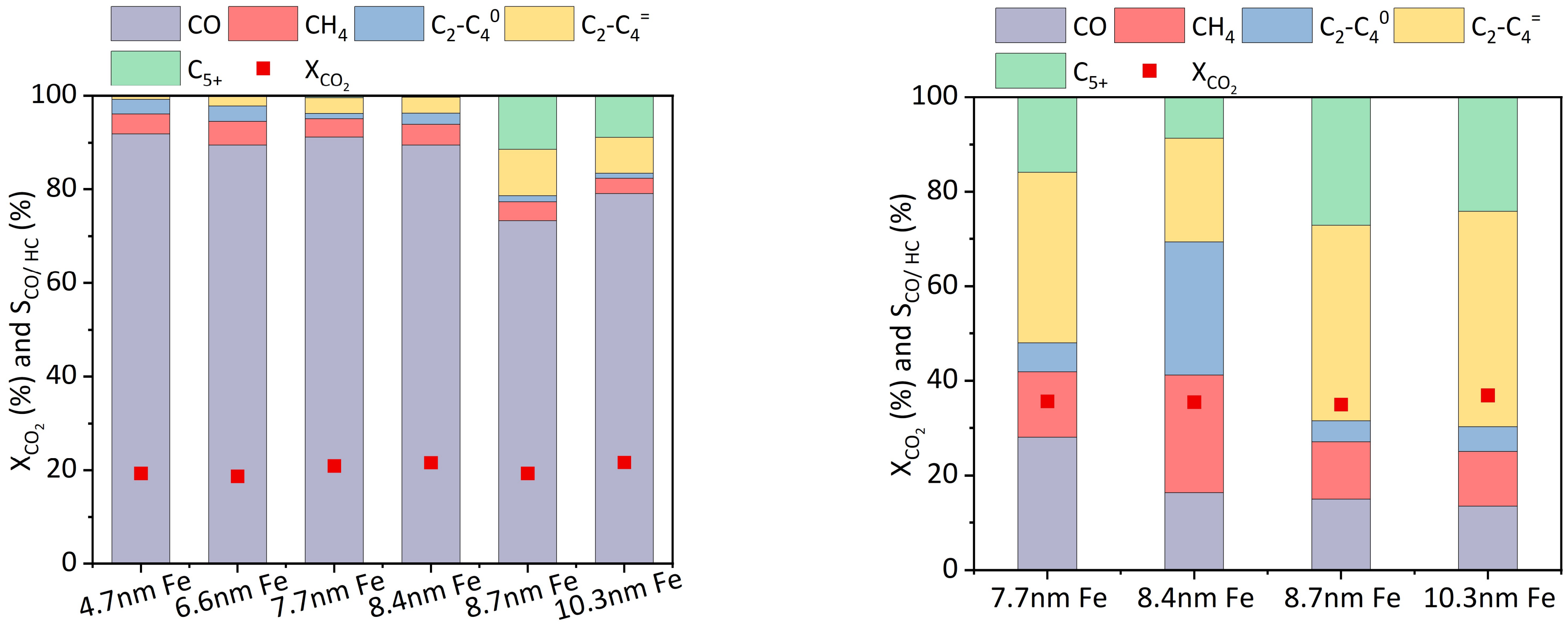
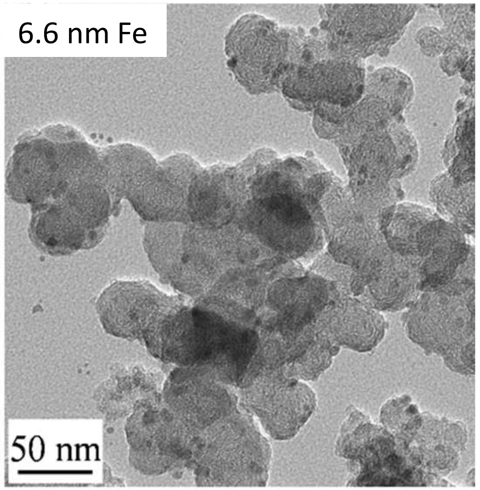
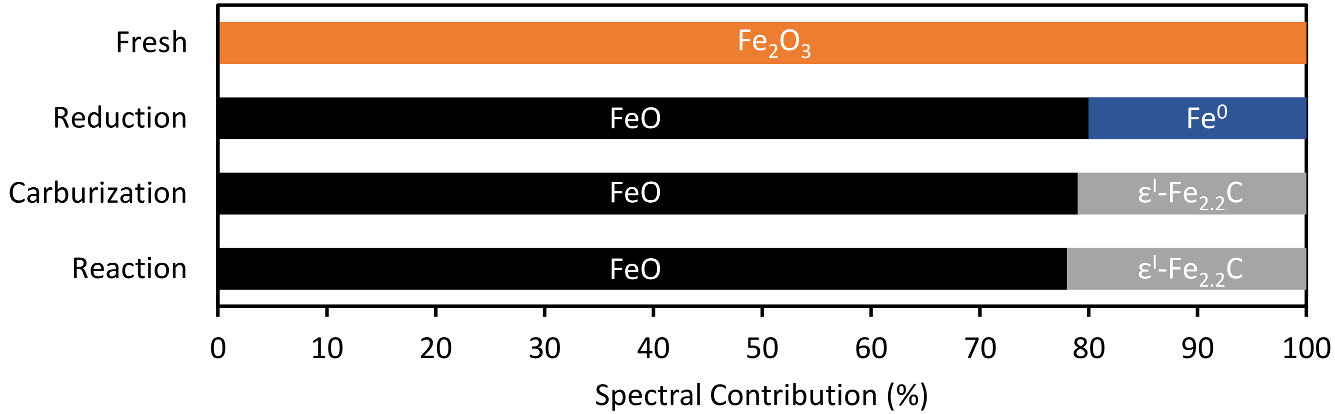
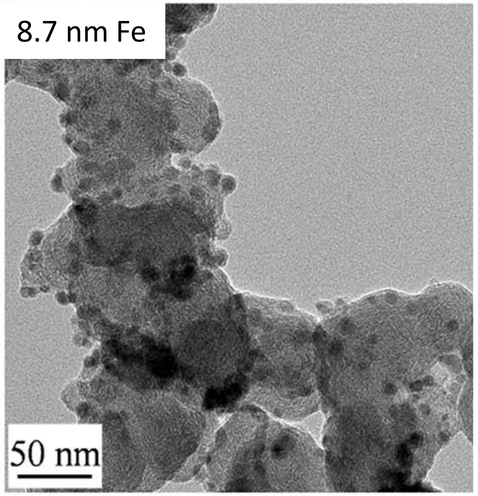


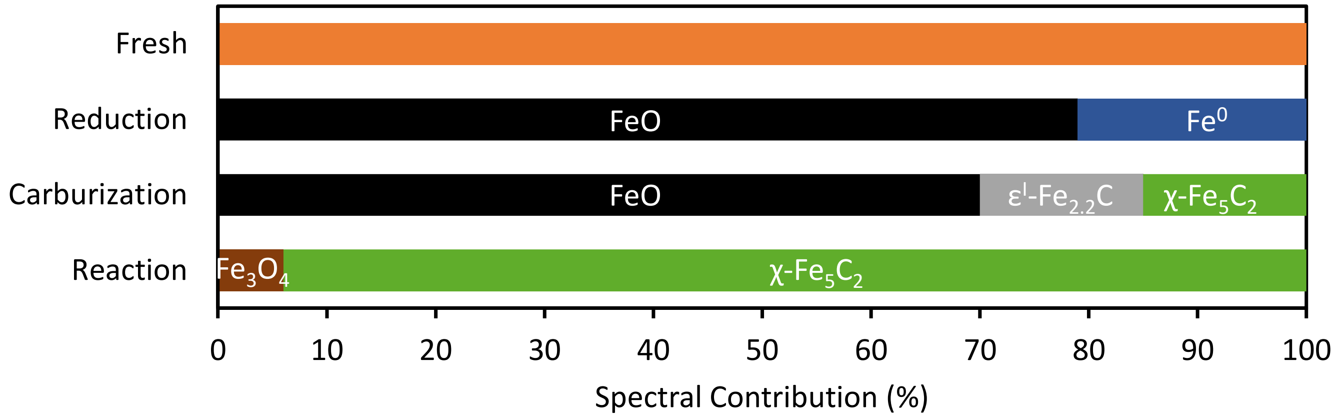
300 °C, 11 bar, H_2/CO_2 = 3, 600 - 72000 mL·g_{cat}^{-1}·h^{-1}

CO_2-FTS

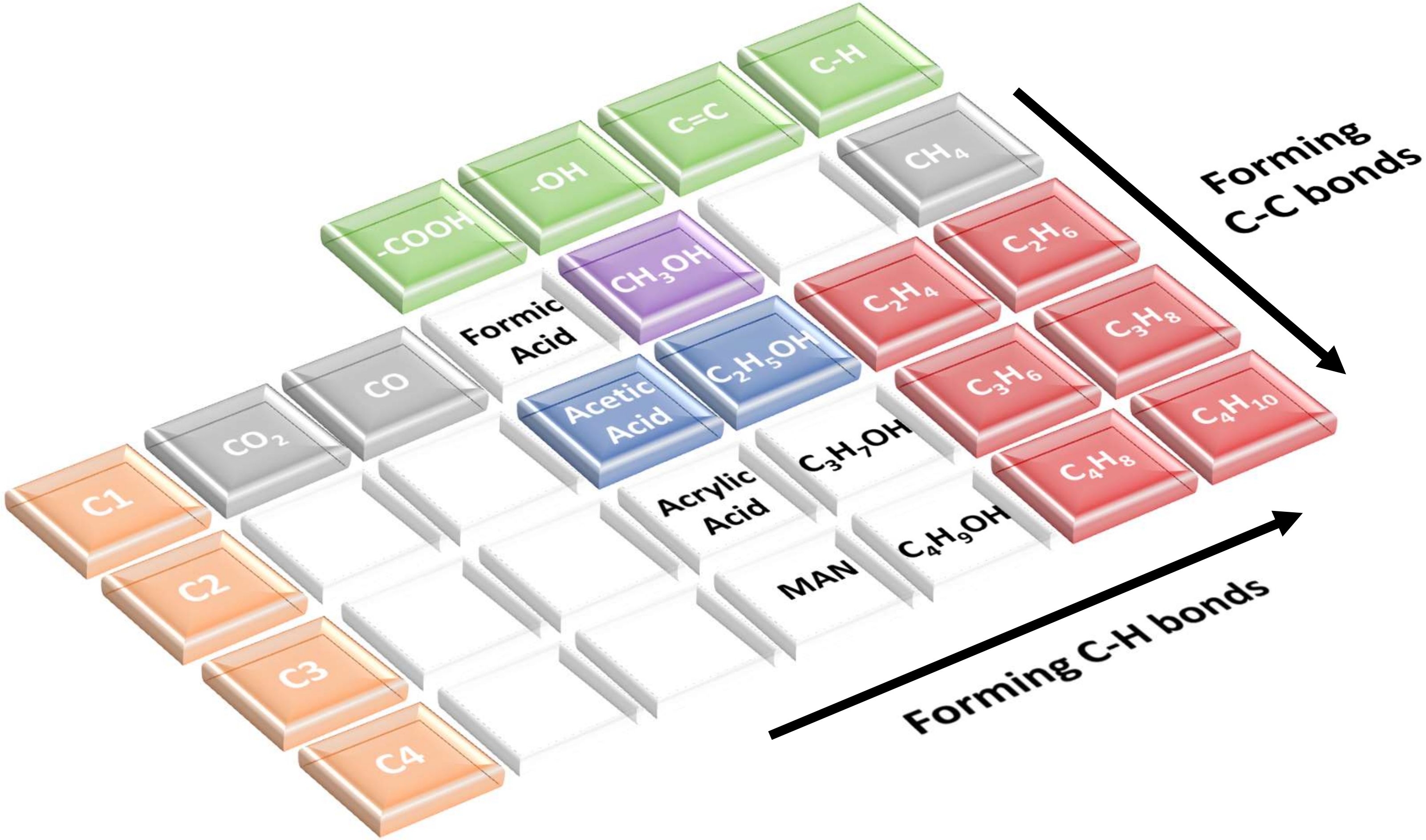

6.6 nm Fe
50 nm


Fresh
Reduction
Carburization
Reaction
Fe_2O_3
FeO
Fe^0
FeO
ε^I-$Fe_{2.2}C$
FeO
ε^I-$Fe_{2.2}C$
0
10
20
30
40
50
60
70
80
90
100
Spectral Contribution (%)


8.7 nm Fe
50 nm


Fresh
Reduction
Carburization
Reaction
FeO
Fe^0
FeO
ε^I-$Fe_{2.2}C$
χ-Fe_5C_2
Fe_3O_4
χ-Fe_5C_2
0
10
20
30
40
50
60
70
80
90
100
Spectral Contribution (%)

New catalysts and processes



Intensified CO_2 to Hydrocarbons

Methanol synthesis (R1) — **Methanol conversion (MTO) (R2)**

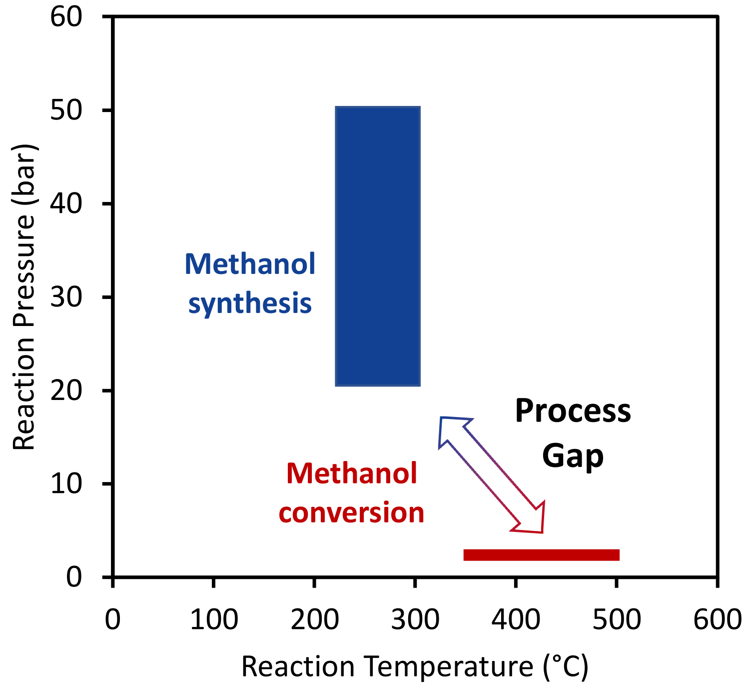
CO_2 ⇌ CH_3OH ⇌ Dimethyl ether ⇌ Hydrocarbons

Advantages:

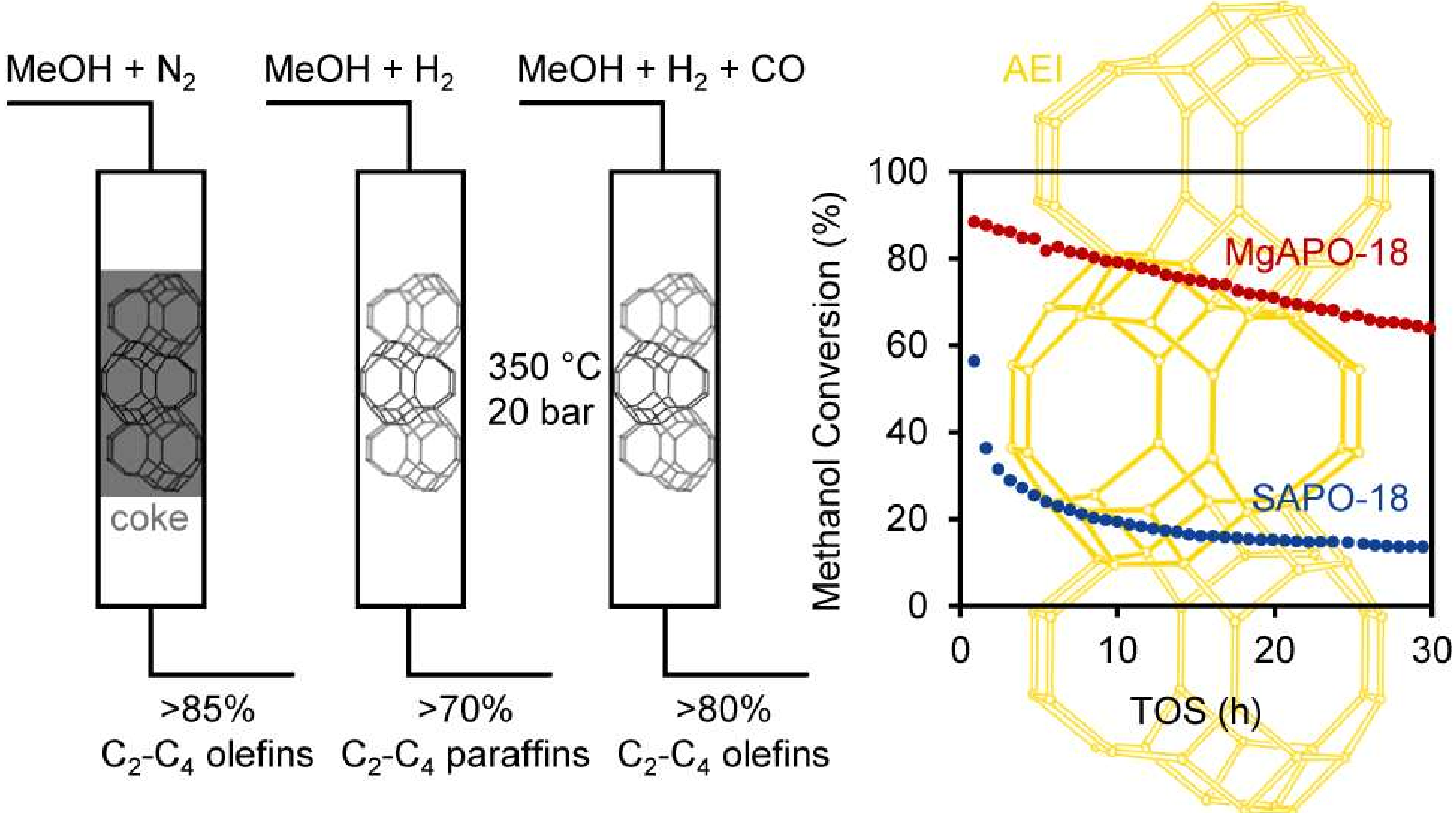
- Shift thermodynamic equilibrium (R1) = less recycling
- Fluidised bed to fixed-bed reactor (R2)
- Reduce separation and purification units
- Savings in energy and costs

Challenges:

- Process conditions
- Catalysts
- Hydrogenation of olefin products



Intensified Methanol to Olefins



J. Xie et al. *ACS Catal.* **2022**, 12, 1520

Intensified CO_2 to Hydrocarbons

CHEMICAL REVIEWS

pubs.acs.org/CR Review

The Oxygenate-Mediated Conversion of CO_x to Hydrocarbons—On the Role of Zeolites in Tandem Catalysis

Jingxiu Xie and Unni Olsbye*

Cite This: https://doi.org/10.1021/acs.chemrev.3c00058 Read Online

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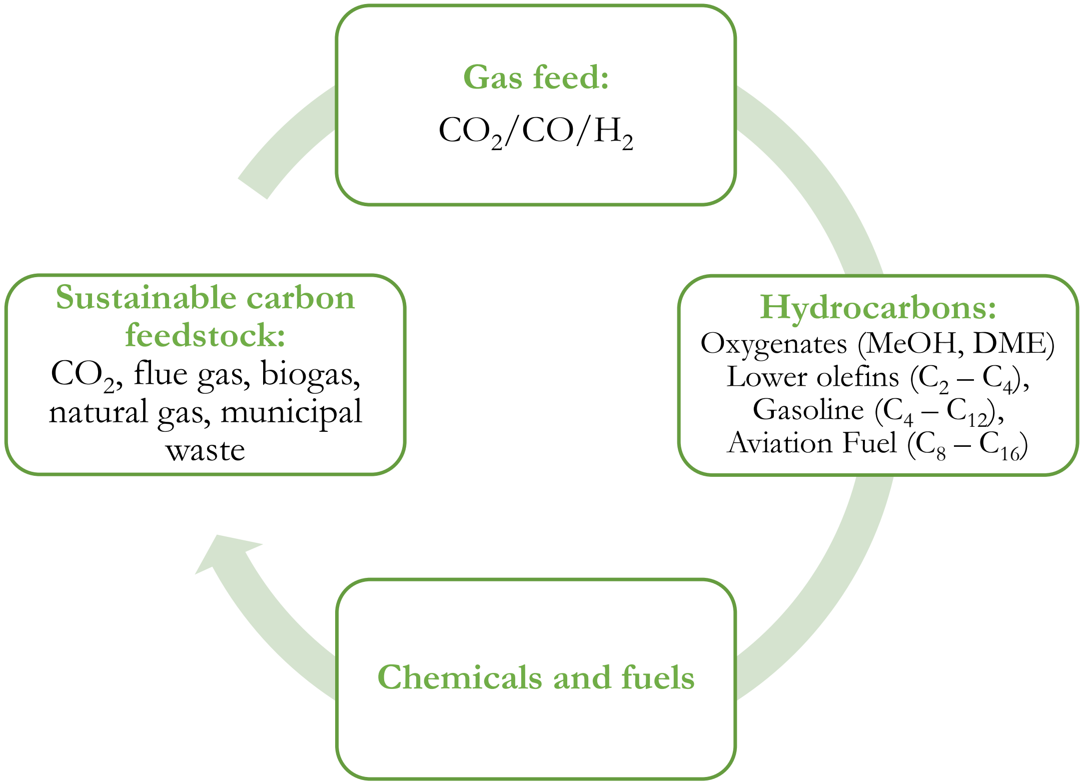

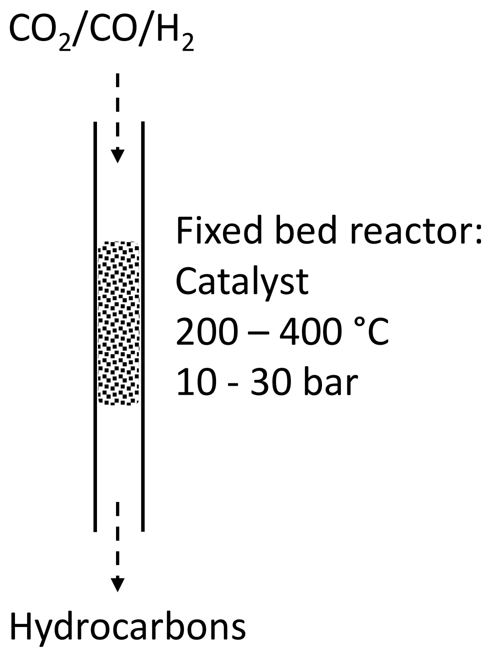

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