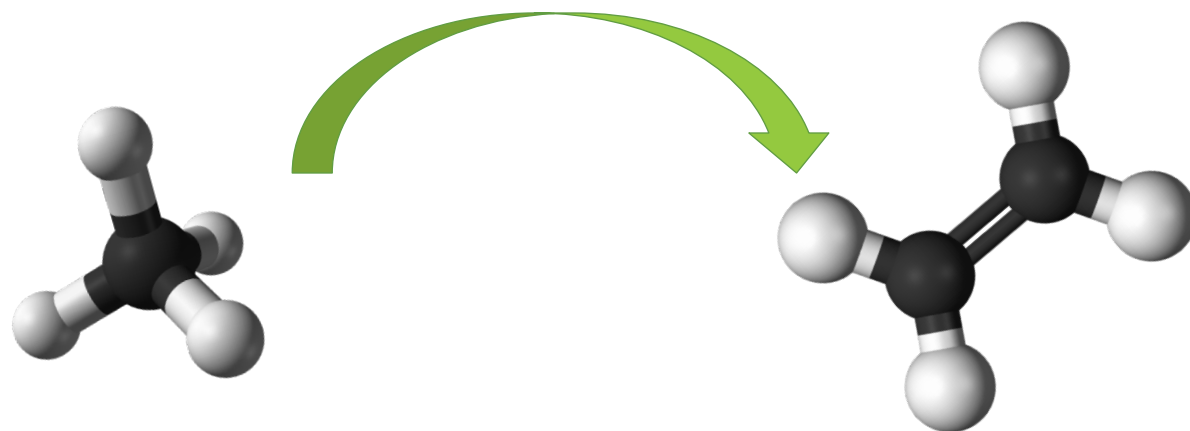


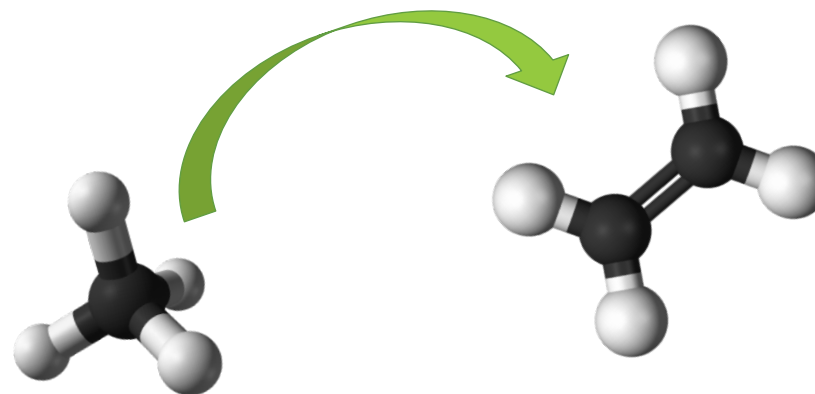
Oxidative conversion of methane on shaped catalyst

CNRS
Jordan Guillemot
Yves Schuurman
David Farrusseng



Content

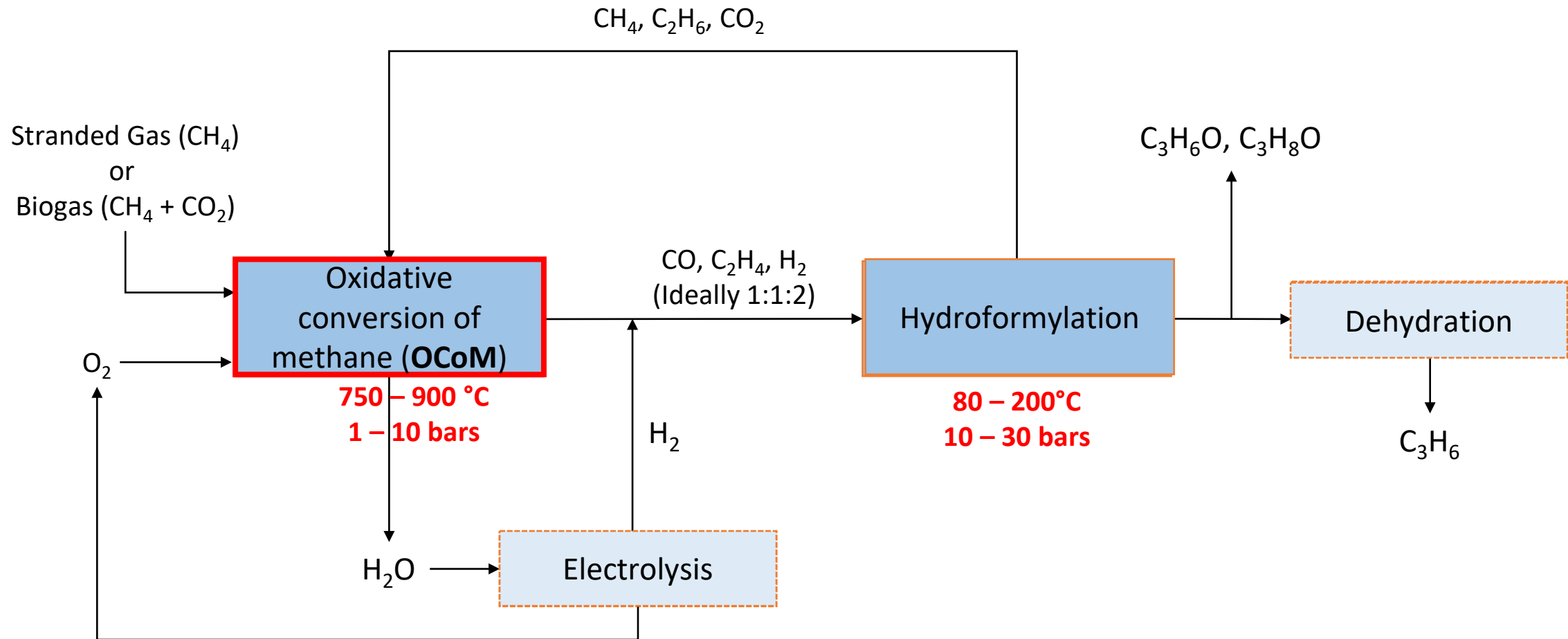
1. Introduction
 1. CNRS tasks in C123
 2. OCM vs. OCoM
 3. Test Rig
2. Results on catalytic powders – Effects of
 1. CO₂
 2. Reactor pressure
3. Results on supported catalyst – Effects of
 1. CO₂
 2. Reaction temperature
4. Conclusions & perspectives



Introduction

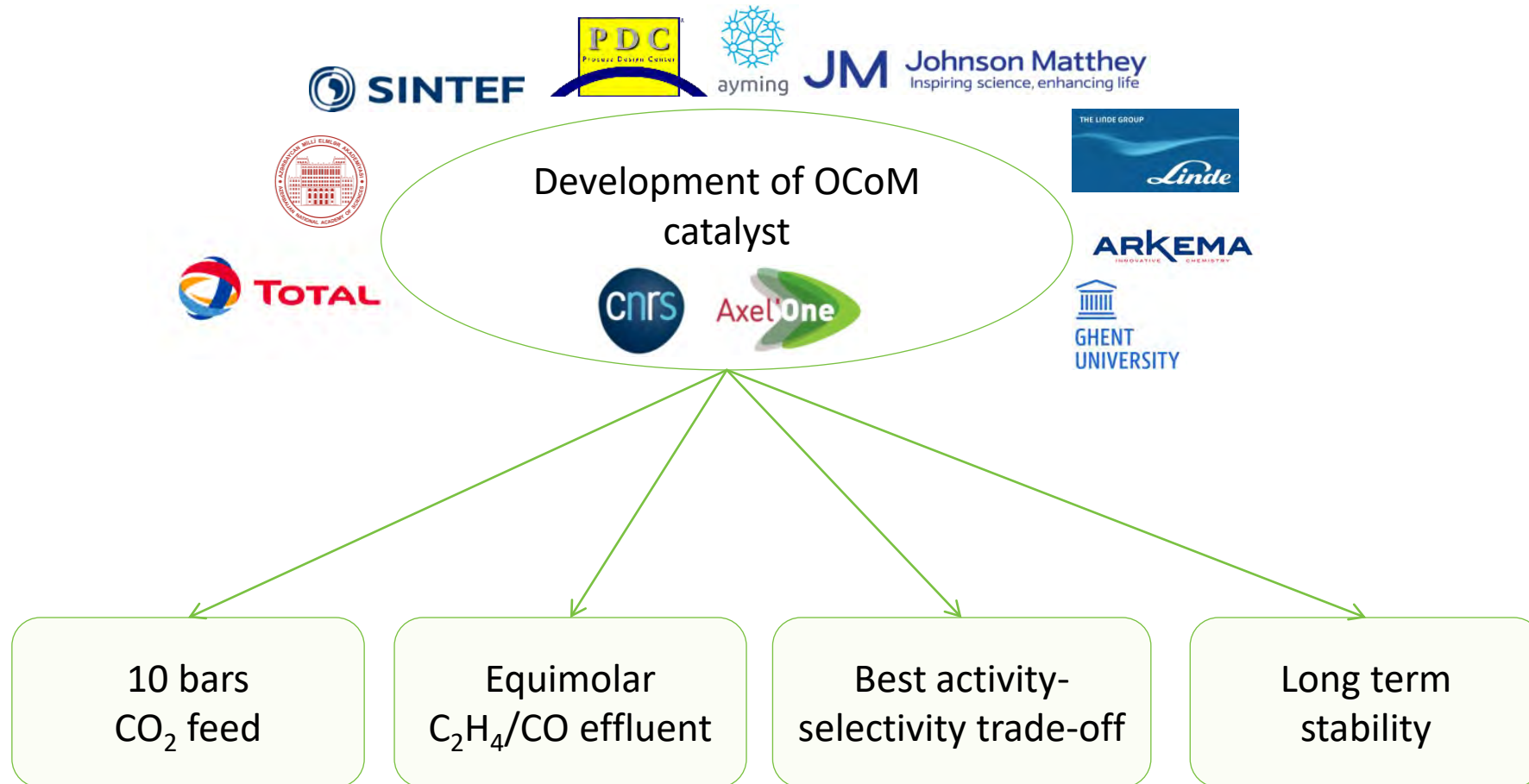
Introduction

- CNRS tasks in C123



Introduction

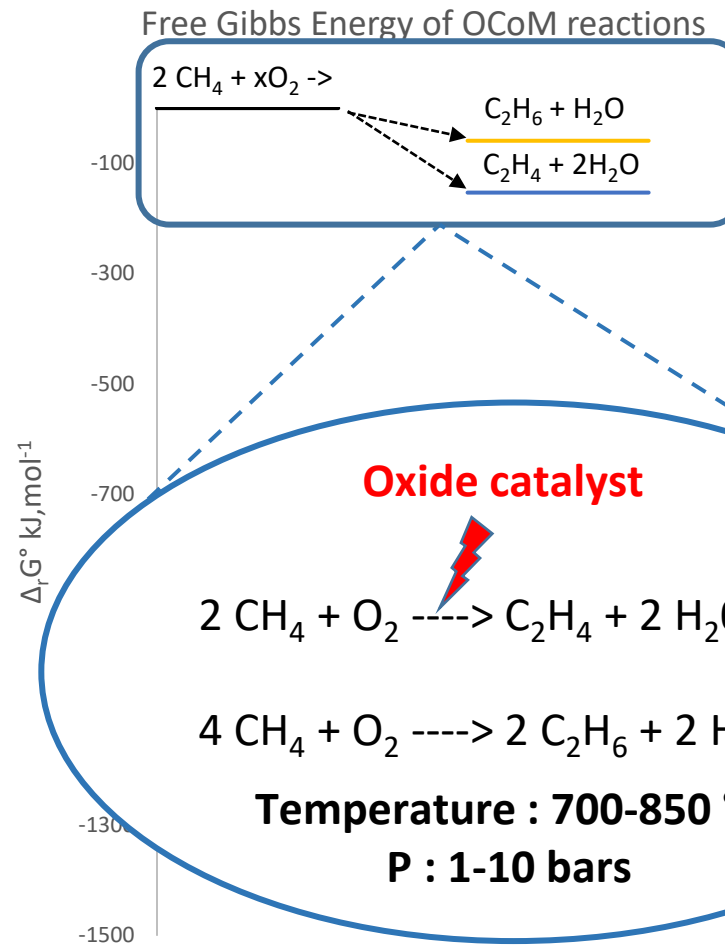
- OCoM specifications



Introduction

■ OCoM reaction

Introduced by Keller and Bhasin in 1982



High exothermicity

1 $\Delta_r G^\circ(800^\circ\text{C}) = -59 \text{ kJ}\cdot\text{mol}^{-1}$

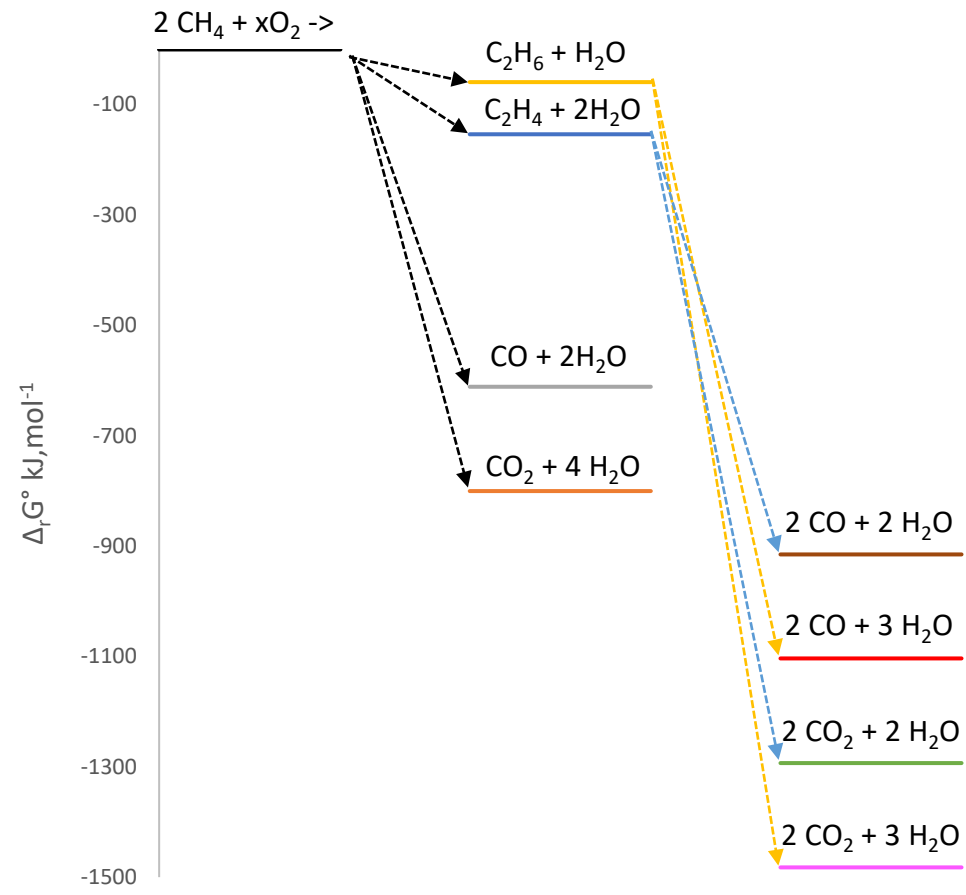
2 $\Delta_r G^\circ(800^\circ\text{C}) = -153 \text{ kJ}\cdot\text{mol}^{-1}$

Introduction

- OCoM reaction

Total oxidations are thermodynamically favored

Free Gibbs Energy of OCoM reactions



- 1 $\Delta_r G^\circ(800^\circ\text{C}) = -59 \text{ kJ}\cdot\text{mol}^{-1}$
- 2 $\Delta_r G^\circ(800^\circ\text{C}) = -153 \text{ kJ}\cdot\text{mol}^{-1}$
- 3 $\Delta_r G^\circ(800^\circ\text{C}) = -611 \text{ kJ}\cdot\text{mol}^{-1}$
- 4 $\Delta_r G^\circ(800^\circ\text{C}) = -800 \text{ kJ}\cdot\text{mol}^{-1}$
- 5 $\Delta_r G^\circ(800^\circ\text{C}) = -915 \text{ kJ}\cdot\text{mol}^{-1}$
- 6 $\Delta_r G^\circ(800^\circ\text{C}) = -1104 \text{ kJ}\cdot\text{mol}^{-1}$
- 7 $\Delta_r G^\circ(800^\circ\text{C}) = -1293 \text{ kJ}\cdot\text{mol}^{-1}$
- 8 $\Delta_r G^\circ(800^\circ\text{C}) = -1482 \text{ kJ}\cdot\text{mol}^{-1}$

Introduction

■ OCM state of the art catalysts

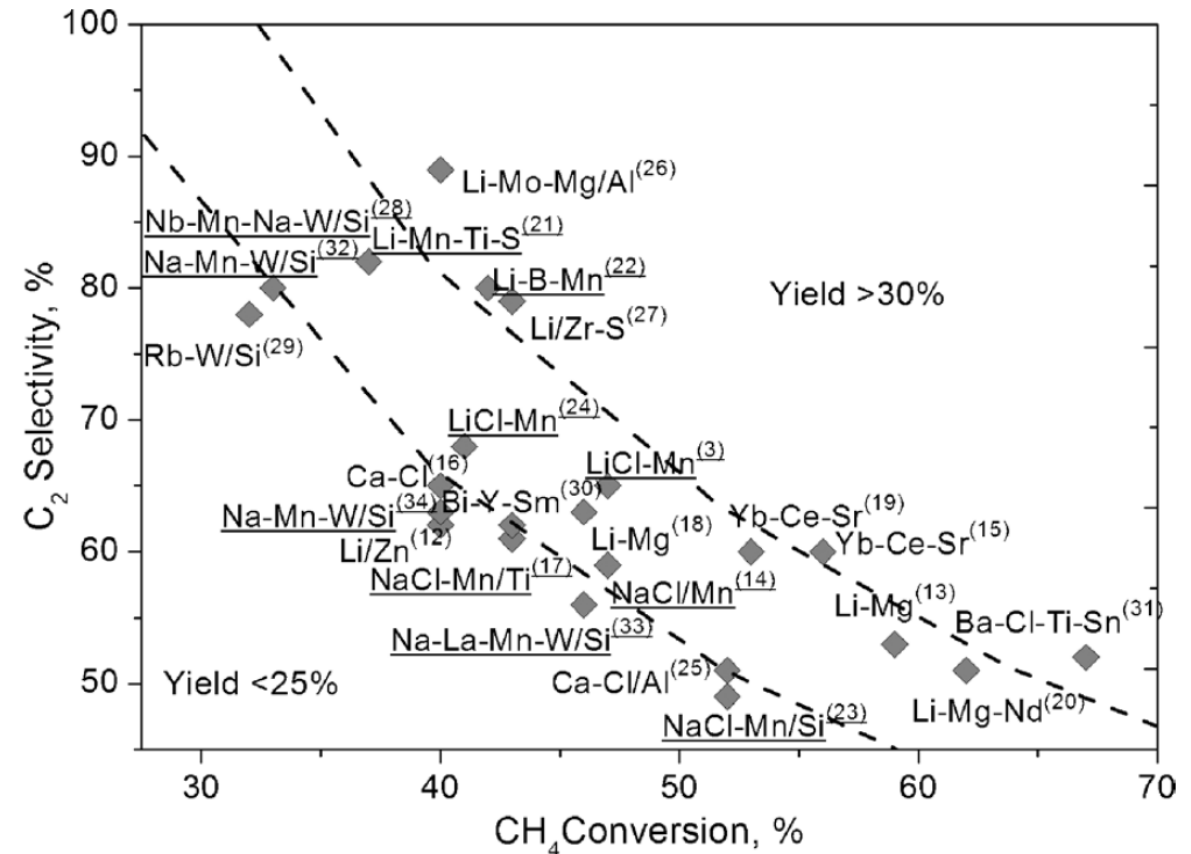
Mn- & La-based catalyst

- Good C₂ yield (selectivity vs activity)
- Good thermal stability (harsh operating conditions)
- Unsupported (powder) catalysts

■ Objective for OCoM

Development of a supported catalyst

- Catalytically inert at high temperature
- Good thermal conductivity (exothermicity)
- Without mass transfert limitation



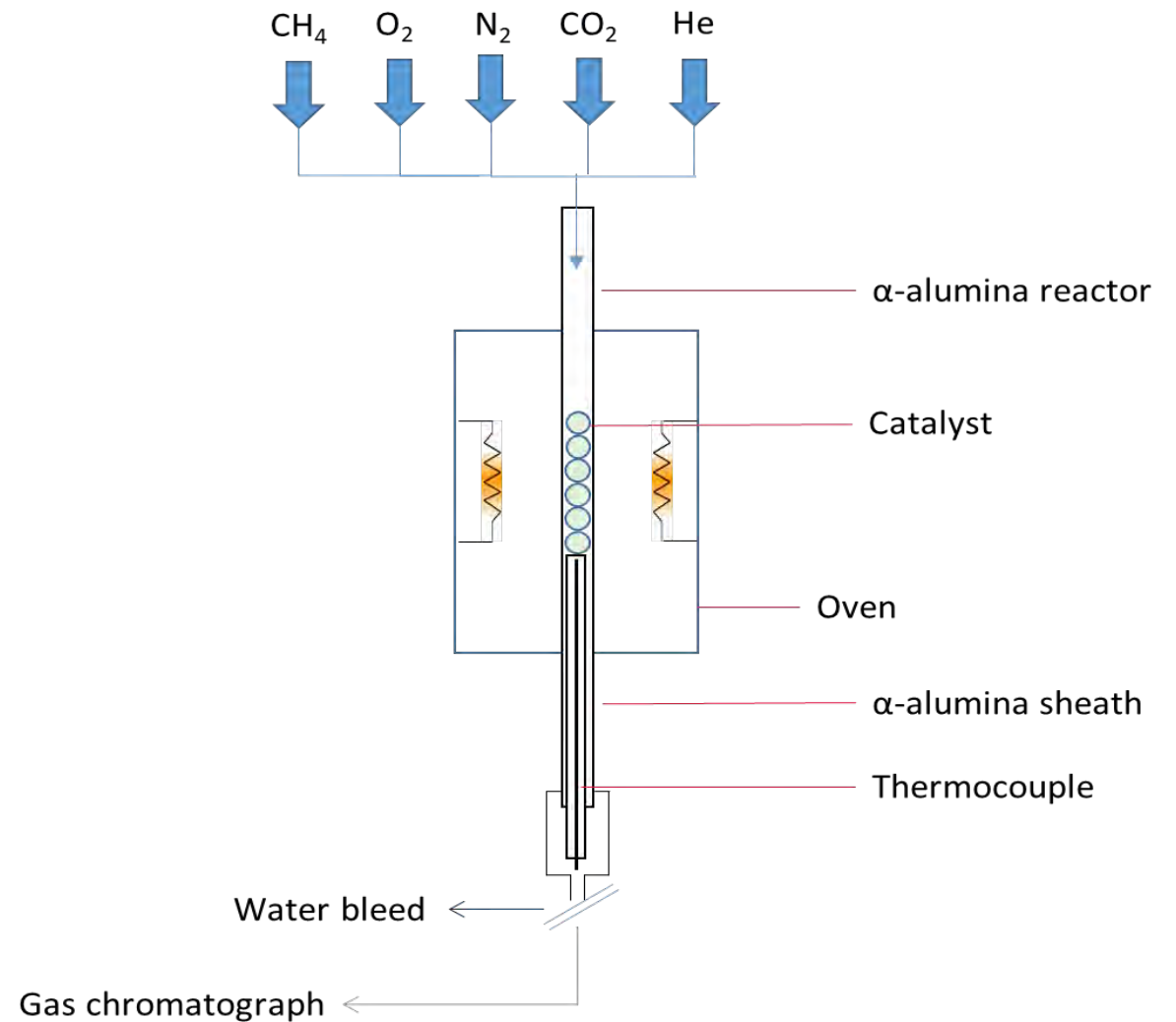
Zavyalova, U., Holena, M., Schlögl, R. and Baerns, M. (2011), Statistical Analysis of Past Catalytic Data on Oxidative Methane Coupling for New Insights into the Composition of High-Performance Catalysts. *ChemCatChem*, 3: 1935-1947

Introduction

Test rig

Standard testing conditions

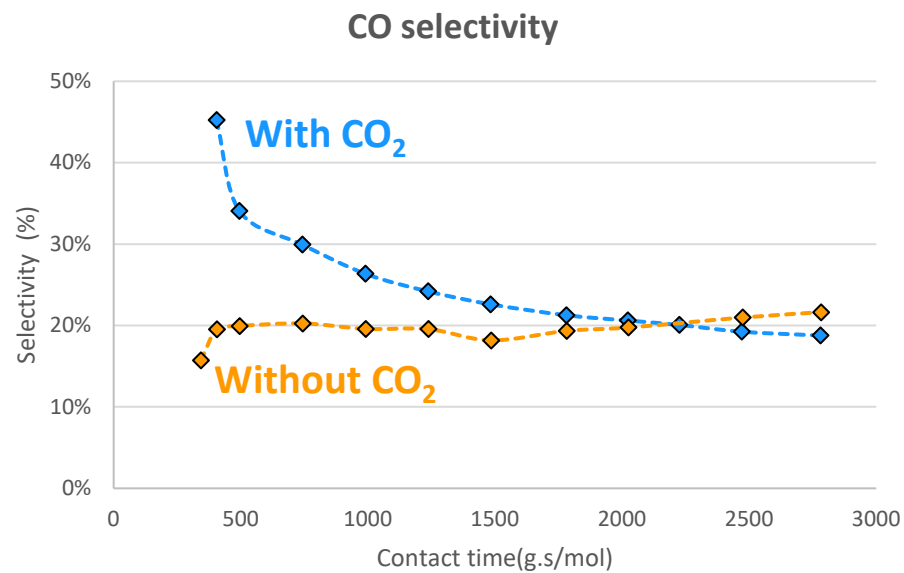
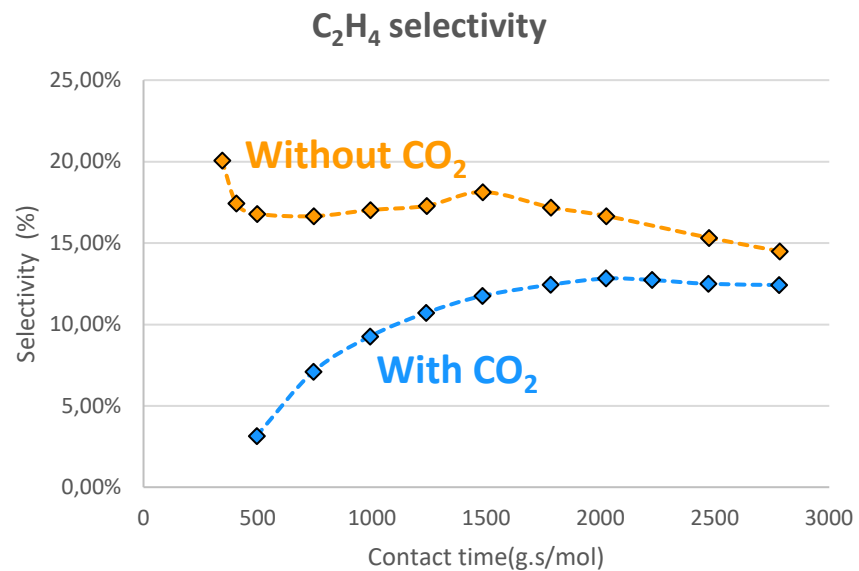
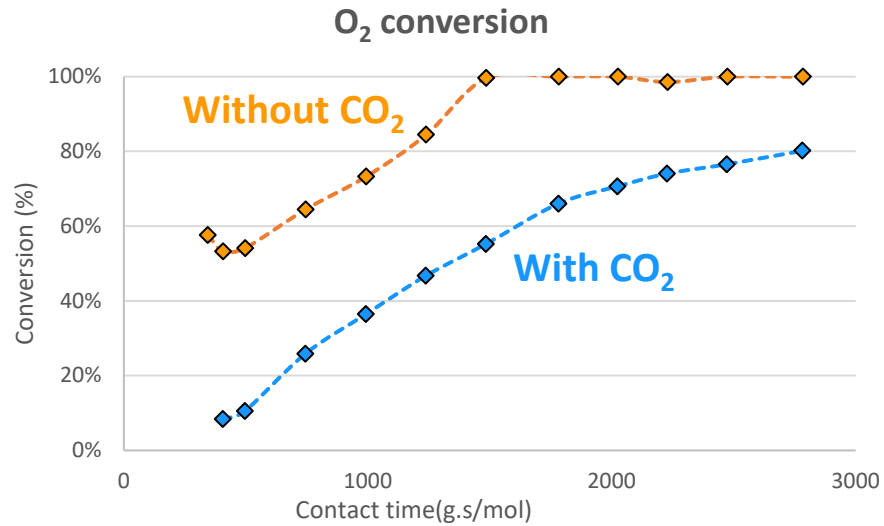
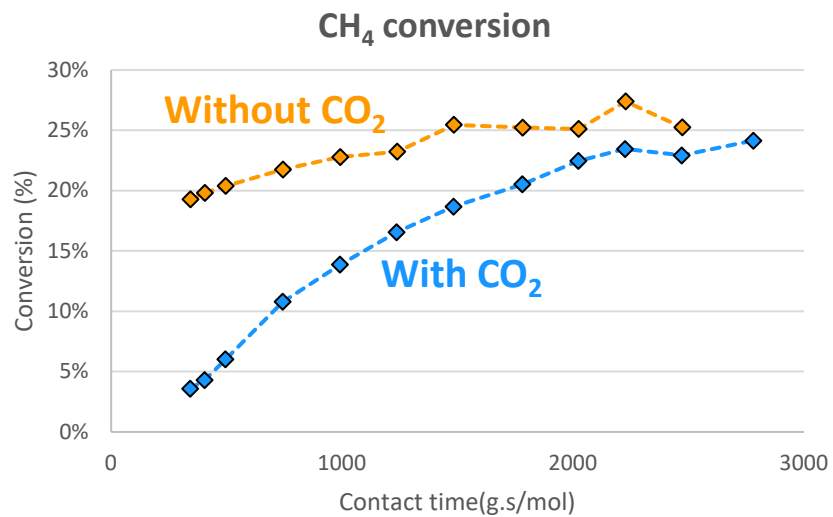
- High Temperature:** 800°C (up to 900°C)
- Medium Pressure:** up to 10 bars
- Reactor diameter:** 3 – 6 mm
- Inlet composition:** CH₄: O₂: N₂: CO₂/He = 60: 15: 15: 10
- GHSV:** 2,000-9,000 h⁻¹
- Either **powder** or **supported** catalysts loading



Results for powders

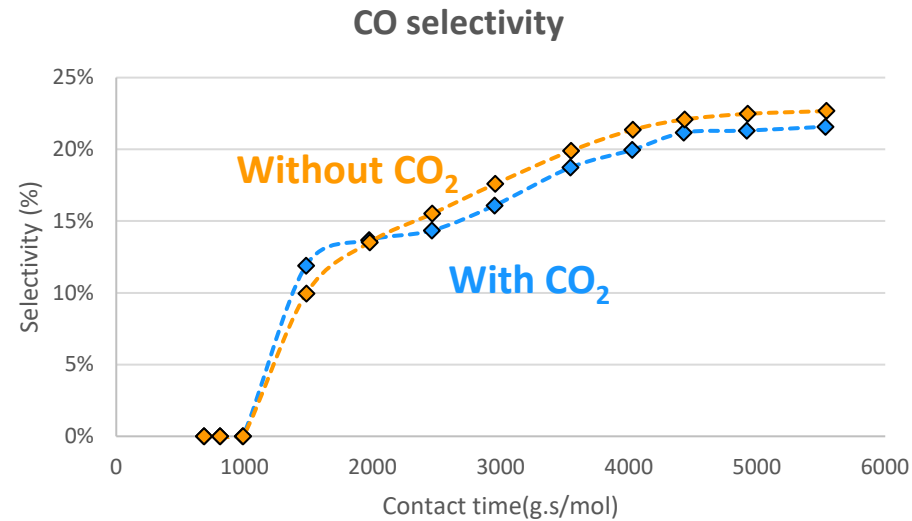
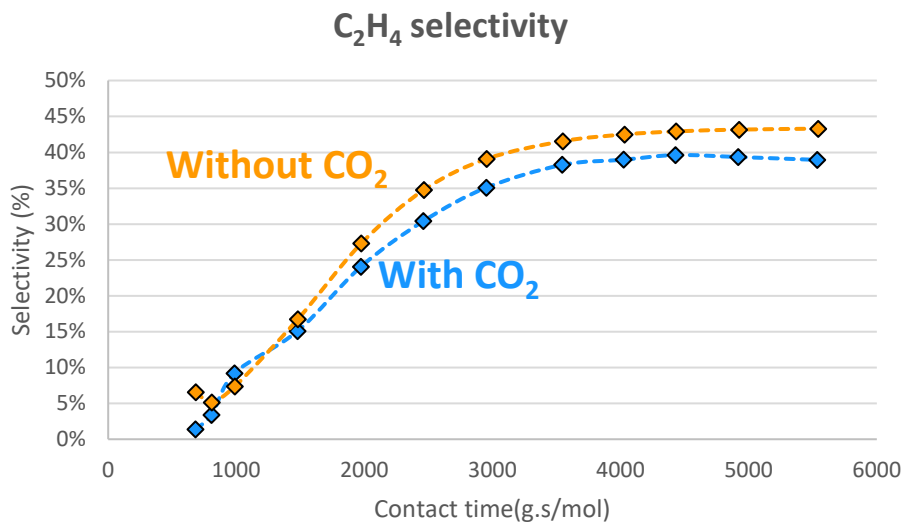
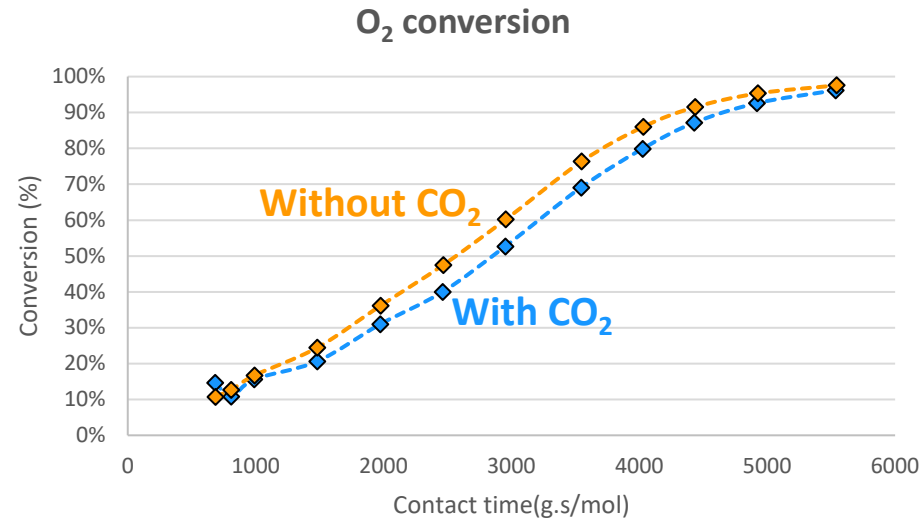
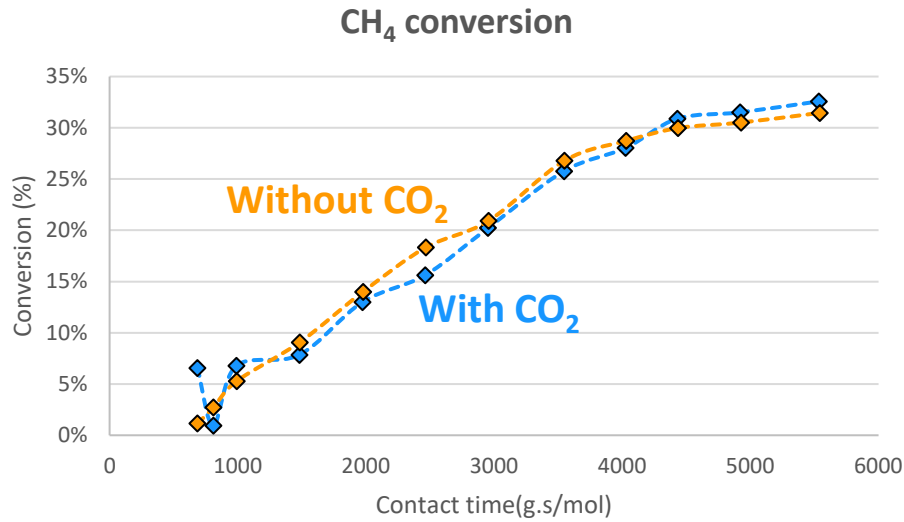
<u>Operating conditions</u>	
<p>Temperature: 800 °C</p> <p>Pressure: 1->3 atm</p> <p>Dilution: 5 %wt of catalyst with 95 %wt SiO₂</p>	
<p>Catalyst: Mn-based / La-based (powder)</p>	
Without CO ₂	With CO ₂
<p>Feed: CH₄, O₂, N₂, He (60/15/15/10 %Vol)</p>	<p>Feed: CH₄, O₂, N₂, CO₂ (60/15/15/10 %Vol)</p>

Powders - La-based catalyst / Effect of CO₂



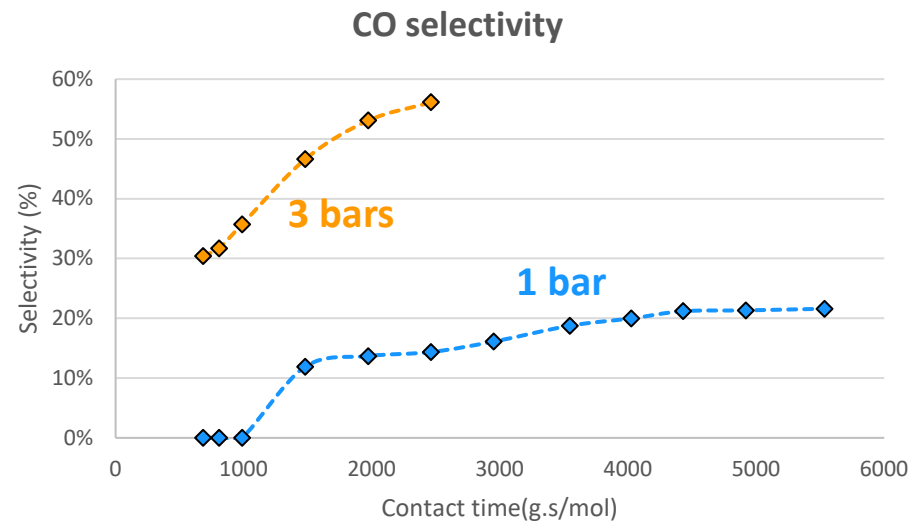
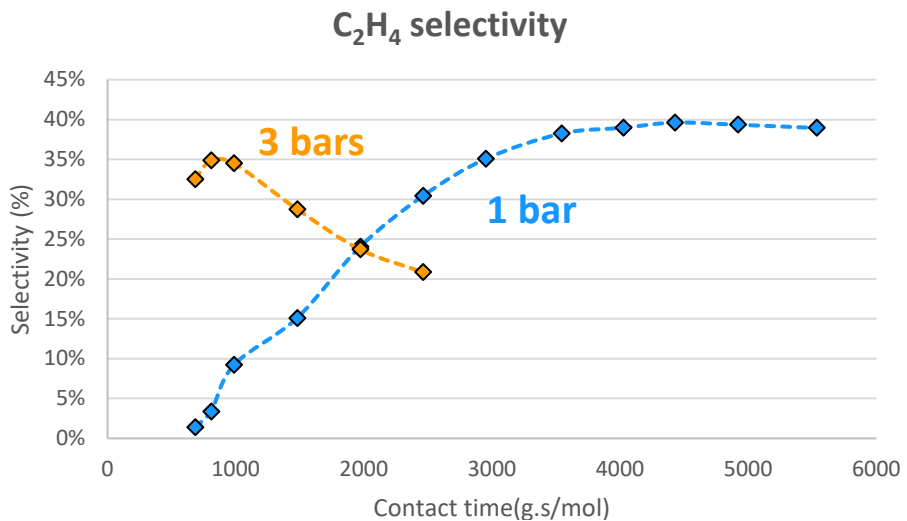
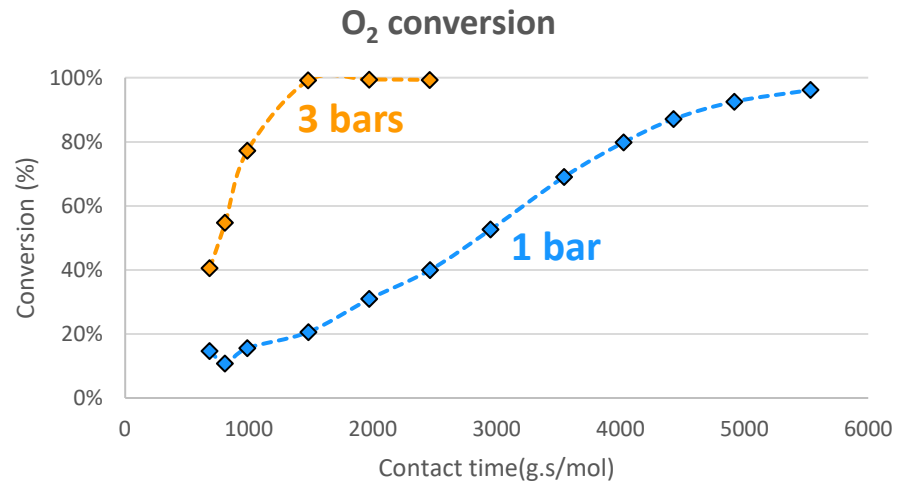
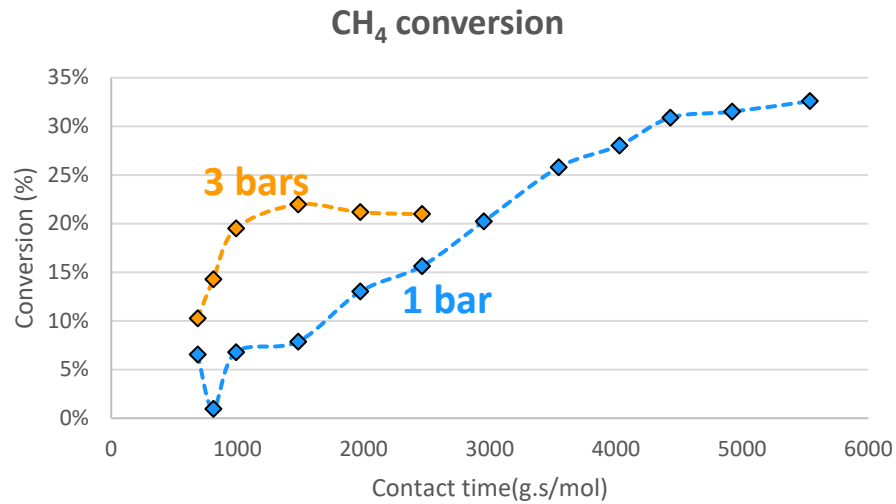
➤ La-based catalysts are affected by the addition of CO₂

Powders - Mn-based catalyst / Effect of CO₂



- Negligible effect of CO₂ on Mn-based catalyst performance
- No deactivation noticed after 1 day of reaction

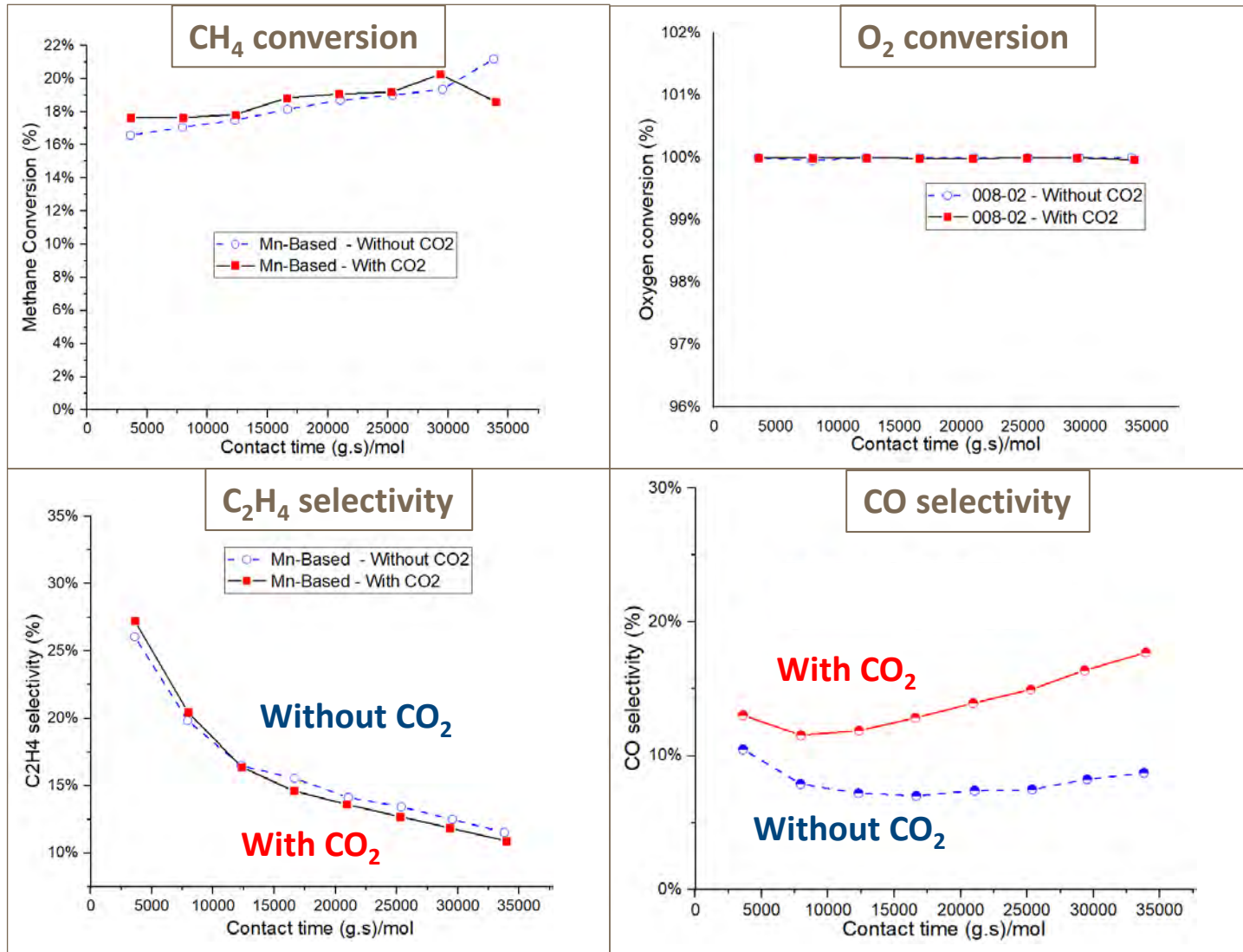
Test on Powders - Mn-based catalyst / Effect of Pressure in the presence of CO₂



- From 1 to 3 bars: x3 activity
- Higher CO selectivity with pressure increase
- Higher pressure (>= 6 bars) do not seem adequate for the OCoM (C₂H₄ selectivity decrease)

Test on supported catalyst

Test on supported catalyst / Effect of CO₂ on Mn-Shaped



CO₂ influence

No negative impact on C₂H₄ productivity

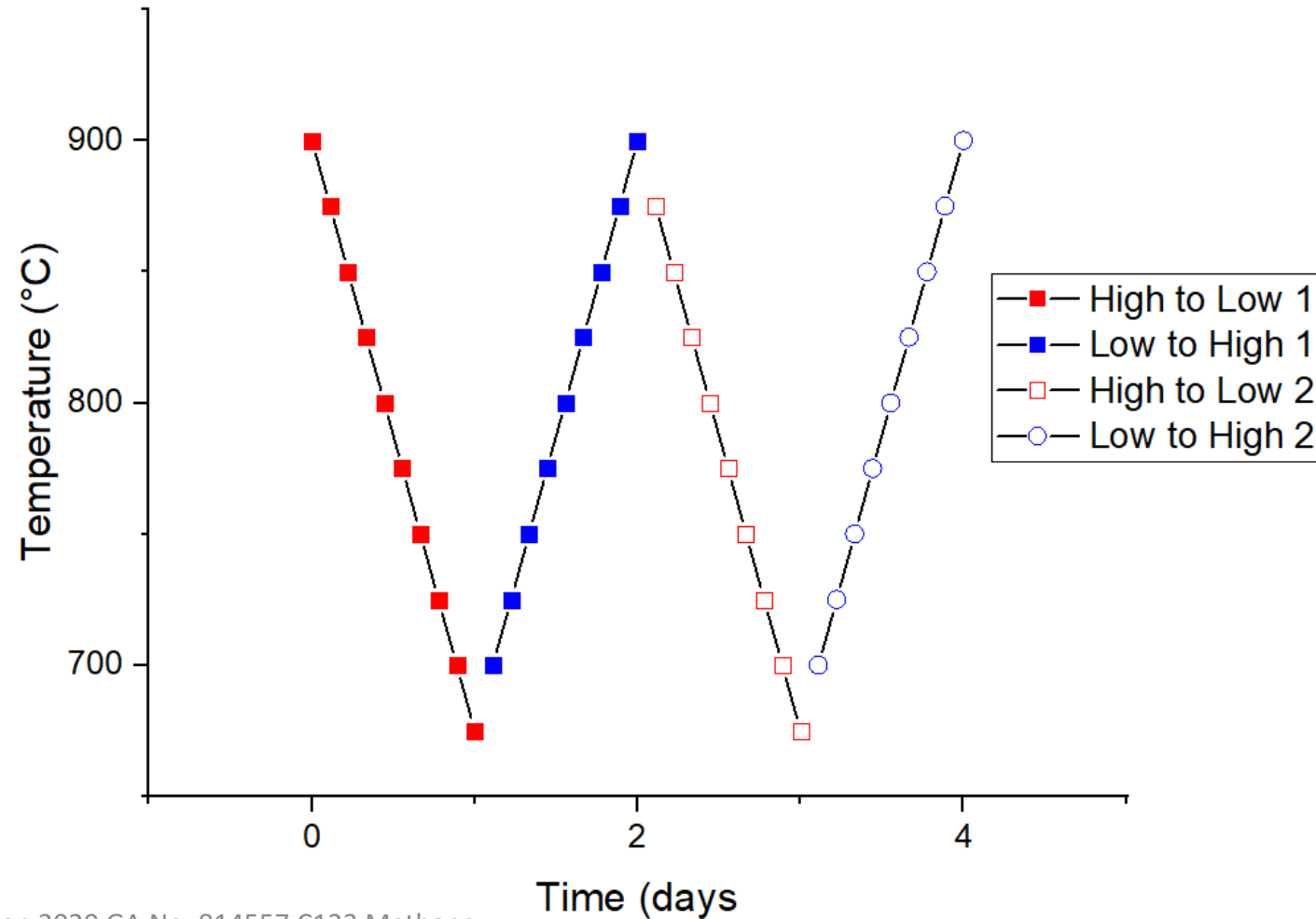
Slight increase of CO selectivity

Higher concentration of CO₂ (up to 40%) were tested with no catalyst deactivation

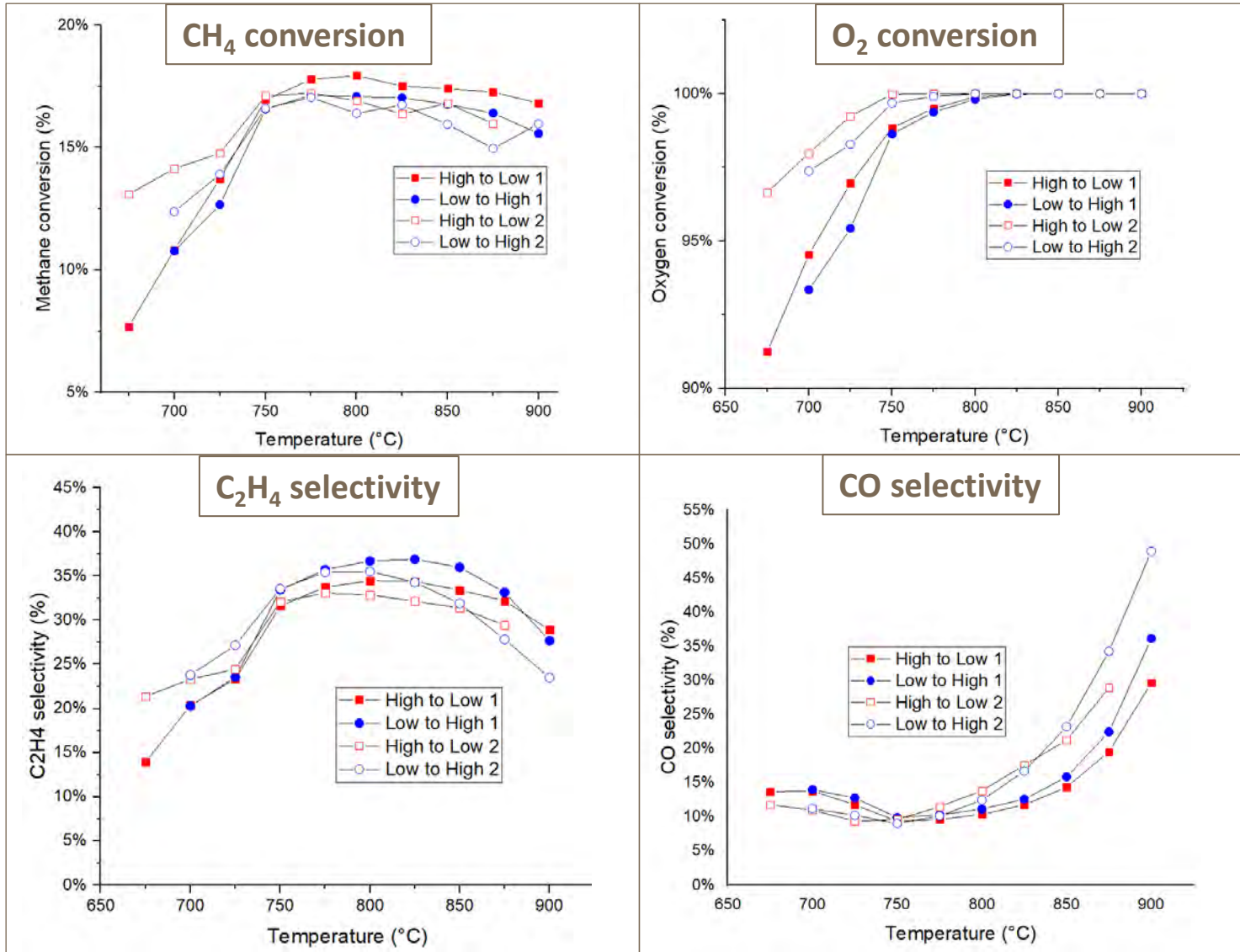
Test on Shaped catalyst / Effect of Temperature on Mn-Shaped

- Temperature influence on **Mn-Shaped**

- Wide temperature range (900°C- 675°C)
- 3 bars with 10%vol of CO₂
- Test over 4 days



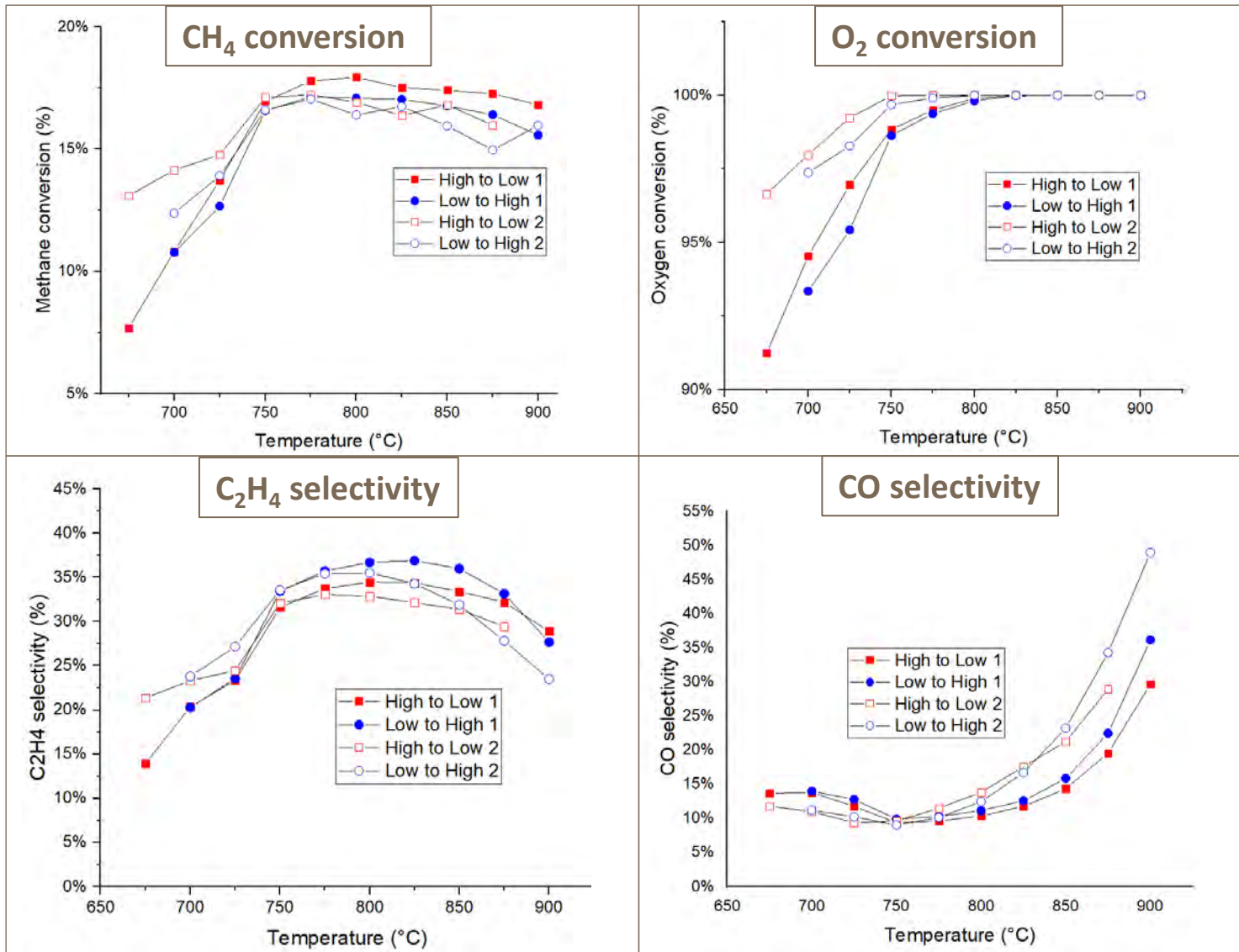
Test on Shaped catalyst/ Effect of Temperature on Mn-Shaped



Temperature influence


- ✓ No major loss of selectivity after 4 days with temperature peaks at 900°C
- CO/C₂H₄ ratio can be tuned by operating temperature


Test on Shaped catalyst / Effect of Temperature on Mn-Shaped



Temperature influence

- ✓ No major loss of selectivity after 4 days with temperature peaks at 900°C
- CO/C₂H₄ ratio can be tuned by operating temperature

 **Coke formation in the reactor**

 **Another run between 750-850°C without coke formation**

Conclusions & Perspective

- From powder to supported catalyst
 - A good C₂H₄ and CO selectivity was maintained with the shaping
 - No deactivation through inlet CO₂ composition was noticed (up to 40% inlet concentration)
 - Thermal stability appears to be good for the supported catalyst

- Perspective
 - Scale-up to industrial pilot
 - Long-term stability test
 - Mechanism study, kinetic modeling

Thank you for your attention!

Acknowledgements



This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 814557.