

# High-purity hydrogen via the sorption-enhanced steam methane reforming reaction over a synthetic CaO-based sorbent and a Ni catalyst

M. Broda<sup>a</sup>, V. Manovic<sup>b</sup>, Q. Imtiaz<sup>a</sup>, A. M. Kierzkowska<sup>a</sup>, E. J. Anthony<sup>c</sup>, C. R. Müller<sup>a</sup>

<sup>a</sup>Laboratory of Energy Science and Engineering, ETH Zurich, Leonhardstrasse 27, 8092 Zurich, Switzerland

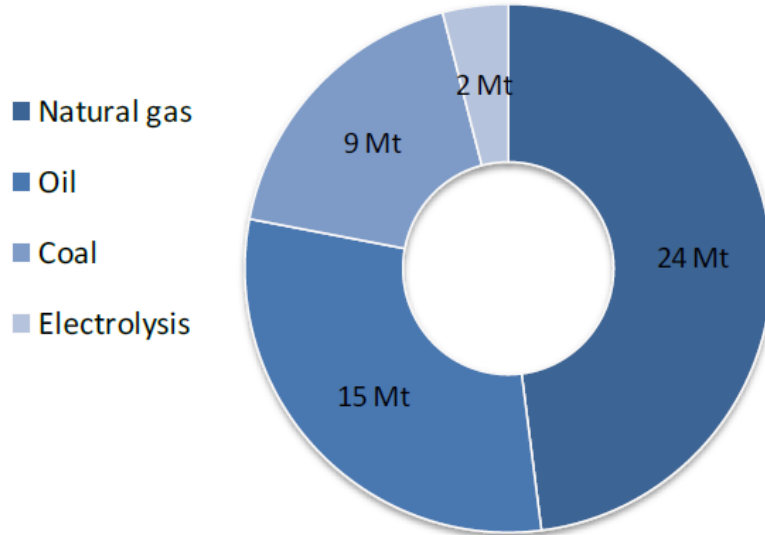
<sup>b</sup>CanmetENERGY, Natural Resources Canada, 1 Haanel Drive, Ottawa K1A 1M1, Canada

<sup>c</sup>School of Applied Science, Cranfield University, Bedfordshire MK43 0AL, England

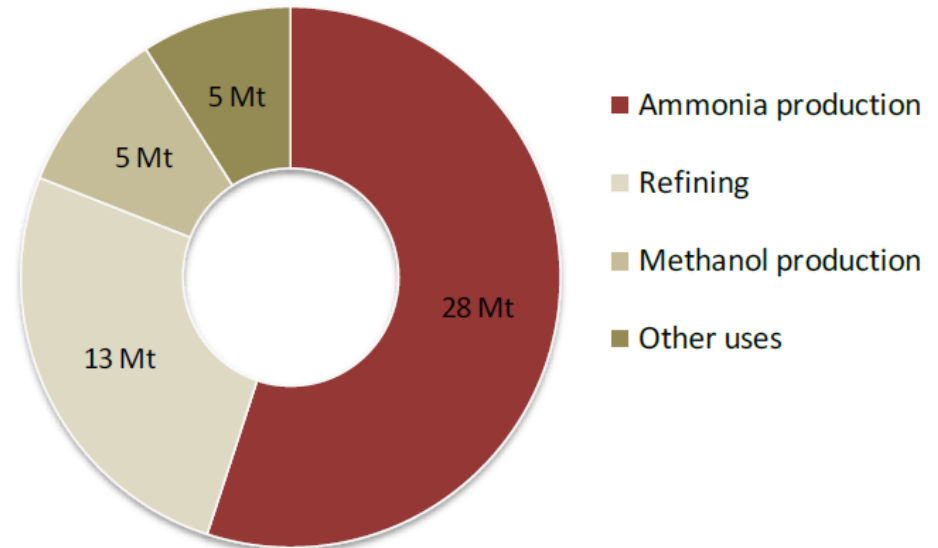


# Introduction

## Global H<sub>2</sub> production (~50 Mt/yr, 2008)



## Global H<sub>2</sub> use



P. Zakkour and G. Cook, CCS industry roadmap-high purity CO<sub>2</sub> sources: final draft sectoral assessment, Carbon Counts, UK, 2010.

# Steam methane reforming accounts for ~50 % of the global hydrogen production

## Reforming reaction:



## Water-gas-shift reaction:

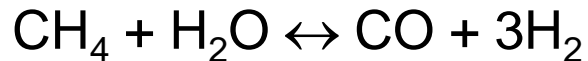


## Disadvantages:

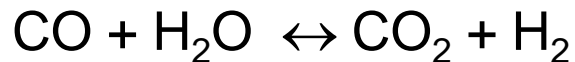
- Highly endothermic
- High operating temperatures → catalyst sintering and coke formation
- Overall process is complex and comprises several unit operations
- Further purification steps are required to produce high-purity hydrogen, e.g. preferential oxidation (PROX)

# Sorption-enhanced steam methane reforming (SE-SMR)

## Reforming and shift reaction:



$$\Delta H^\circ_{25\text{ }^\circ\text{C}} = + 206 \text{ kJ/mol}$$

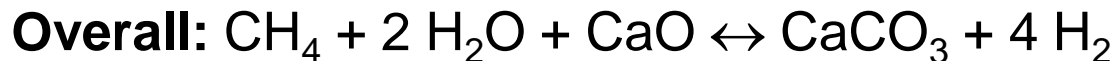


$$\Delta H^\circ_{25\text{ }^\circ\text{C}} = - 41 \text{ kJ/mol}$$

## CO<sub>2</sub> absorption reaction, e.g. carbonation of CaO:



$$\Delta H^\circ_{25\text{ }^\circ\text{C}} = -178 \text{ kJ/mol}$$

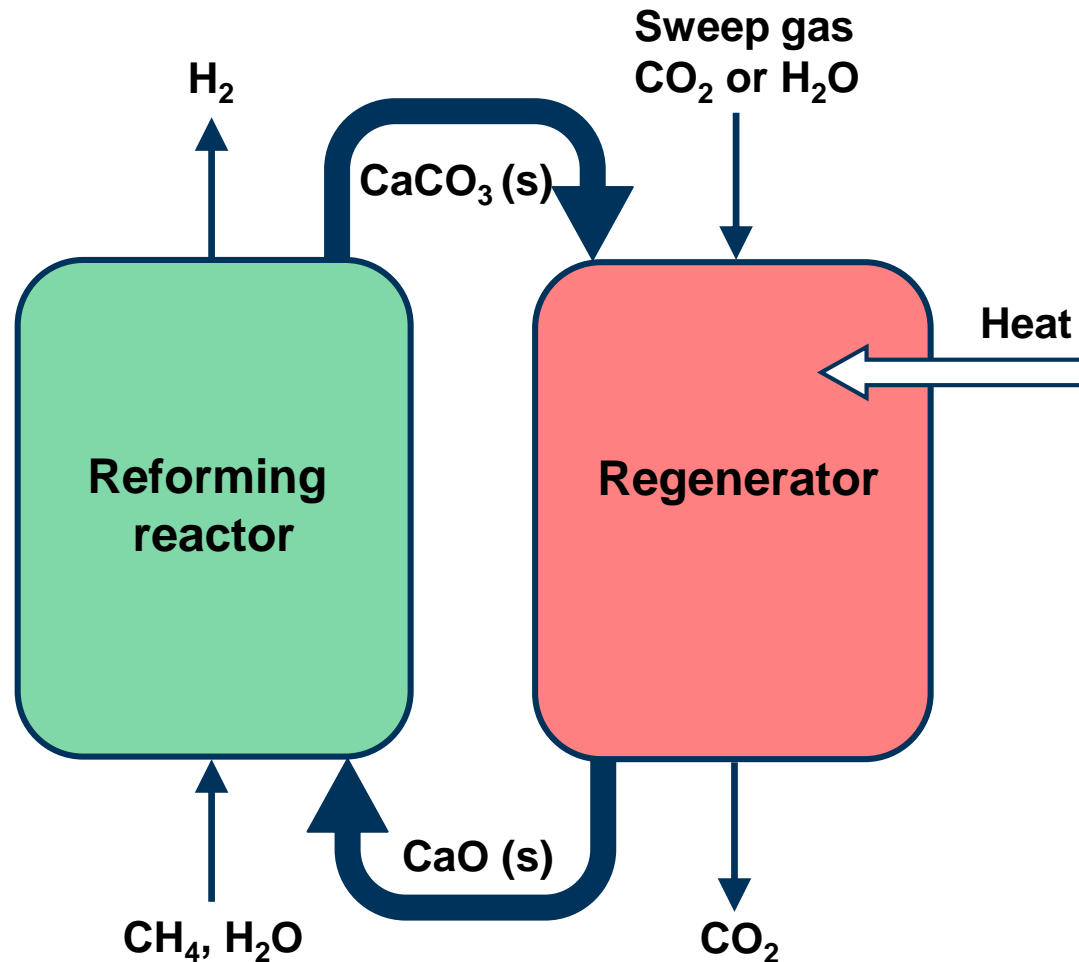


$$\Delta H^\circ_{25\text{ }^\circ\text{C}} = -13 \text{ kJ/mol}$$

## Advantages:

- Reduced operating temperature ~ 450 – 630 °C
- Elimination of the shift reactor and catalyst
- Reduction, or possibly even elimination, of subsequent purification steps

# Schematic diagram of the SE-SMR process

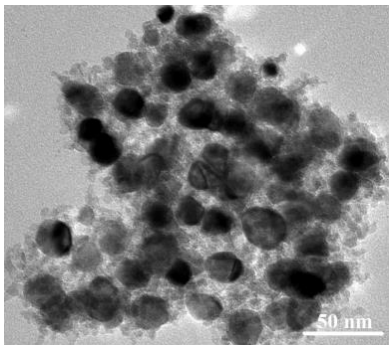


# Material options for the SE-SMR reaction:

1. Limestone + reforming catalyst
2. Synthetic CaO-based sorbent + reforming catalyst
3. Bifunctional catalyst - sorbent

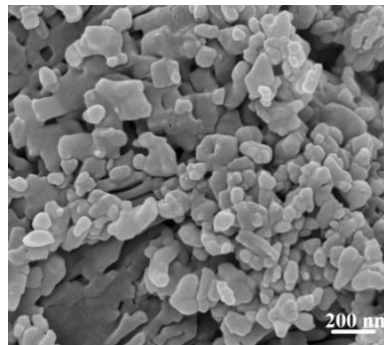
## Materials studied here:

- Ni-based catalyst  
(47 wt.% Ni)



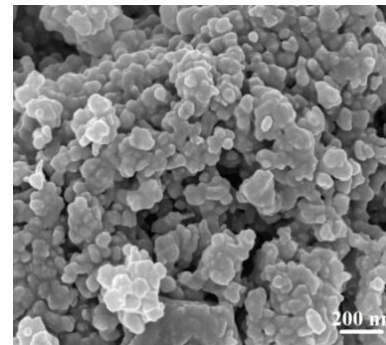
- CaO-based sorbents

Limestone

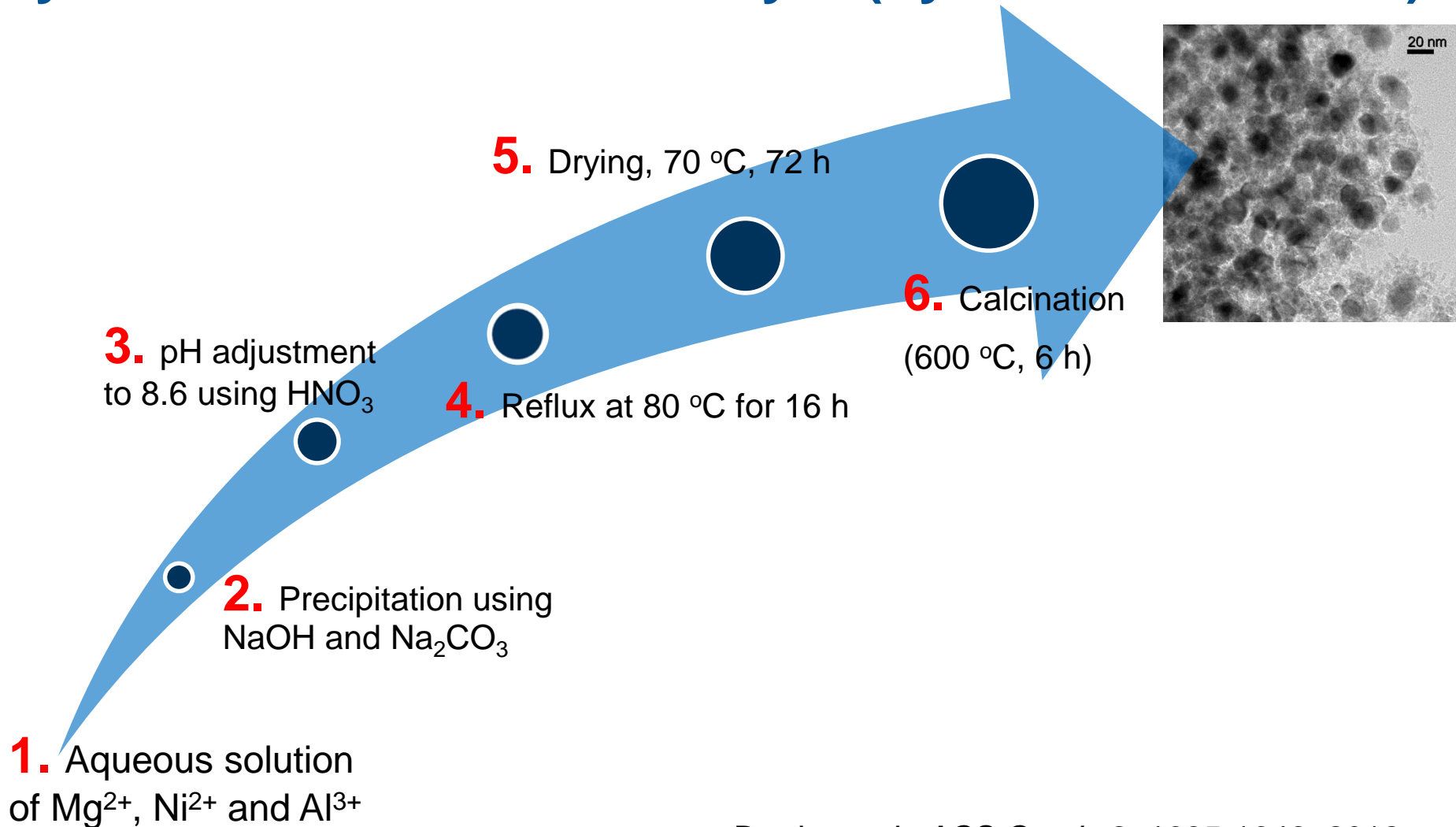


Pellets

(90 wt.% CaO, 10 wt.% cement)

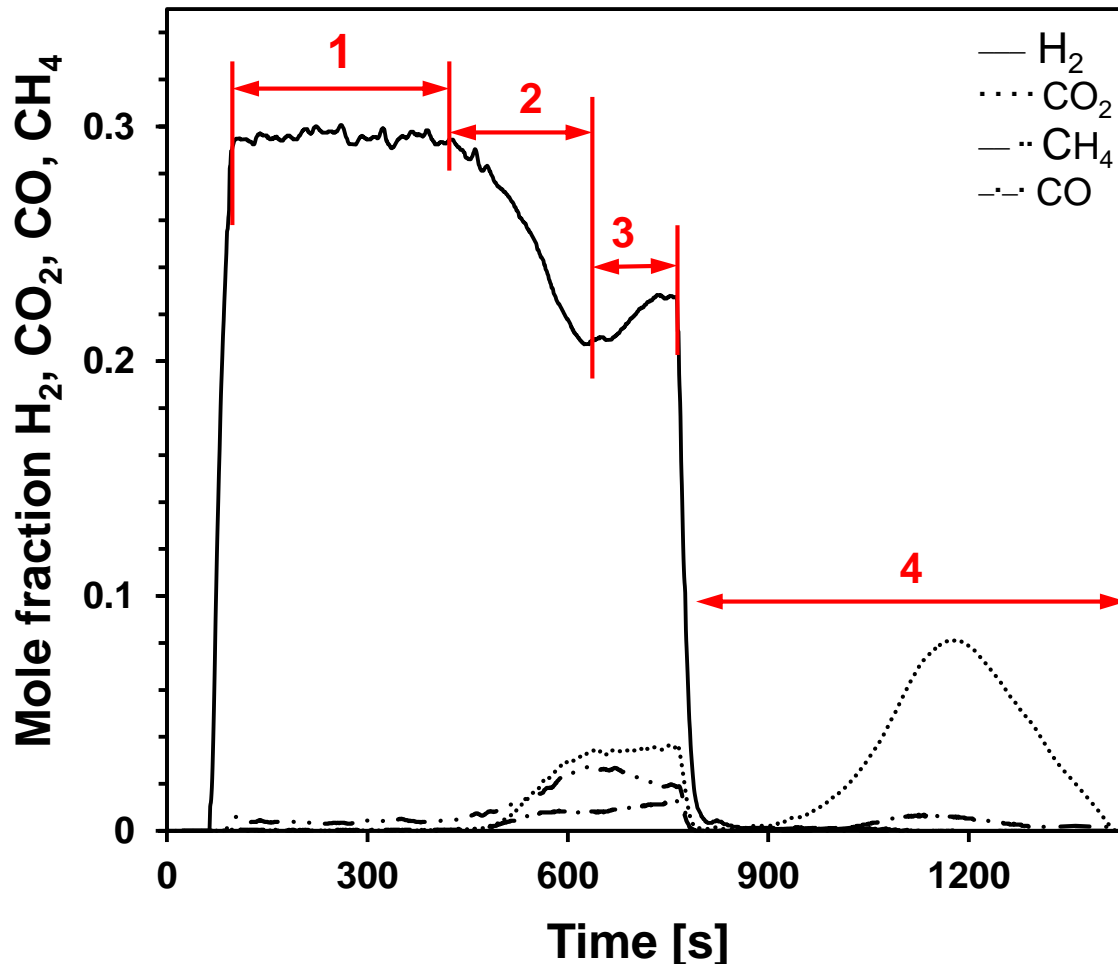


# Synthesis of Ni-based catalyst (hydrotalcite-based)



Broda *et al.*, *ACS Catal.*, 2, 1635-1646, 2012

# SE-SMR reaction + regeneration



## 1. Pre-breakthrough period

- Complete CH<sub>4</sub> conversion and high H<sub>2</sub> selectivity
- Fast absorption of CO<sub>2</sub> via the formation of CaCO<sub>3</sub>

## 2. Breakthrough period

- Fairly sharp decrease in the mole fraction of H<sub>2</sub> and breakthrough of CO<sub>2</sub>

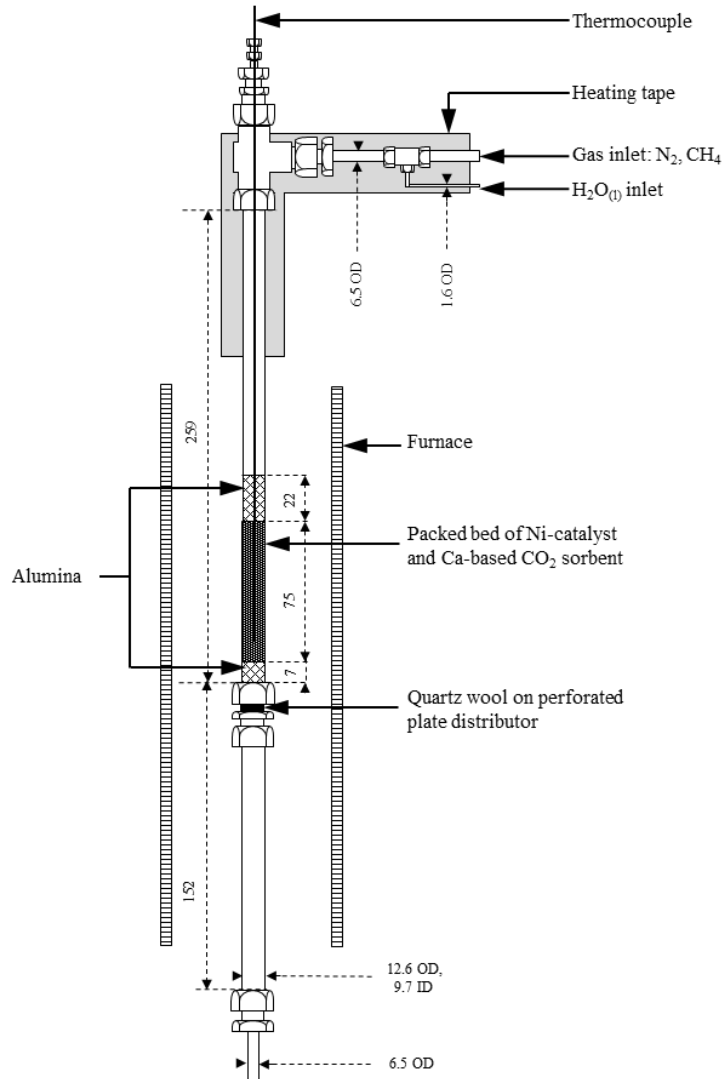
## 3. Post-breakthrough period

## 4. Calcination



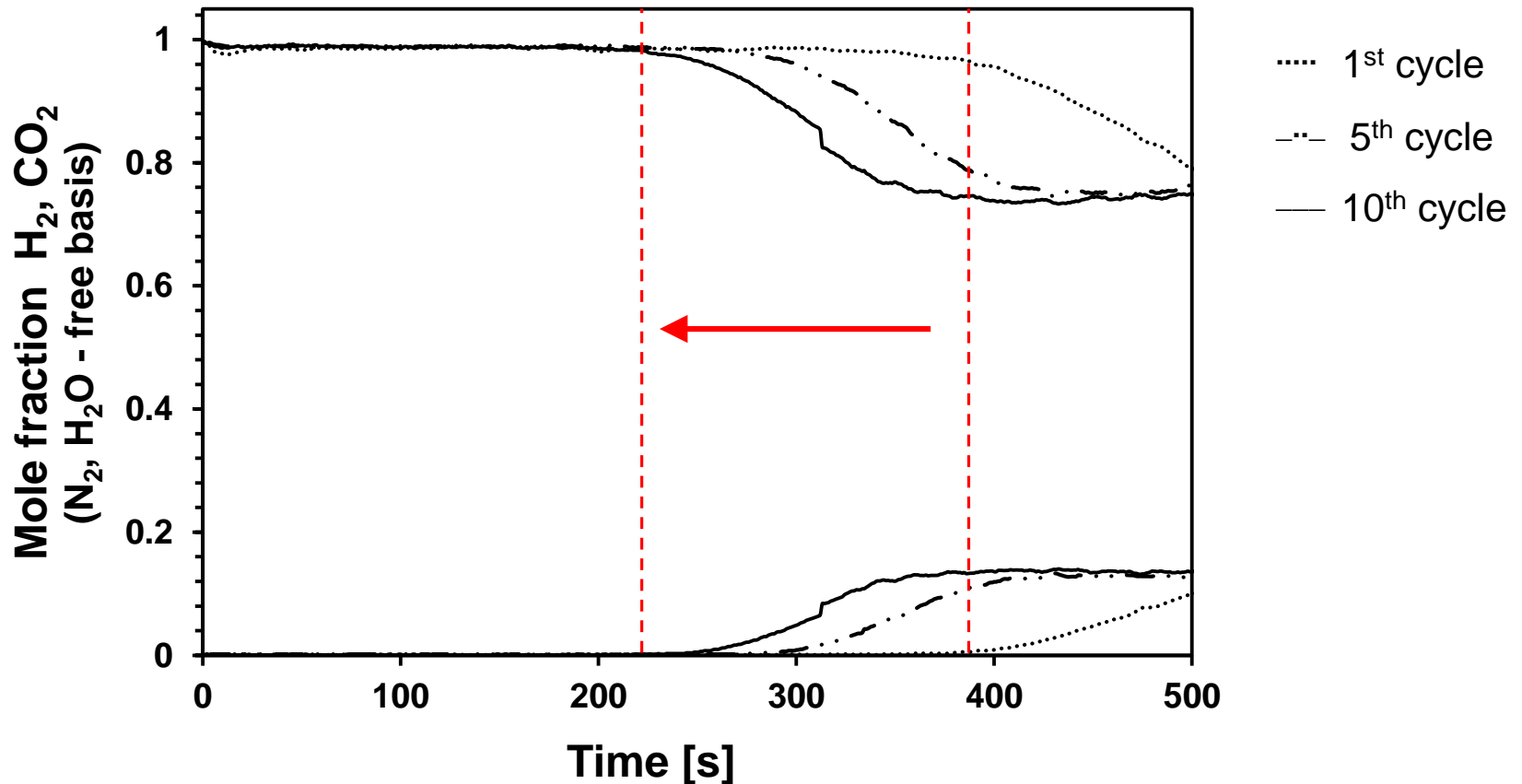
# Fixed-bed reactor

- Particle size: 300-710  $\mu\text{m}$
- Reforming temperature: 550  $^{\circ}\text{C}$
- Calcination temperature: 750  $^{\circ}\text{C}$
- $\text{H}_2\text{O}/\text{CH}_4$  ratio: 4



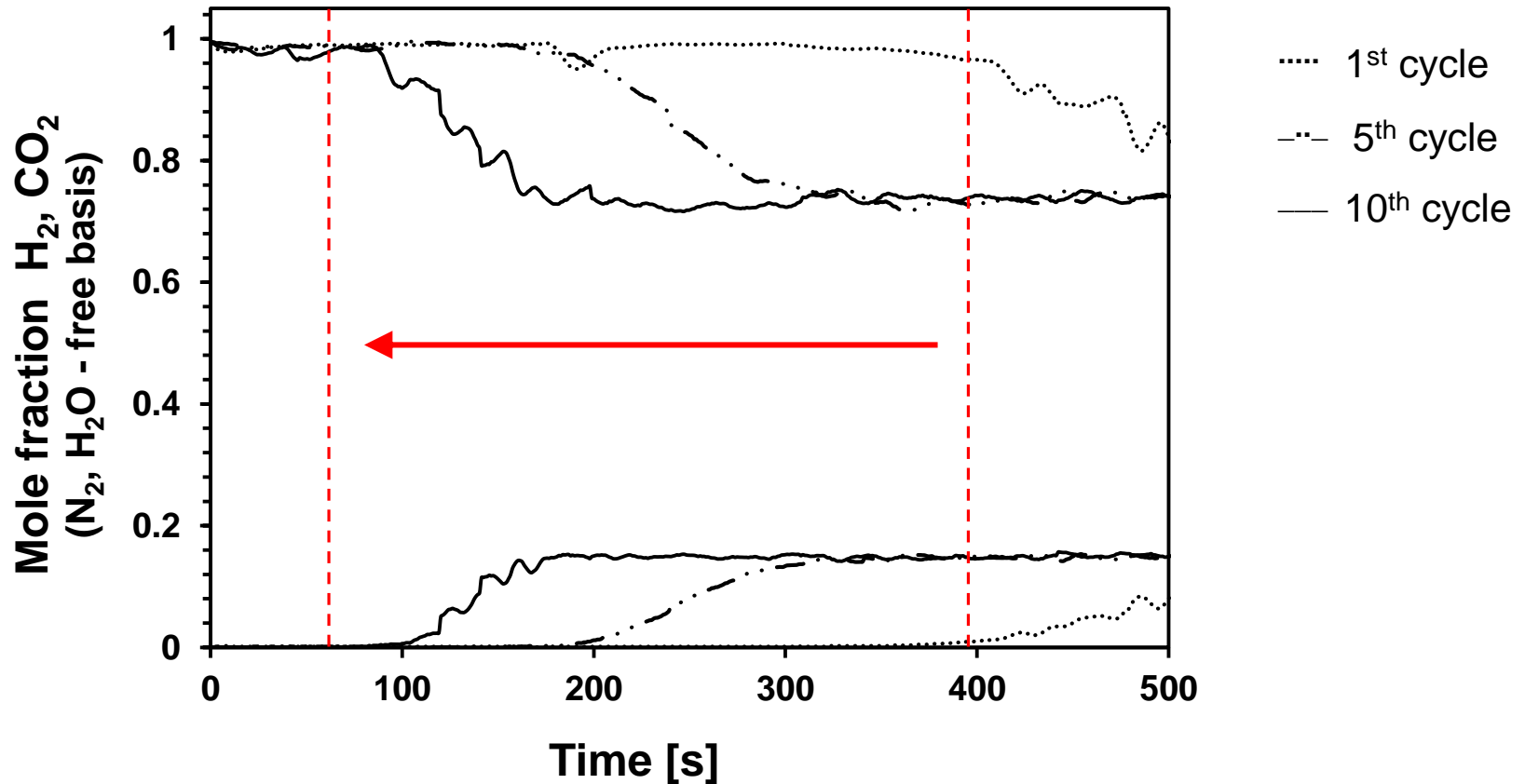
Broda *et al.*, *ACS Catal.*, 2, 1635-1646, 2012

# SE-SMR reaction (Ni-catalyst + pellets)



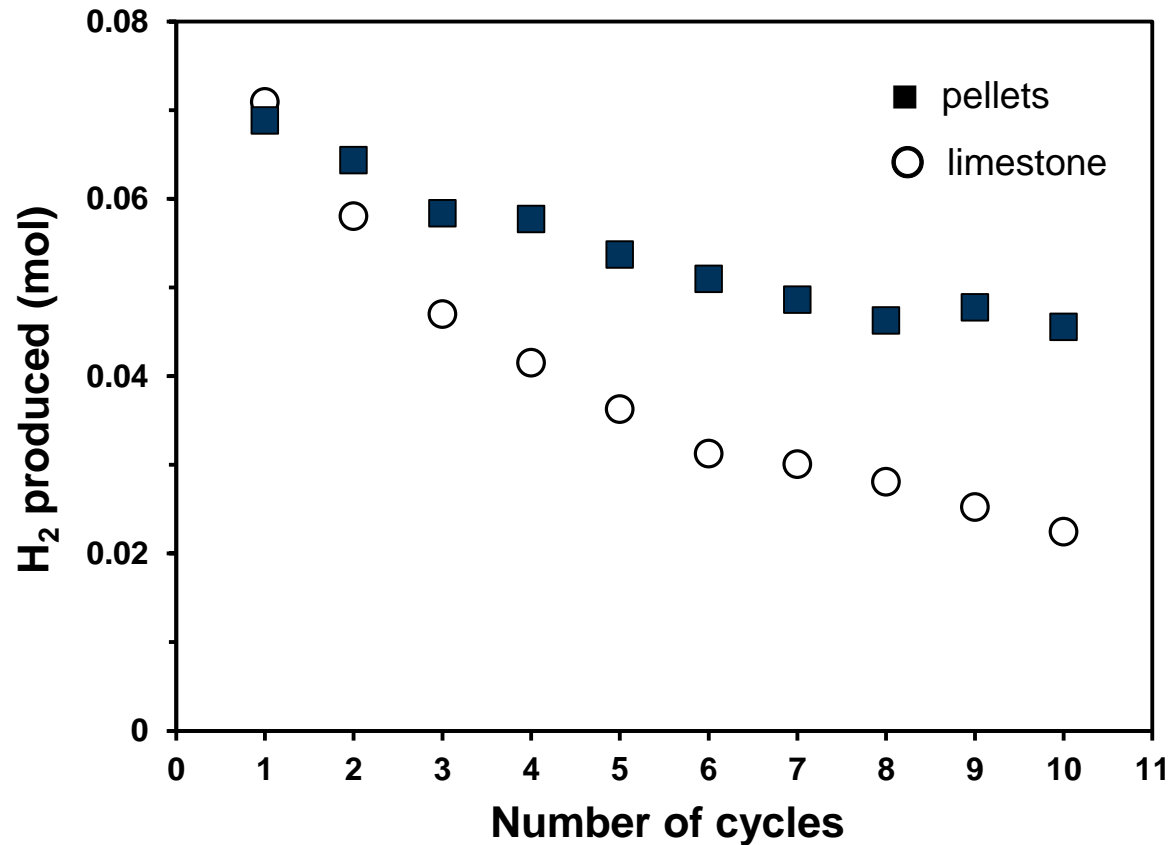
The time at which breakthrough occurs decreased from ~380 to ~280 s, but stabilized after the 5<sup>th</sup> cycle.

# SE-SMR reaction (Ni-catalyst + limestone)



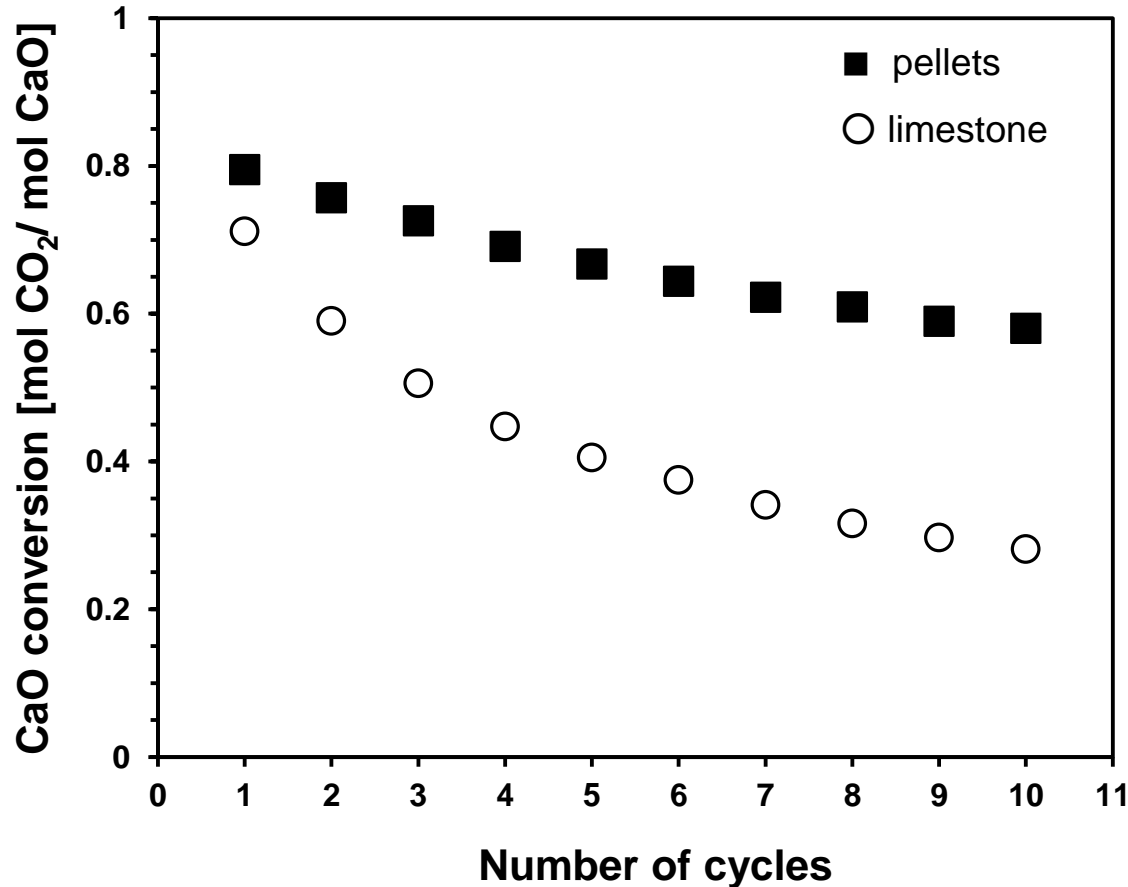
For limestone, the time at which breakthrough occurs decreased continuously from ~370 s in the 1<sup>st</sup> cycle to 95 s in the 10<sup>th</sup> cycle.

# H<sub>2</sub> production



- After the 8<sup>th</sup> cycle, Ni-catalyst + pellets show a stable pre-breakthrough production of H<sub>2</sub>
- Continuous deactivation of Ni-catalyst + limestone.

# CaO conversion



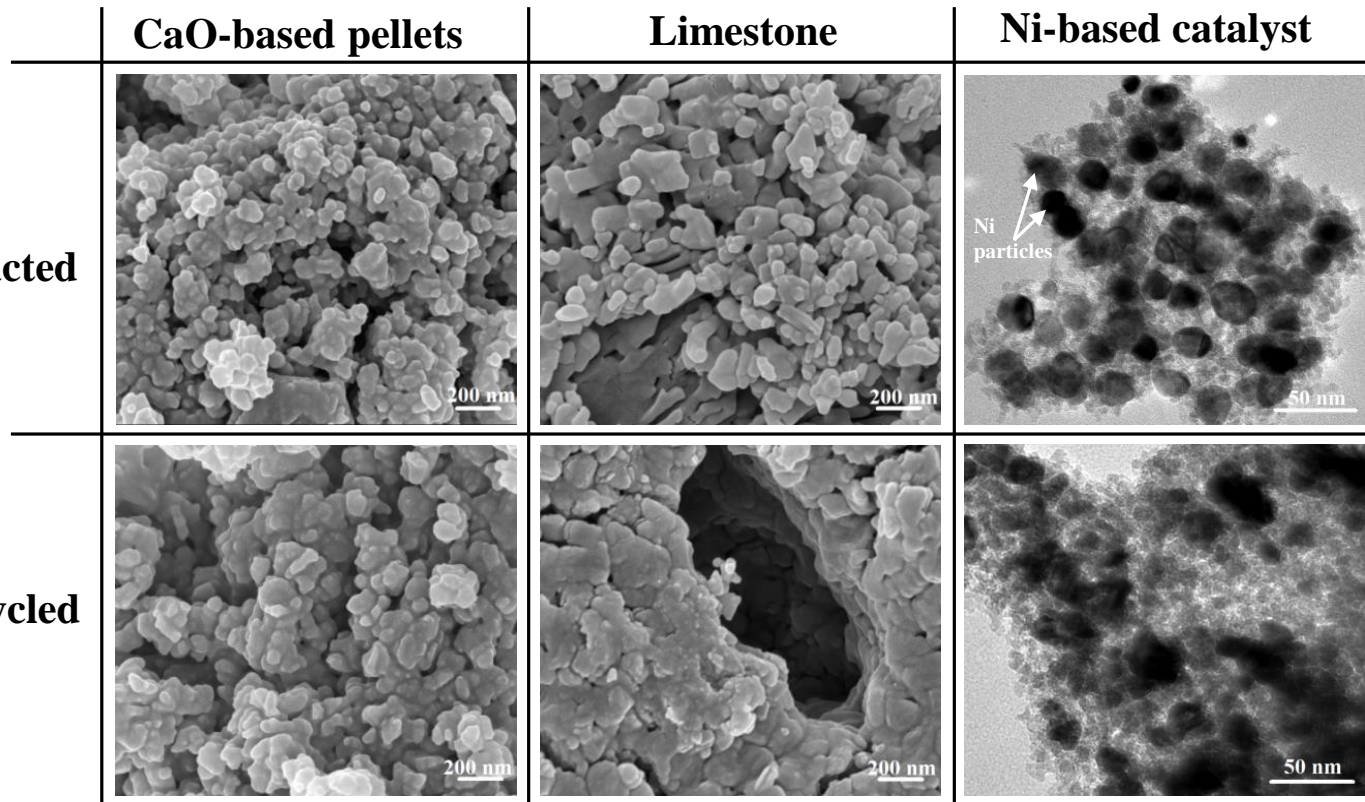
After 10 cycles, the pellets showed a ~110 % higher CaO conversion than the reference limestone.

# Characterisation of the materials

| Unreacted materials                  |                   |           |                   |
|--------------------------------------|-------------------|-----------|-------------------|
|                                      | CaO-based pellets | Limestone | Ni-based catalyst |
| BET surface area [m <sup>2</sup> /g] | 28                | 30        | 175               |
| BJH pore volume [cm <sup>3</sup> /g] | 0.35              | 0.32      | 0.36              |
| After 10 SE-SMR cycles               |                   |           |                   |
| BET surface area [m <sup>2</sup> /g] | 18                | 9         | 93                |
| BJH pore volume [cm <sup>3</sup> /g] | 0.15              | 0.06      | 0.33              |

- The BET surface area and BJH pore volume of limestone drastically decreased over 10 SE-SMR cycles.
- The Ni-based catalyst and the pellets possessed good thermal stability.

# Structural changes with SE-SMR cycles



- The initial morphology of the synthetic CO<sub>2</sub> sorbent and Ni-based catalyst did not change appreciably over 10 cycles.
- The cycled limestone lost its nano-structured morphology completely due to its intrinsic lack of a support.

# Conclusions

- At a reaction temperature of 550 °C and using a steam-to-methane ratio of 4, equilibrium conversion of methane was achieved for both systems, resulting in the production of high-purity hydrogen (~99%).
- The pellets showed better performance in the SE-SMR reaction than limestone, demonstrated by a high cyclic CaO conversion, and in a higher quantity of H<sub>2</sub> produced during the pre-breakthrough period.
- The favourable performance of the pellets was attributed to their stable nano-structured morphology stabilized by homogeneously dispersed mayenite.
- The cycled limestone lost its nano-structured morphology completely over 10 SE-SMR cycles due to its intrinsic lack of a support component.



# Acknowledgment

Swiss National Science Foundation for financial support (Project 200021\_135457/1)



Electron Microscopy Center of ETH Zurich (EMEZ) for providing access and training to electron microscopes.