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Oxidative conversion of methane on shaped catalyst

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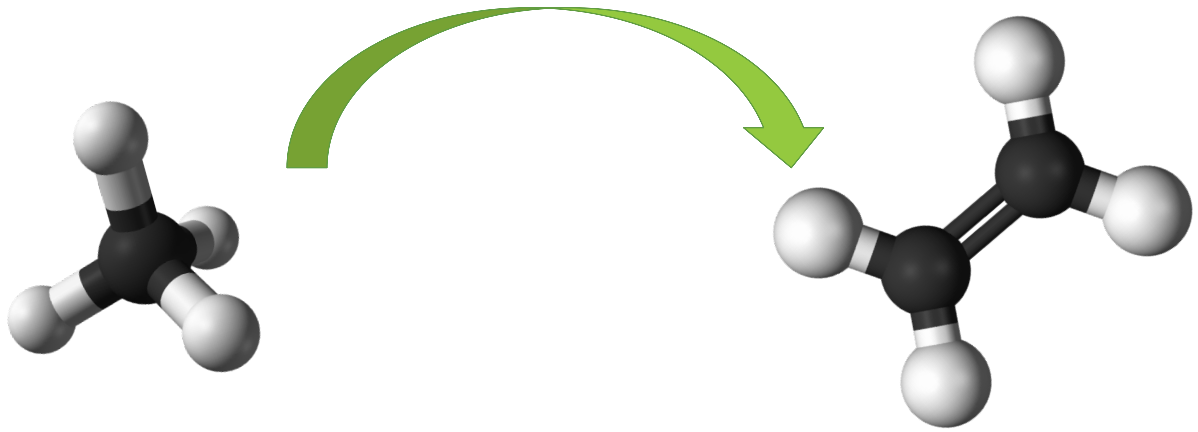

C123
VALORISING METHANE RESOURCES

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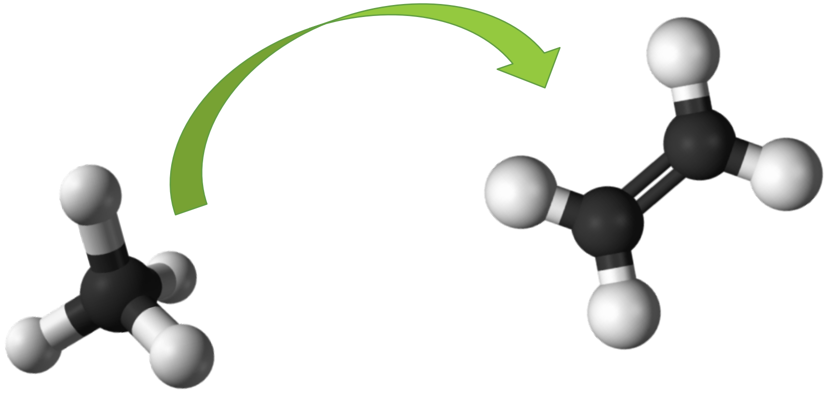
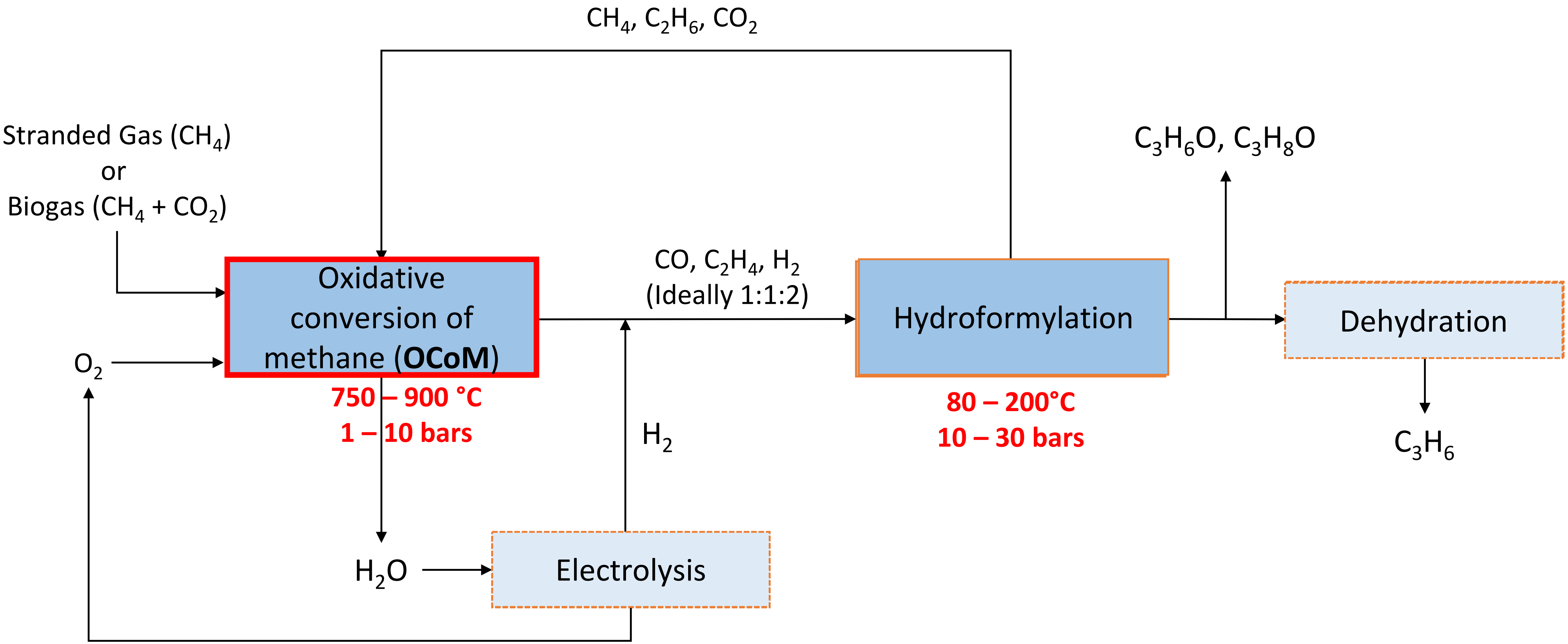


Introduction

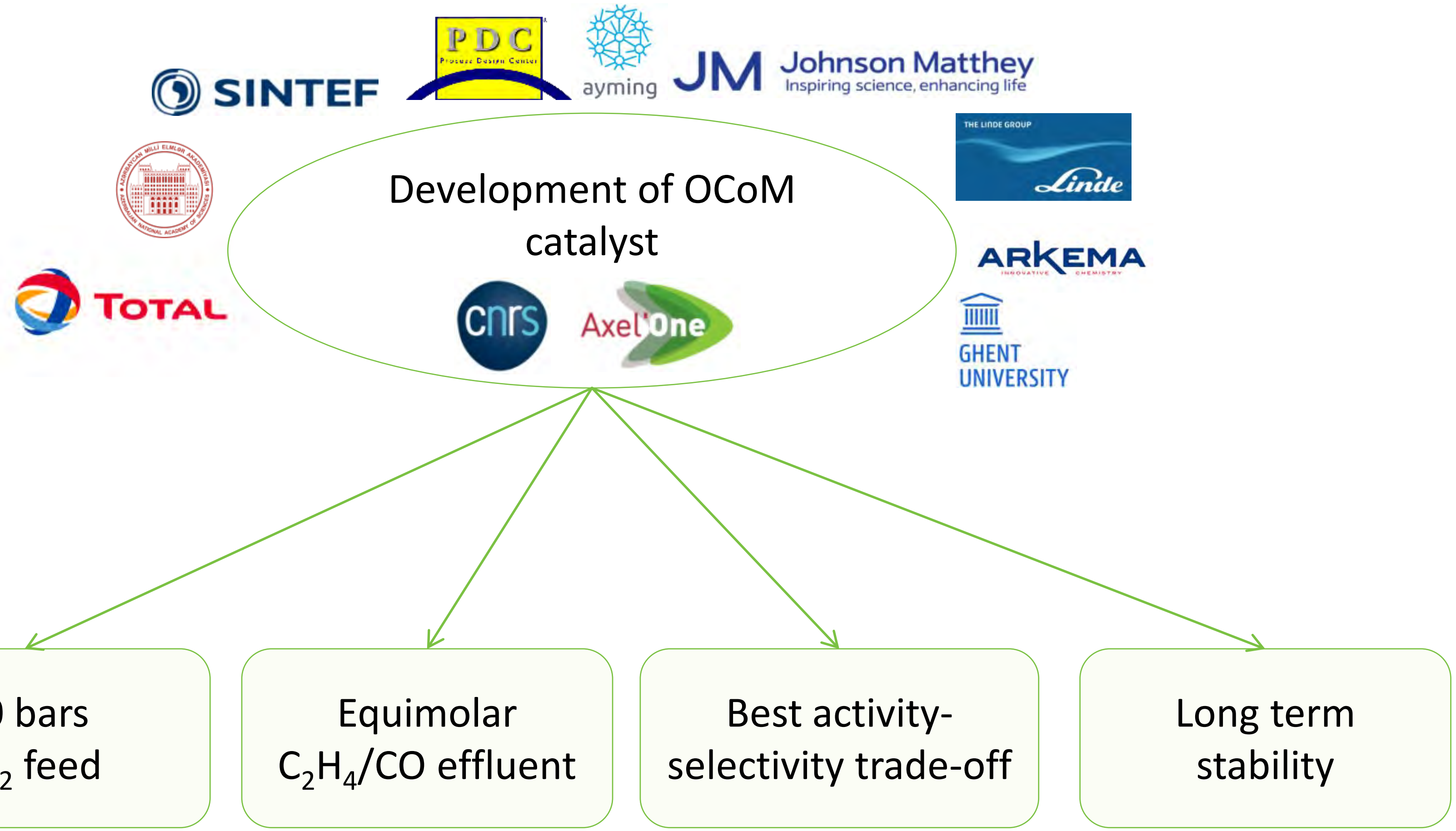
Introduction

- **CNRS tasks in C123**



Introduction

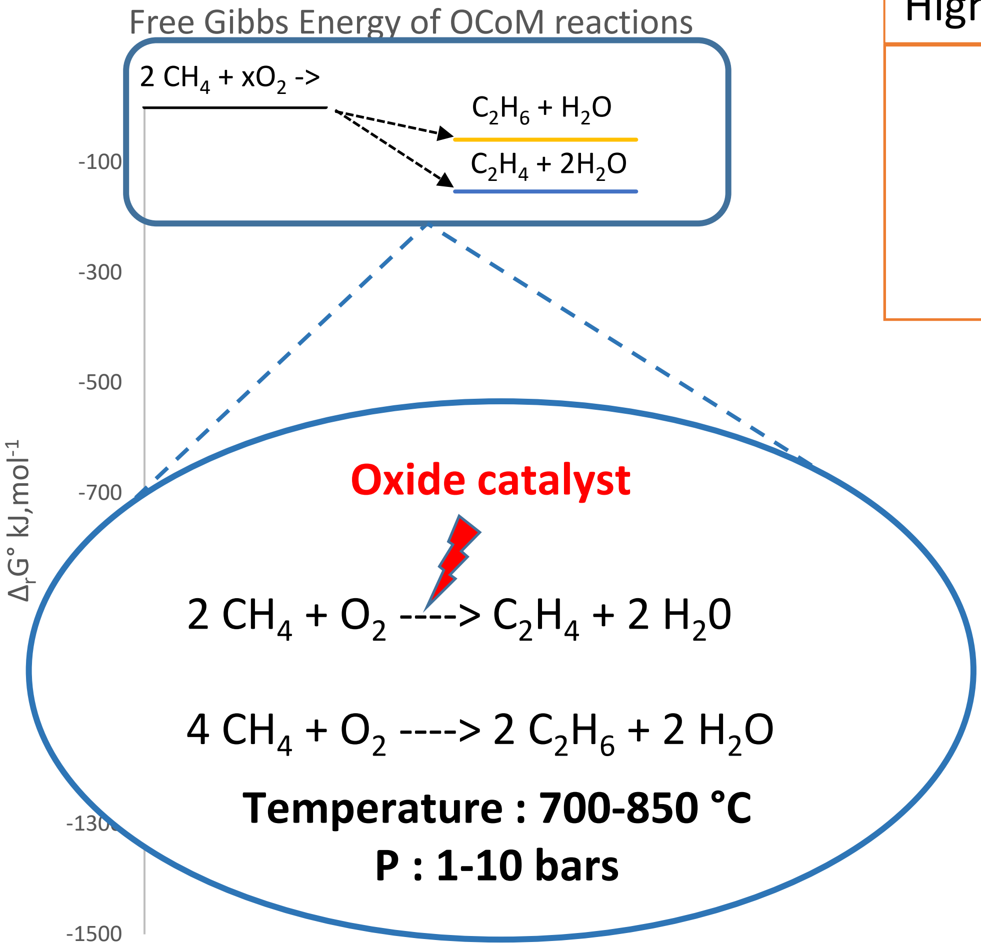
- **OCoM specifications**



Introduction

- **OCoM reaction**

Introduced by Keller and Bhasin in 1982



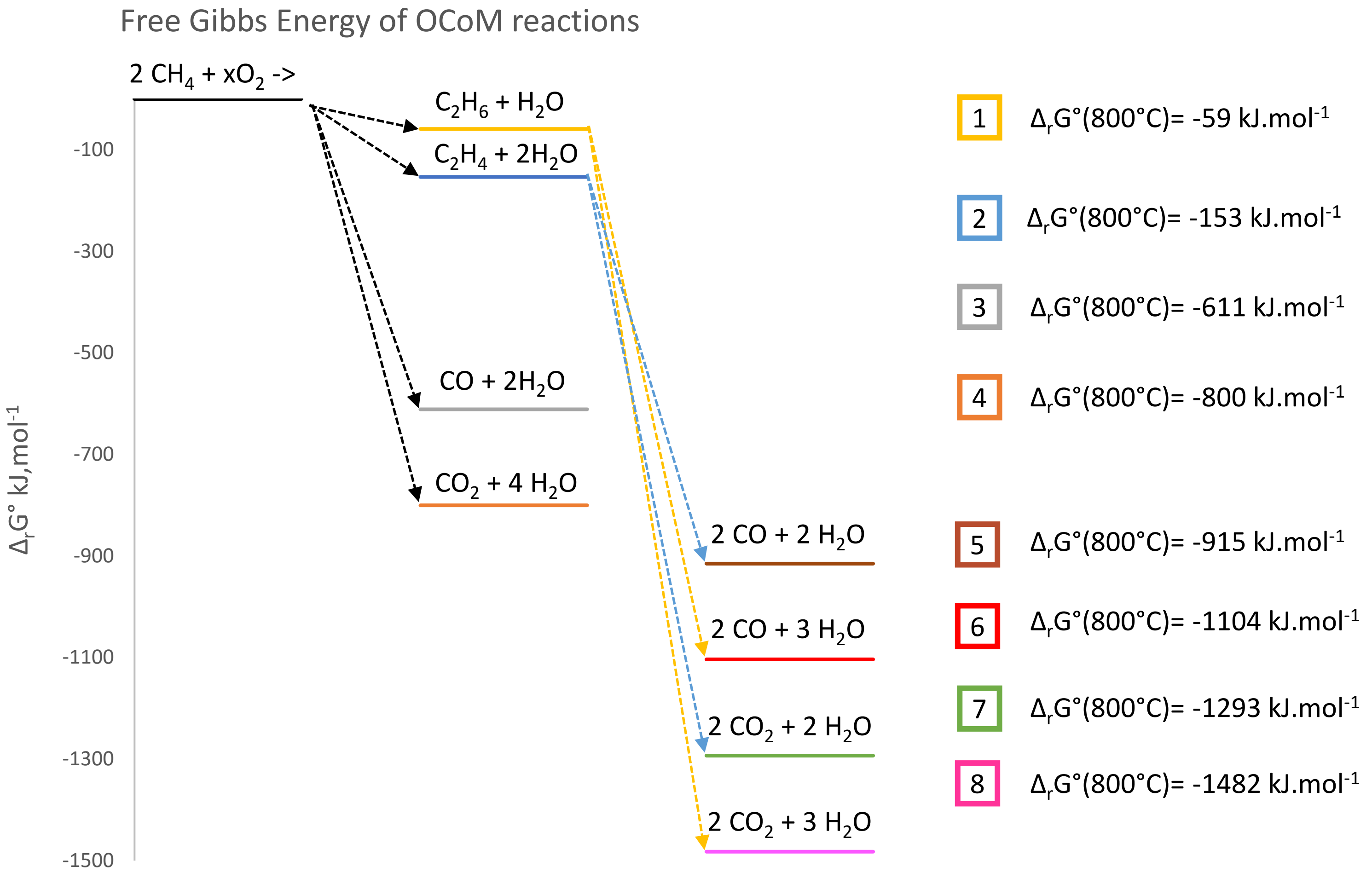
High exothermicity

1. $\Delta_r G°(800°C) = -59\ kJ.mol^{-1}$
2. $\Delta_r G°(800°C) = -153\ kJ.mol^{-1}$

Introduction

- **OCoM reaction**

Total oxidations are thermodynamically favored

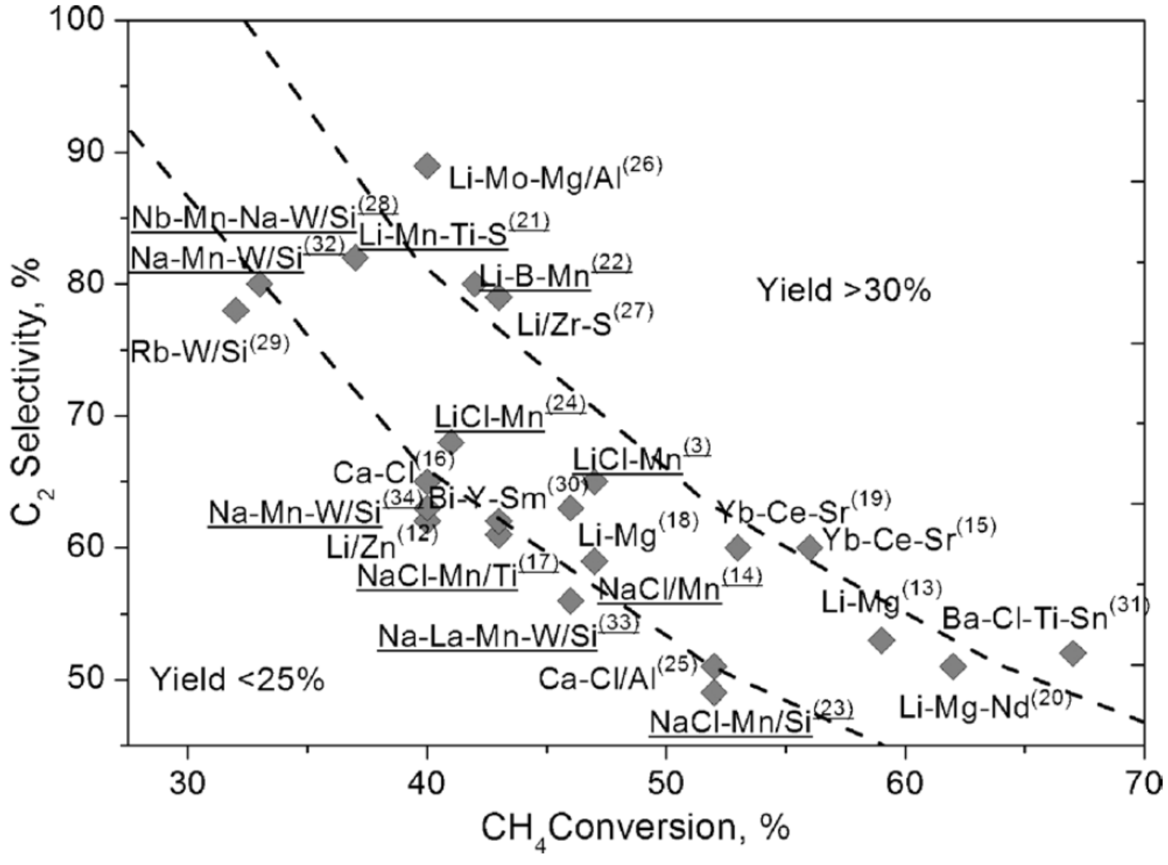


Introduction

- **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



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

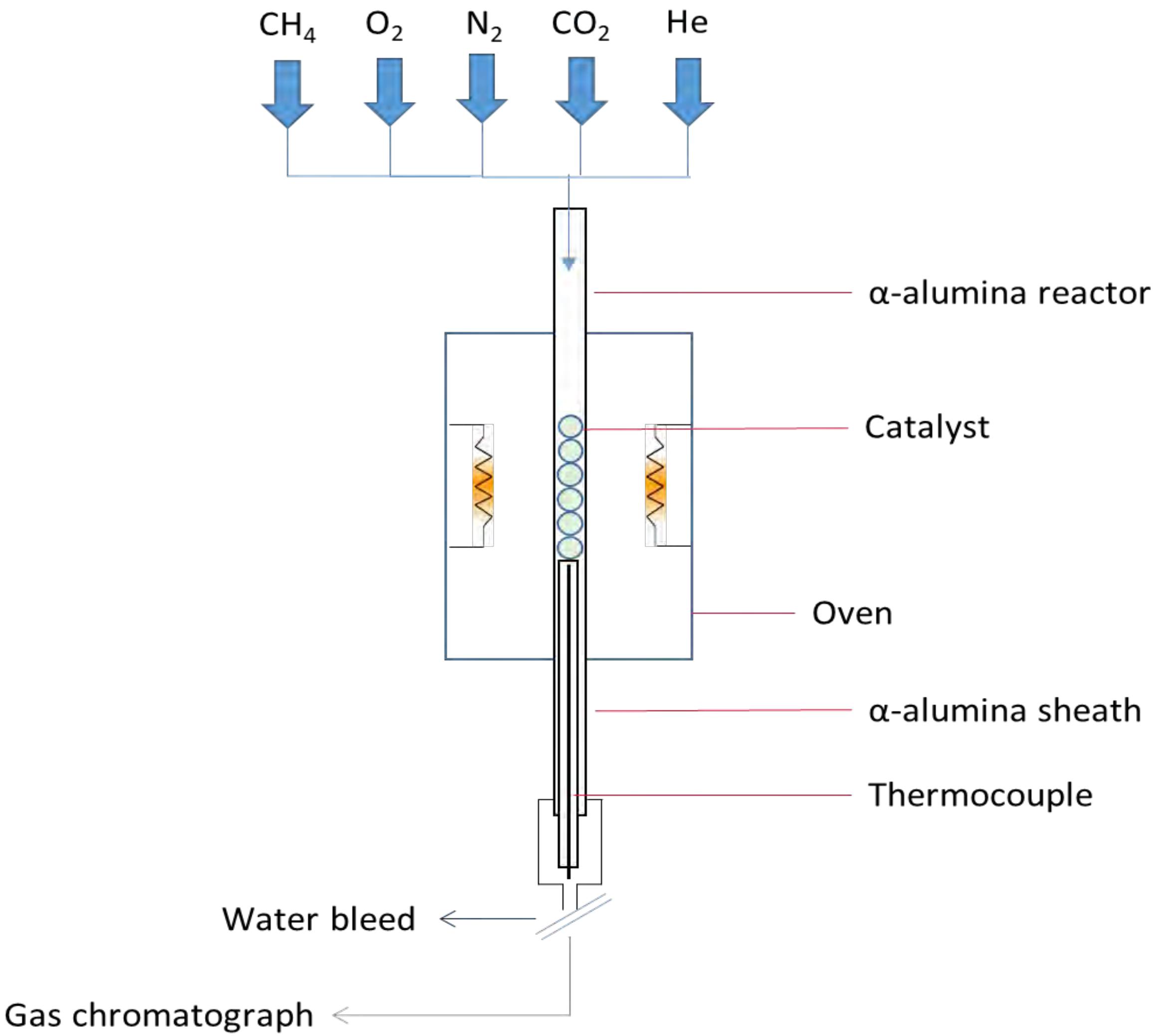
- **Objective for OCoM**

Development of a supported catalyst

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

Introduction

- **Test rig**



Standard testing conditions

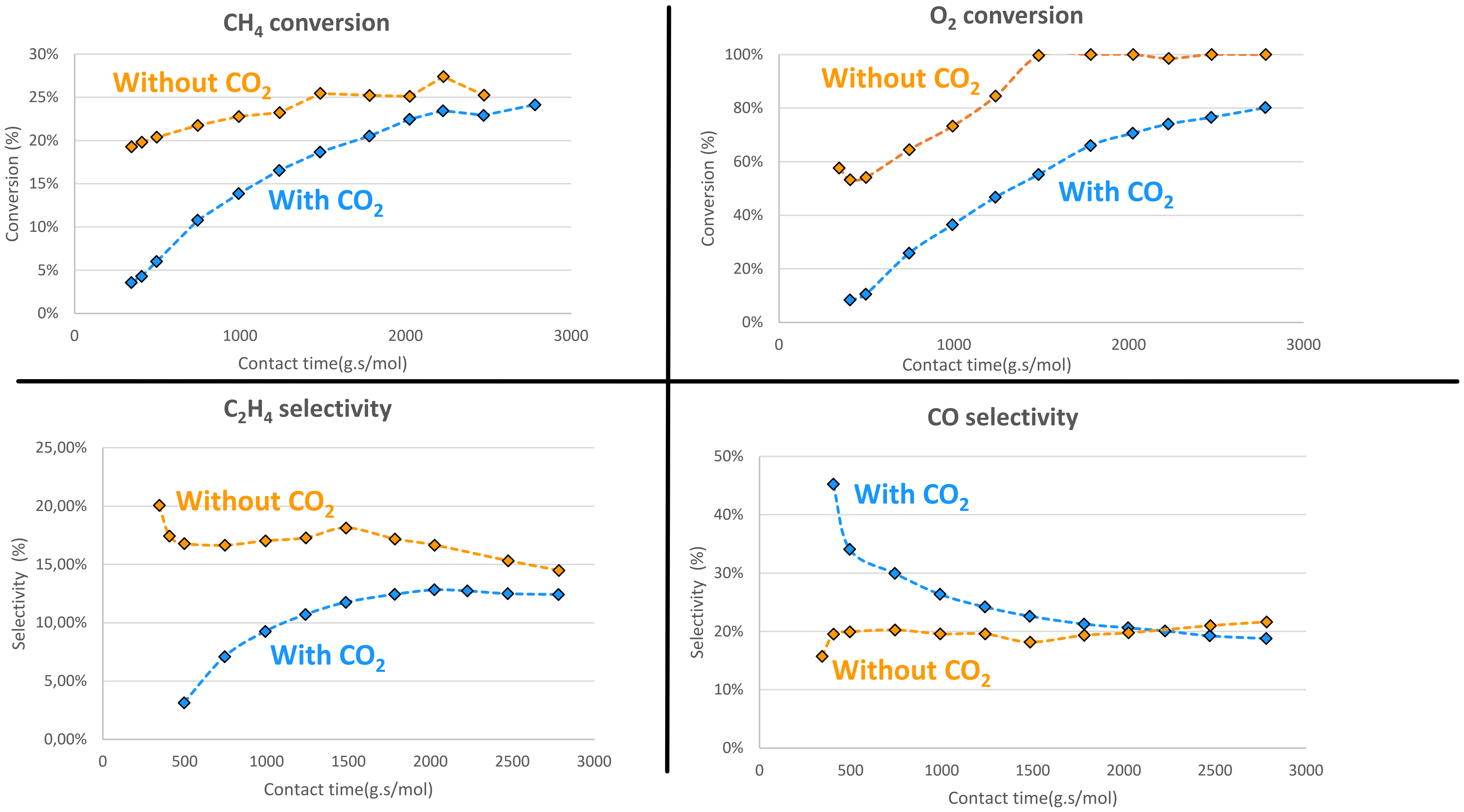
- **High Temperature:** 800°C (up to 900°C)
- **Medium Pressure:** up to 10 bars
- **Reactor diameter**: 3 – 6 mm
- **Inlet composition**: CH4: O2: N2: CO2/He = 60: 15: 15: 10
- **GHSV**: 2,000-9,000 h^{-1}
- Either **powder** or **supported** catalysts loading

Results for powders

Operating conditions
Temperature: 800 °C
Pressure: 1->3 atm
Dilution: 5 %wt of catalyst with 95 %wt SiO_2
Catalyst: Mn-based / La-based (**powder**)

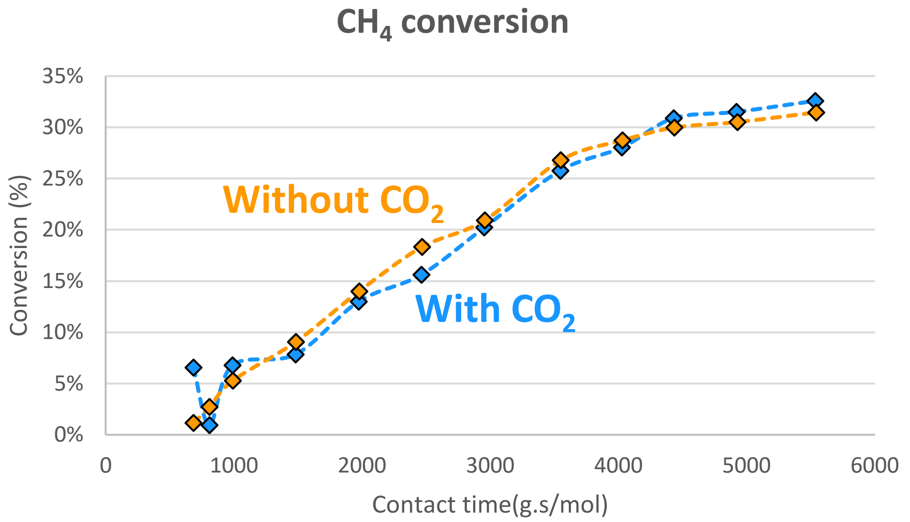
Without CO_2	With CO_2
Feed: CH_4, O_2, N_2, **He** (60/15/15/10 %Vol)	Feed: CH_4, O_2, N_2, $\mathbf{CO_2}$ (60/15/15/10 %Vol)

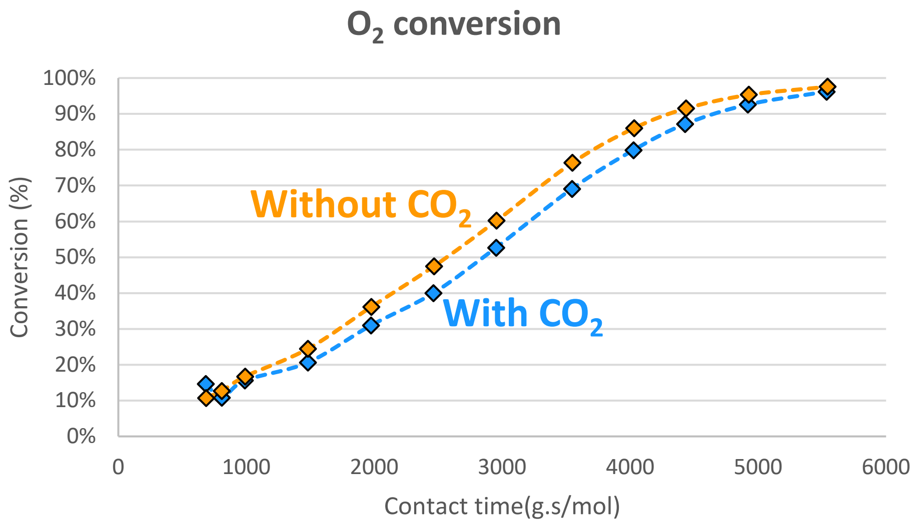
Powders - **La-based** catalyst / Effect of CO_2

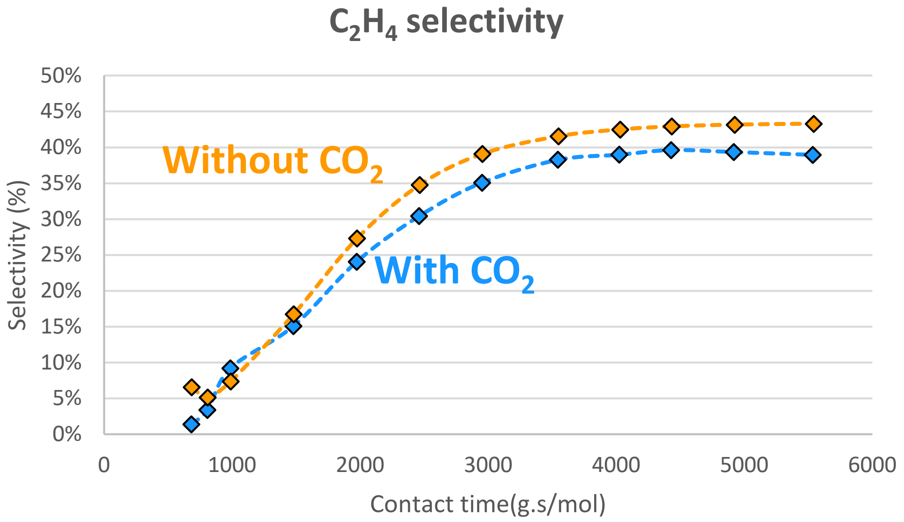


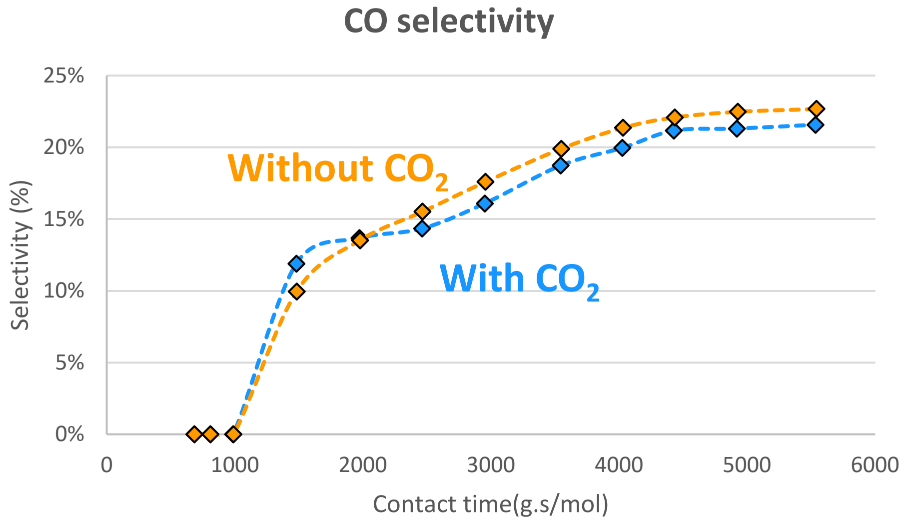
➢ La-based catalysts are affected by the addition of CO_2

Powders - **Mn-based** catalyst / Effect of CO_2



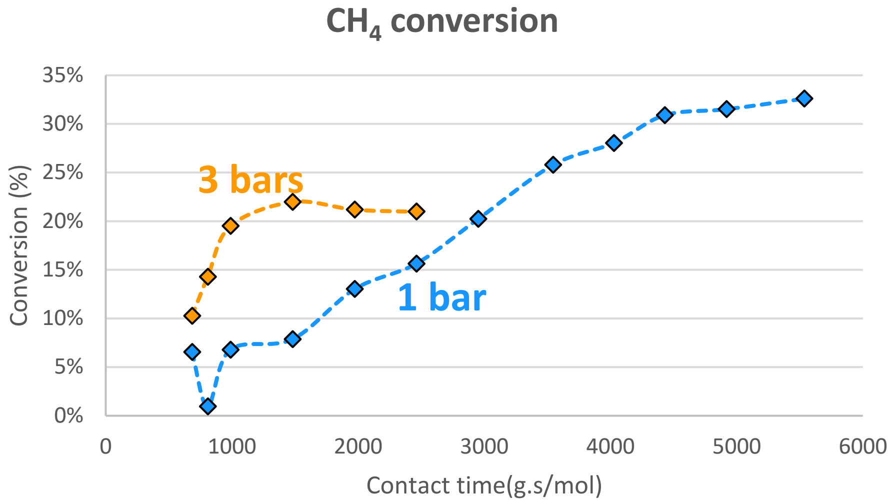


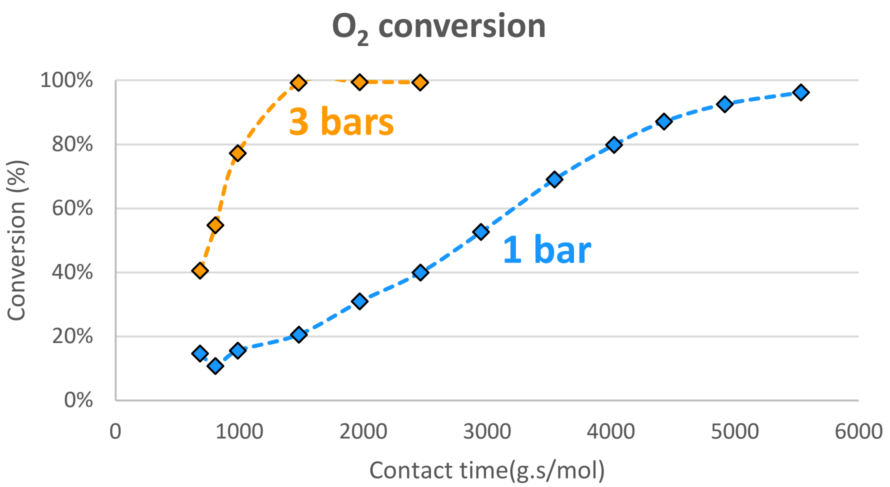


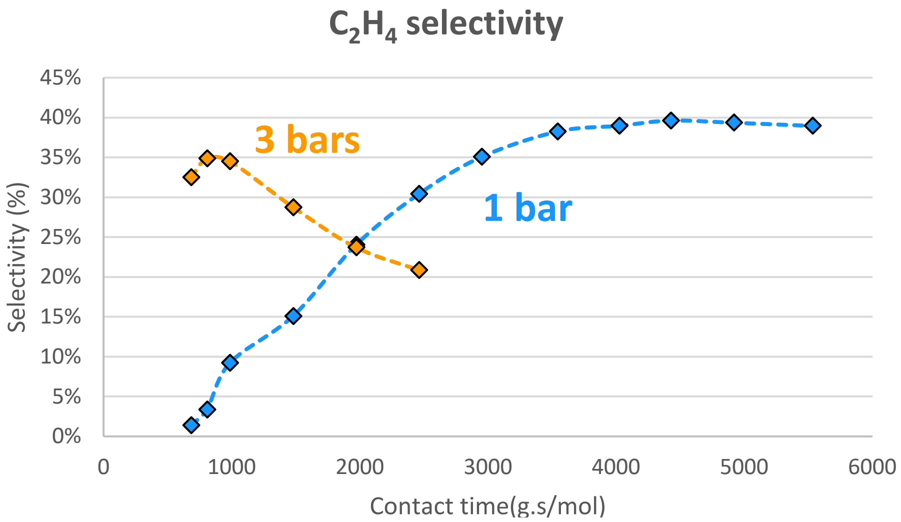


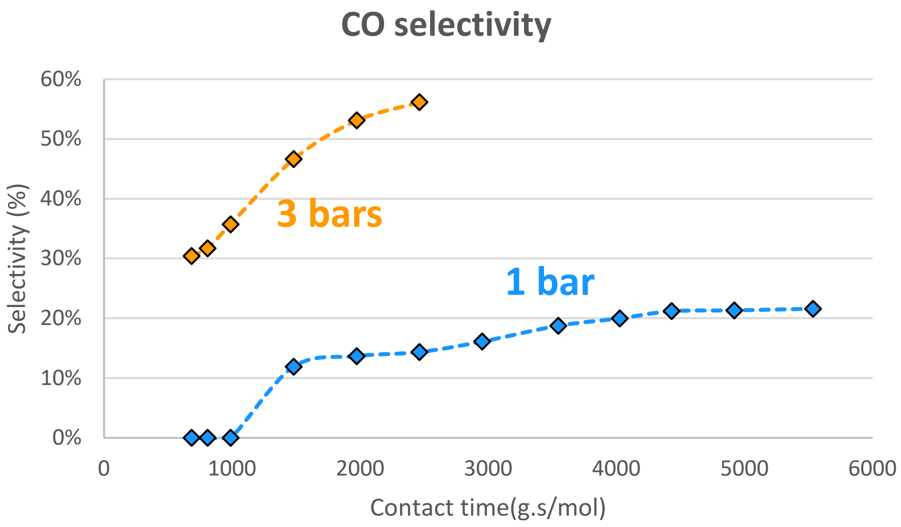
- Negligeable effect of CO_2 on Mn-based catalyst performance
- No deactivation noticed after 1 day of reaction

Test on Powders - **Mn-based** catalyst /Effect of **Pressure** in the presence of CO_2





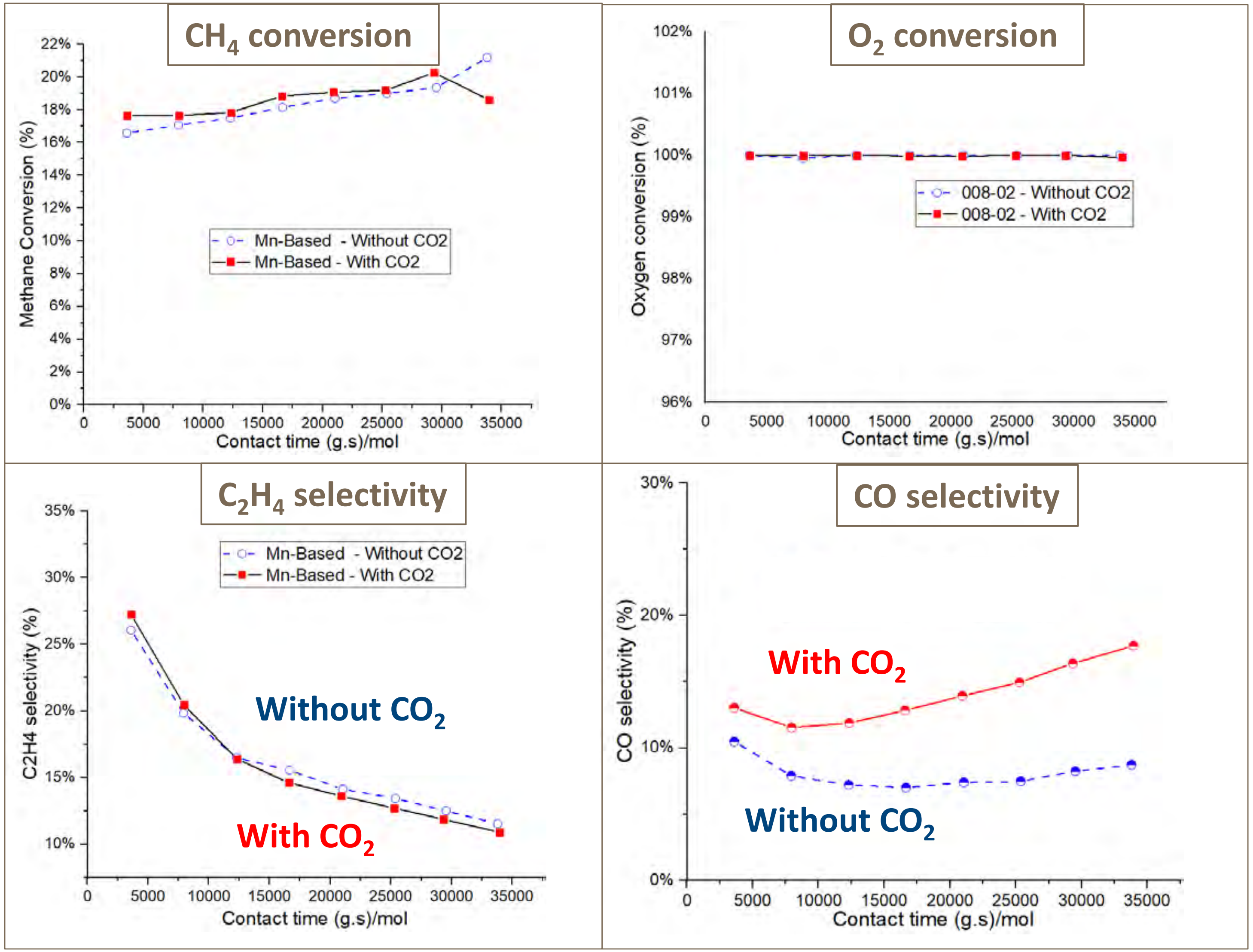




- From 1 to 3 bars: x3 activity
- Higher CO selectivity with pressure increase
- Higher pressure (>= 6 bars) do not seem adequate for the OCoM (C_2H_4 selectivity decrease)

Test on supported catalyst

Test on supported catalyst / Effect of CO_2 on Mn-Shaped



CO2 influence

No negative impact on C_2H_4 productivity

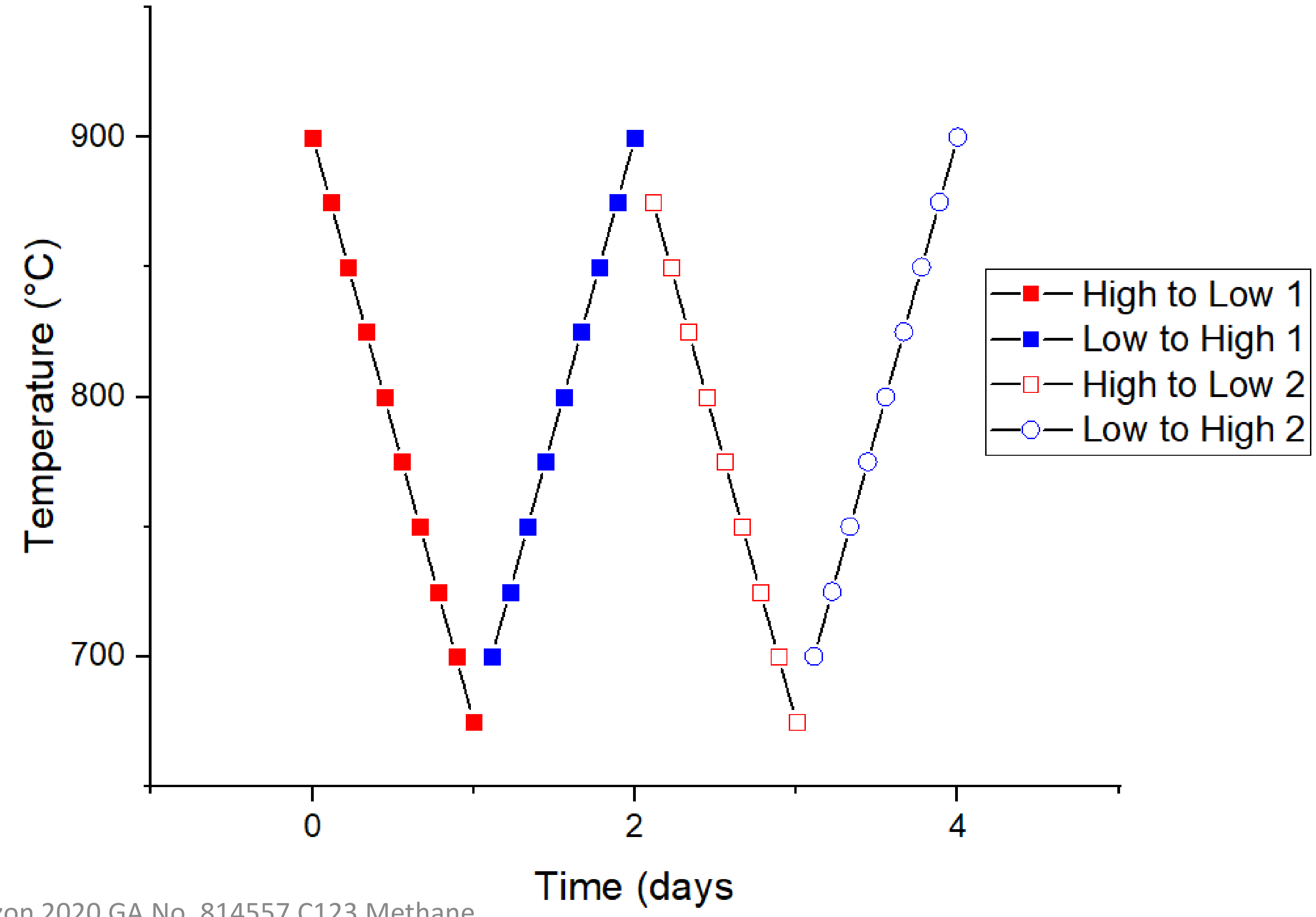
Slight increase of CO selectivity

Higher concentration of CO_2 (up to 40%) were tested with no catalyst deactivation

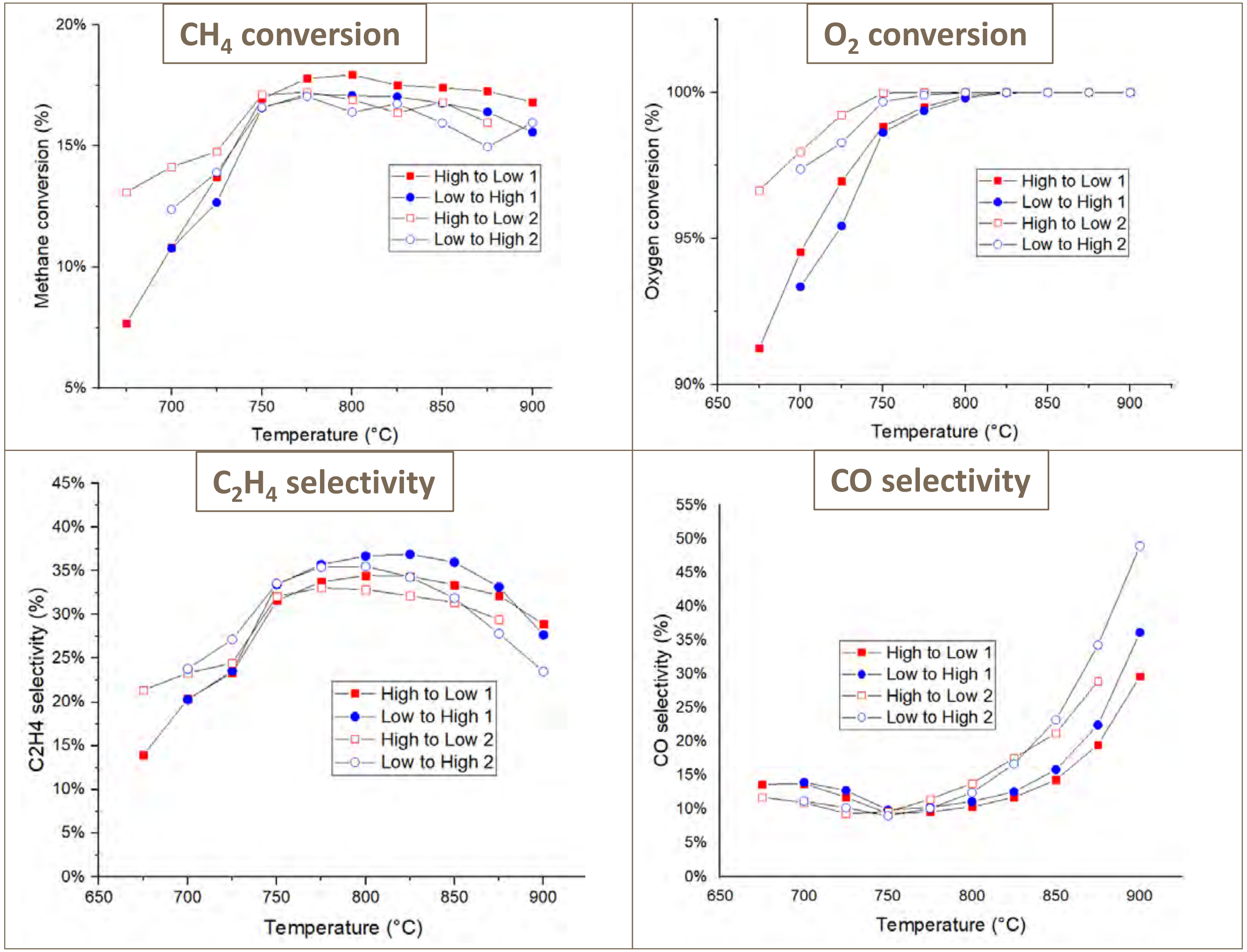
Test on Shaped catalyst / Effect of **Temperature** on Mn-Shaped

- Temperature influence on **Mn-Shaped**

    - Wide temperature range (900°C- 675°C)
    - 3 bars with 10%vol of CO_2
    - Test over 4 days



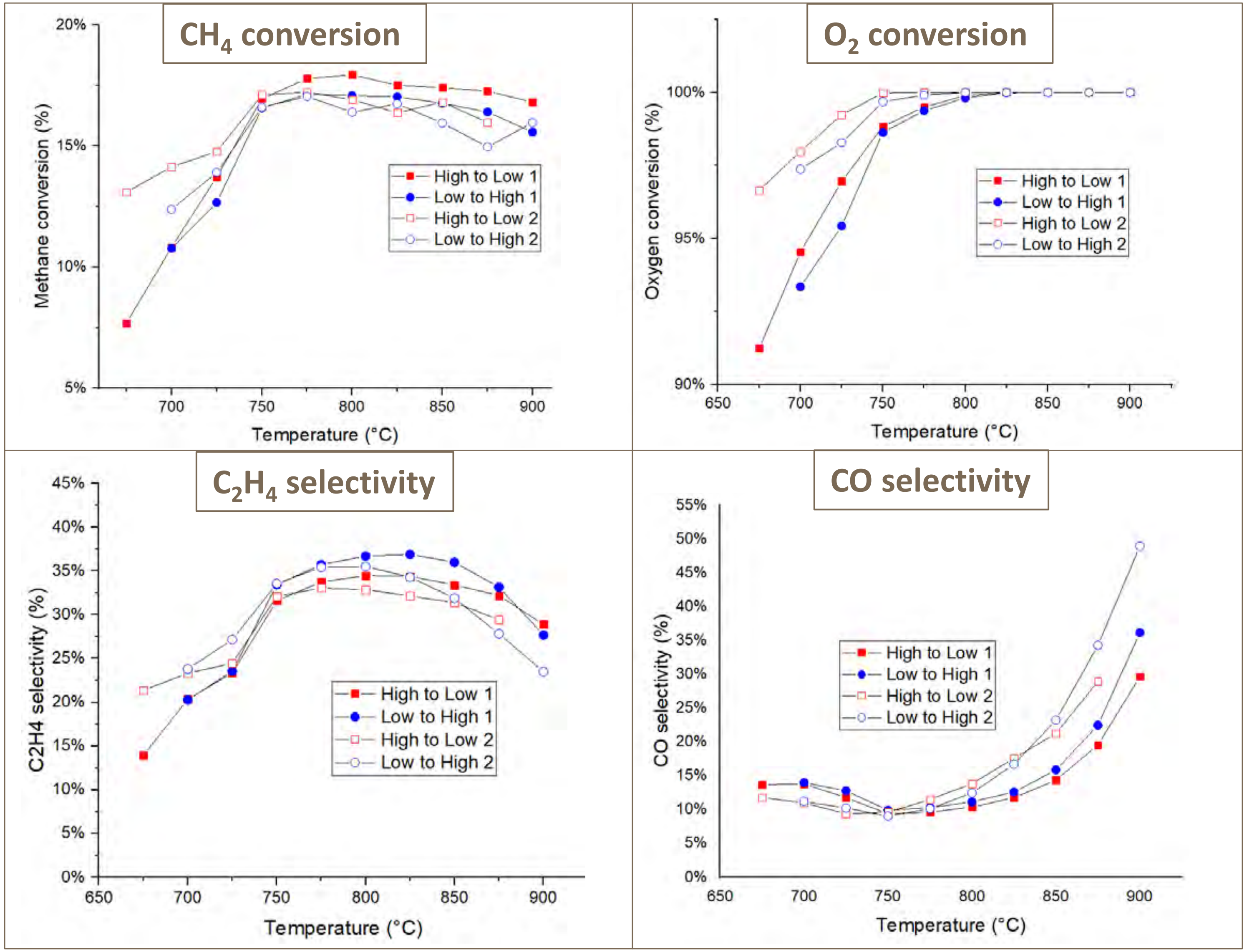
Test on Shaped catalyst/ Effect of **Temperature** on Mn-Shaped



Temperature influence

- ✓ No major loss of selectivity after 4 days with temperature peaks at 900°C
- ➢ CO/C_2H_4 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/C_2H_4 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 C_2H_4 and CO selectivity was maintained with the shaping
  - No deactivation through inlet CO_2 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

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