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Advanced pre-combustion CO_2 capture (ADhOC-CCS)

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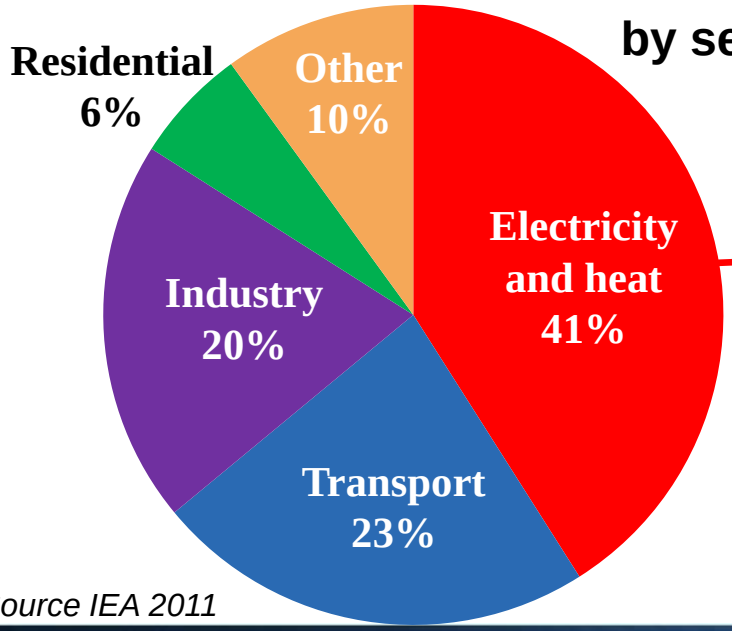
CO_2 emissions

The use of coal for electricity generation for selected countries

Poland	93 %	**Israel**	71 %*	**Czech Rep.**	59 %
South Africa	93 %*	**Kazakhstan**	70 %*	**Greece**	58 %
Australia	80 %	**India**	69 %*	**USA**	50 %
PR China	78 %*	**Morocco**	69 %*	**Germany**	47 %

Source IEA 2007
** Only 2005 data available for these countrie*

Global CO_2 emissions by sector in 2009



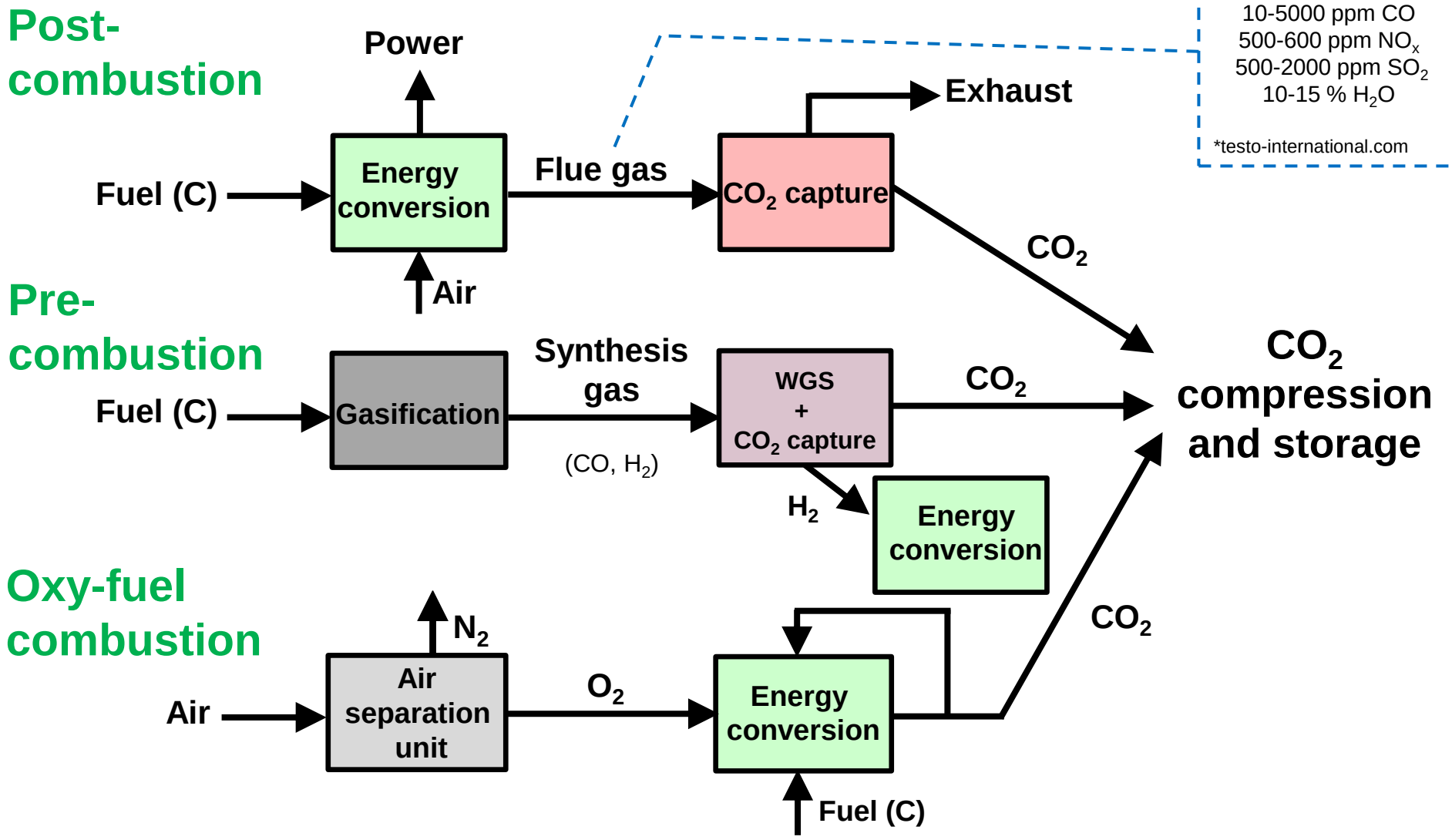
relies heavily on coal

Source IEA 2011

The three different CO_2 capture concepts

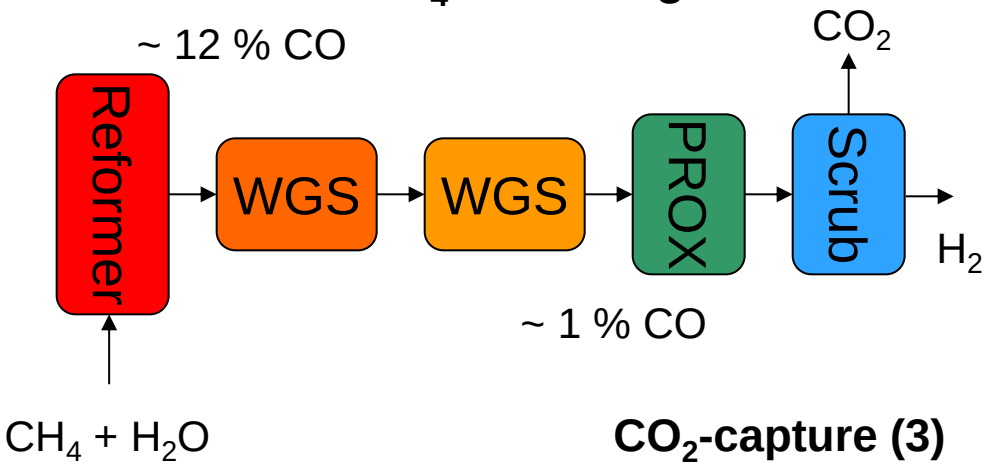
15-18 % CO_2
5-9 % O_2
10-5000 ppm CO
500-600 ppm NO_x
500-2000 ppm SO_2
10-15 % H_2O

*testo-international.com



Sorbent-enhanced steam methane reforming

Conventional CH_4 reforming



Steam methane reforming (1)

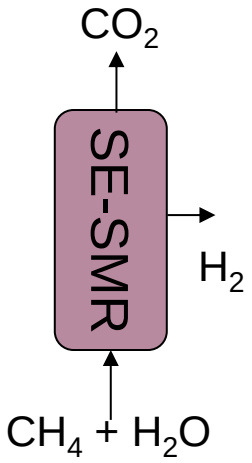
$CH_4 + H_2O \rightarrow CO + 3\ H_2$;
ΔH^0_{293K} = + 206 kJ/mol

Water-gas-shift (2)

$CO + H_2O \rightarrow CO_2 + H_2$;
ΔH^0_{293K} = -41 kJ/mol

CO_2-capture (3)

+ $CaO + CO_2 \rightarrow CaCO_3$;
ΔH^0_{293K} = -178 kJ/mol



Sorbent enhanced steam methane reforming (1-3)

$CH_4 + 2\ H_2O + CaO \rightarrow CaCO_3 + 4\ H_2$; ΔH^0_{293K} = -13 kJ/mol

CO_2 sorbent

- Different CO_2 sorbents have been proposed including Li_2ZrO_3, $KLiZrO_3$, Li_4SiO_4, Na_2ZrO_3, CaO or K-promoted hydrotalcite

- The CO_2 sorbent has to fulfill the following criteria:

  (i) high CO_2 capture capacity (g CO_2/g sorbent)
  (ii) cyclic capture stability
  (iii) fast kinetics for the CO_2 capture and release reaction
  (iv) suitable thermodynamics

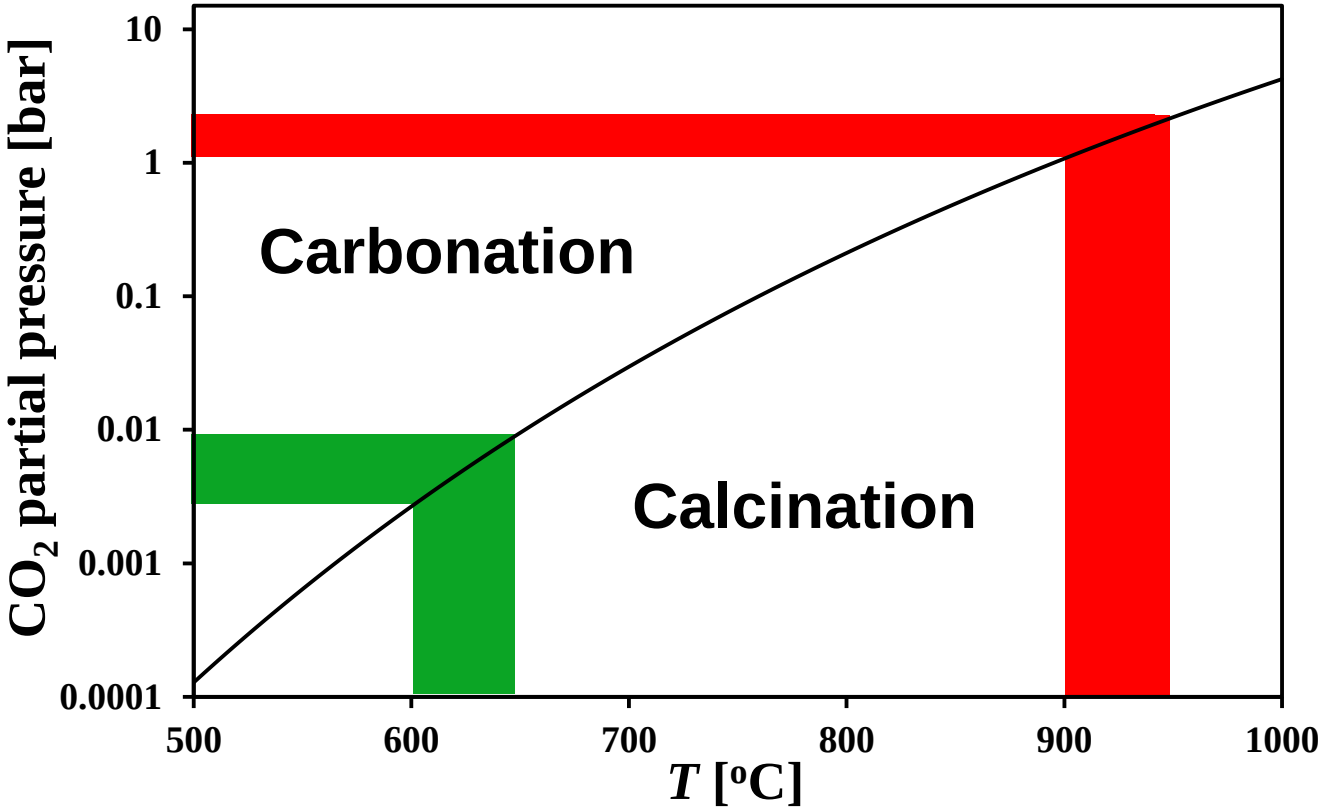
- Ochoa-Fernández et al. argued that CaO fullfils criteria (i-iv) best, e.g. the CO_2 capacity of pure CaO is 0.79 g CO_2/g sorbent.

- However, the major disadvantage of pure CaO is its rapidly decreasing, cyclic CO_2 uptake.

Calcium looping process

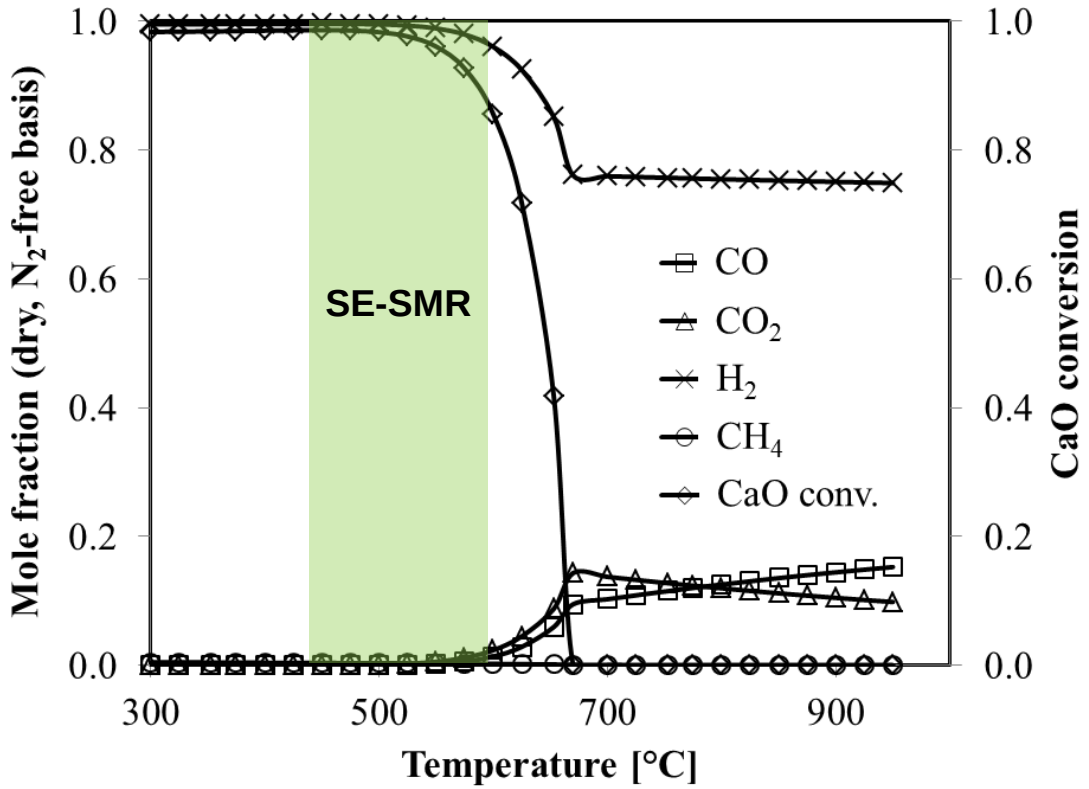
Capture of CO_2 (carbonation): $CaO + CO_2 \rightarrow CaCO_3 \quad \Delta H^0_{25°C} = -178\ kJ/mol$

Sorbent regeneration (calcination): $CaCO_3 \rightarrow CaO + CO_2 \quad \Delta H^0_{25°C} = +178\ kJ/mol$



Broda *et al.*, *Porous materials for carbon dioxide capture*, *Springer-Verlag*, Berlin Heidelberg, 2014
Barin and Platzki, *Thermochemical data of pure substances. VCH Verlagsgesellschaft*, Weinheim, 1995

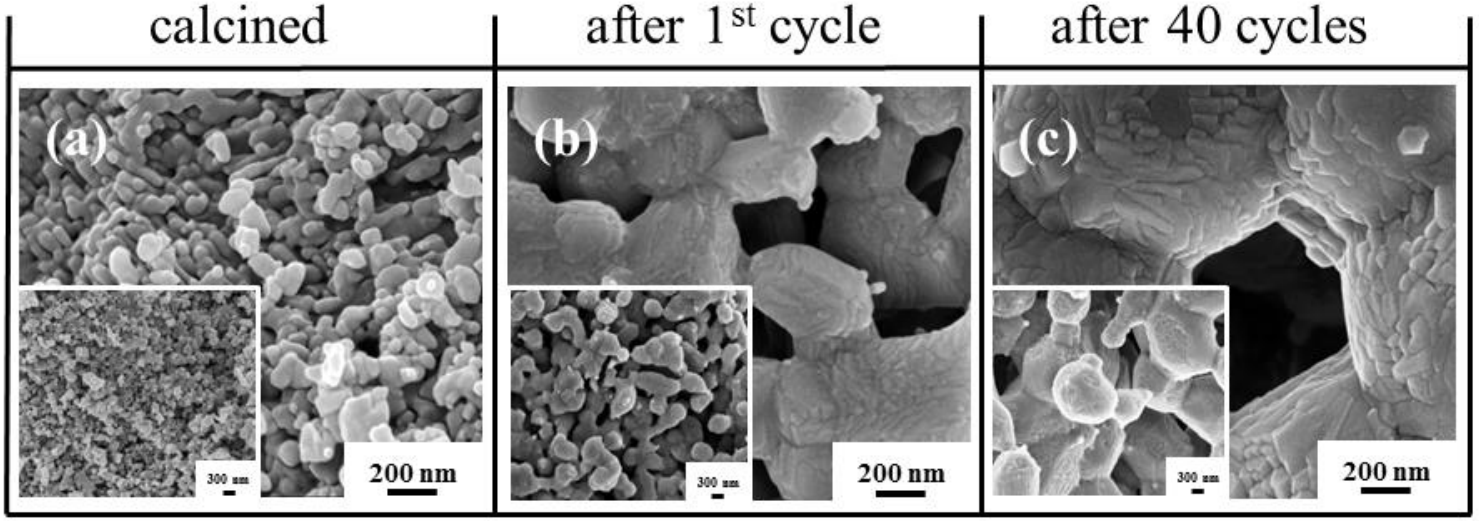
Equilibrium thermodynamics

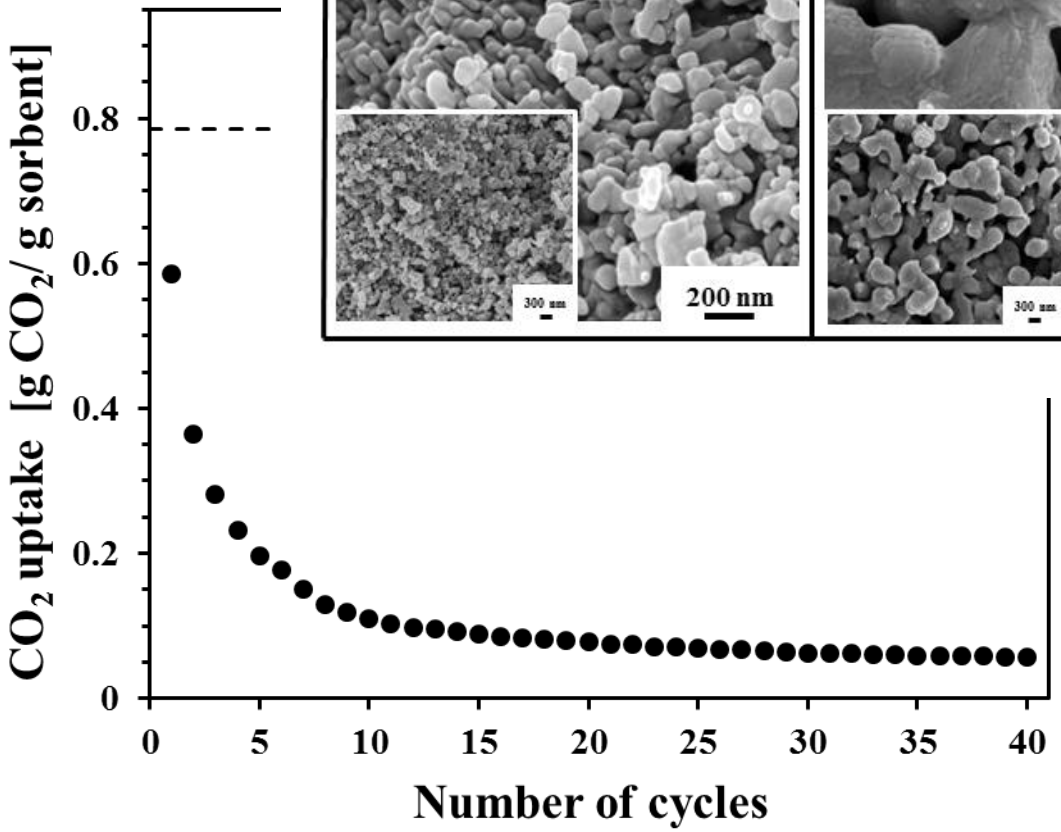


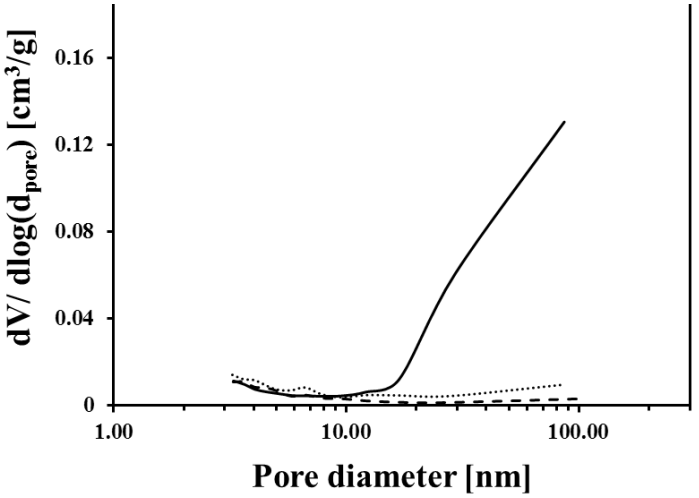
T < 575 °C equilibrium is almost completely on product side → high purity H_2

T > 675 °C decomposition of $CaCO_3$ → conventional SMR reaction

Natura

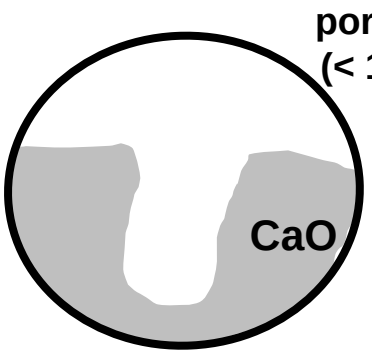

calcined
after 1st cycle
after 40 cycles
(a)
(b)
(c)
300 nm
200 nm


CO2 uptake [g CO2/ g sorbent]
0
0.2
0.4
0.6
0.8
0
5
10
15
20
25
30
35
40
Number of cycles

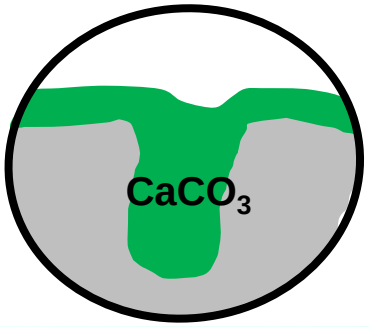

dV/ dlog(dpore) [cm3/g]
0
0.04
0.08
0.12
0.16
1.00
10.00
100.00
Pore diameter [nm]

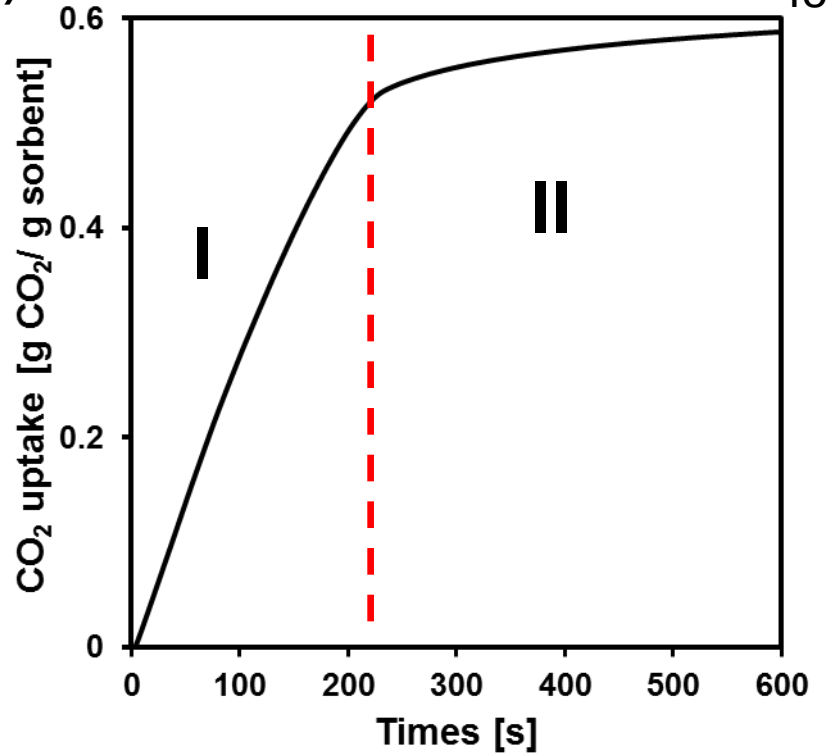
Characteristics of the carbonation reaction

Molar volume $CaCO_3$/molar volume CaO ~ 2

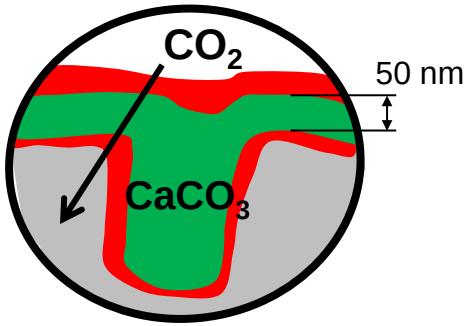


I reaction step
Fast, pore filling reaction mechanism





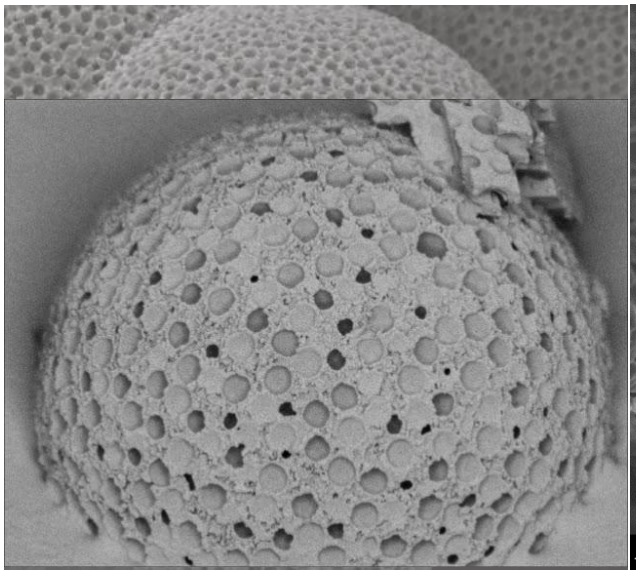
II reaction step
Slow, product layer forming reaction mechanism



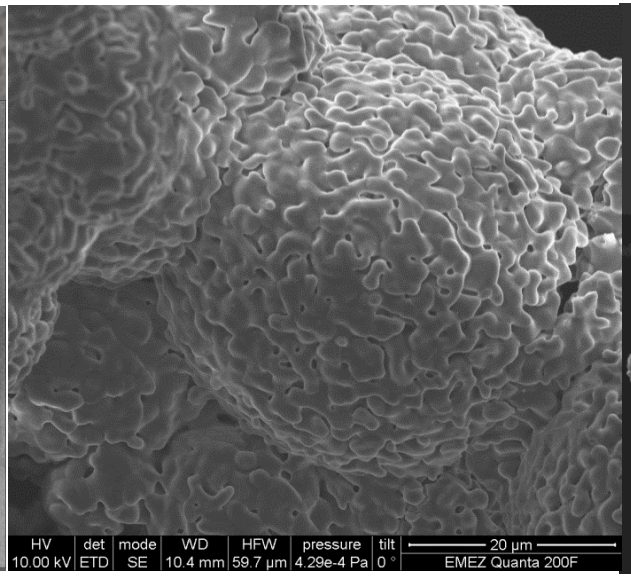
Critical product layer thickness: ~ 50 nm (Alvarez and Abanades; *Ind. Eng. Chem. Res.*, 44, 5608-5615, 2005)

Sintering of un-supported CaO

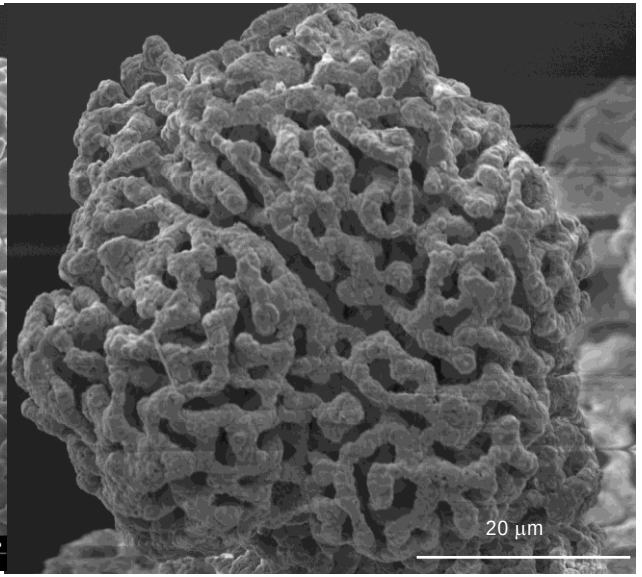
Template removed



Carbonated

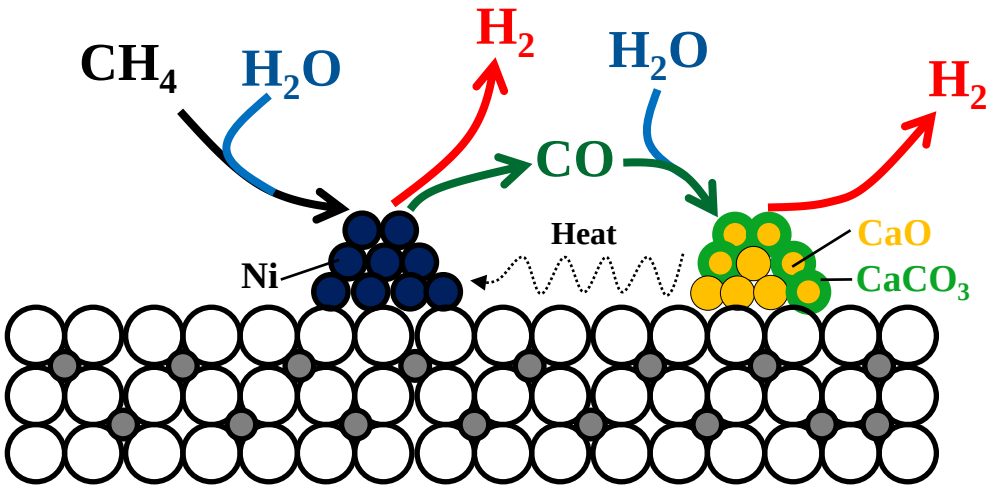


After 8 cycles



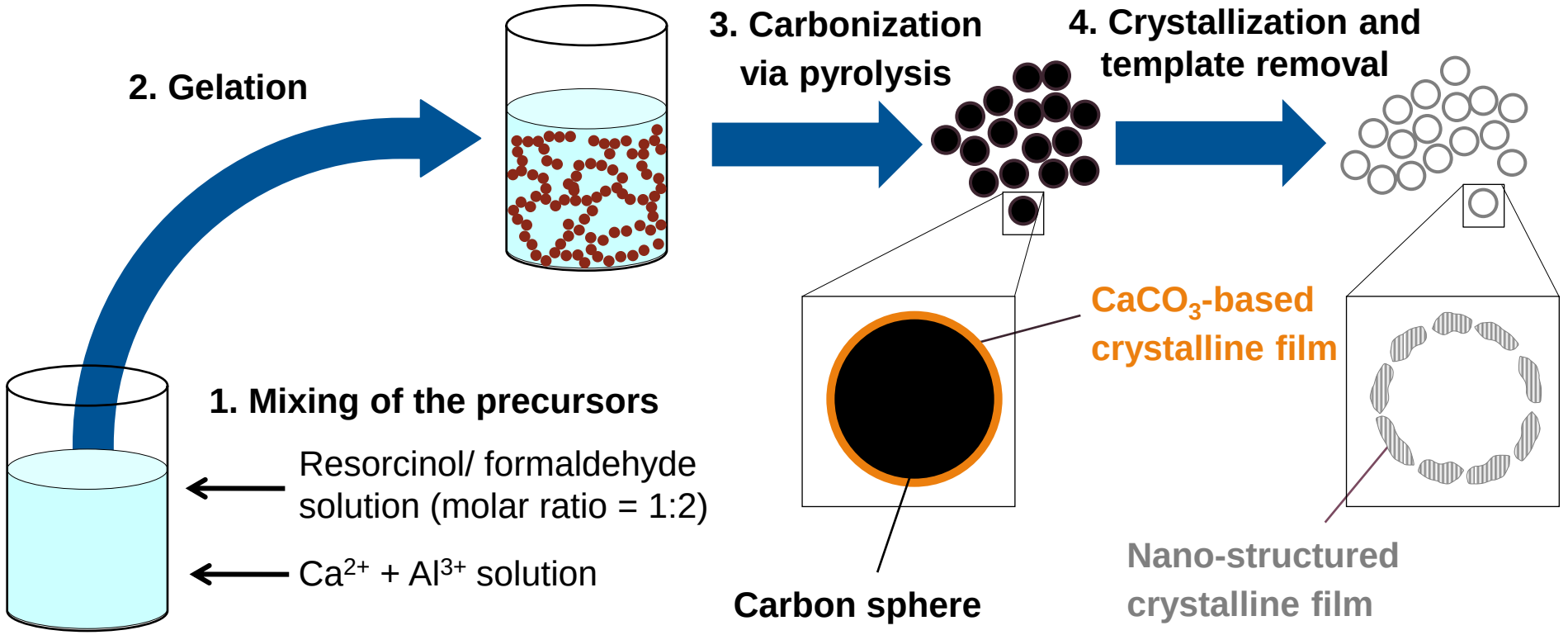
Material options for the SE-SMR reaction:

1. **Limestone + reforming catalyst**
2. **Synthetic sorbent + dedicated reforming catalyst**
3. **Bifunctional catalyst - sorbent**



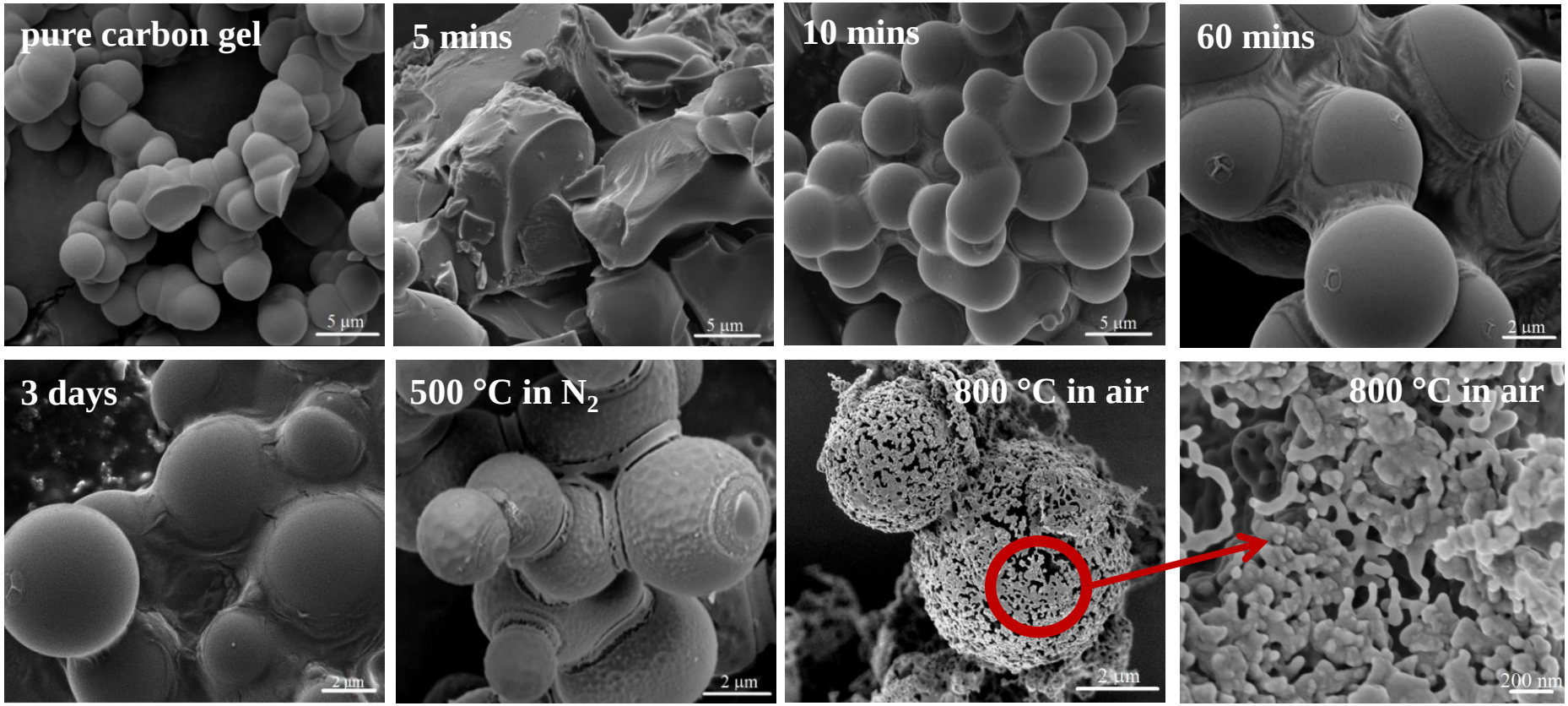
Synthesis of highly efficient CO_2 sorbents

Synthesis of Ca-Al-based, CO_2 sorbents with a hierarchical porosity



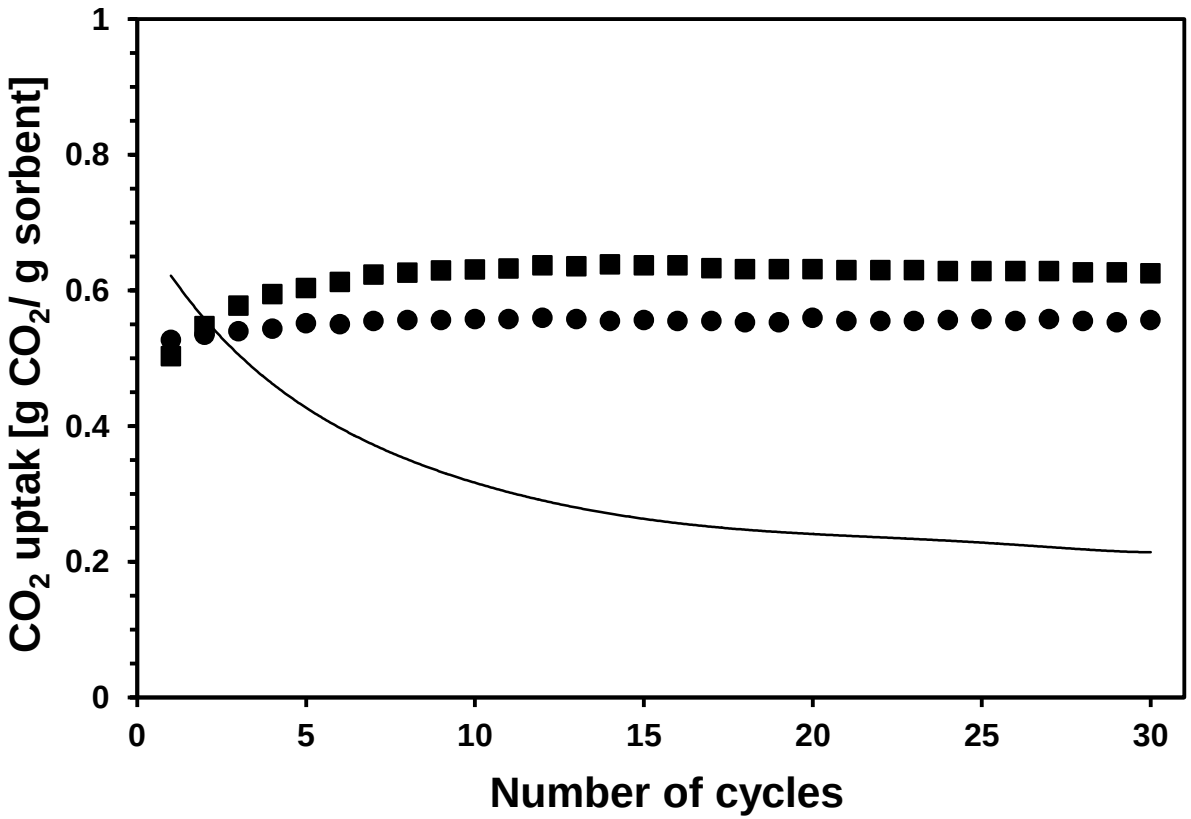
Broda *et al*., *Adv. Mat.*, 24, 3059-3064, 2012

SEM images of the synthesis steps



Broda *et al*., *Adv. Mat.*, 24, 3059-3064, 2012

Cyclic CO_2 uptake of the new sorbent (TGA)



(■) Ca:Al_95:5,

(●) Ca:Al_90:10,

(—) limestone.

The new sorbent exceeds the CO_2 uptake of limestone by 200 %.

Broda *et al*., *Adv. Mat.*, 24, 3059-3064, 2012

Synthesis of a bifunctional catalyst-sorbent

Bi-functional catalyst-sorbent (Ni-Ca-Htlc)

1. Aqueous solution of Ca^{2+}, Mg^{2+}, Ni^{2+} and Al^{3+}

2. Precipitation using NaOH and Na_2CO_3

3. pH adjustment to 8.6 using HNO_3

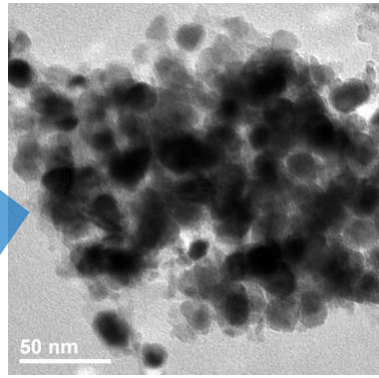
4. Reflux at 80 ^oC for 16 h

5. Drying, 70 ^oC, 72 h

6. Calcination:

a) 600 ^oC, 6 h

b) 800 ^oC, 2 h



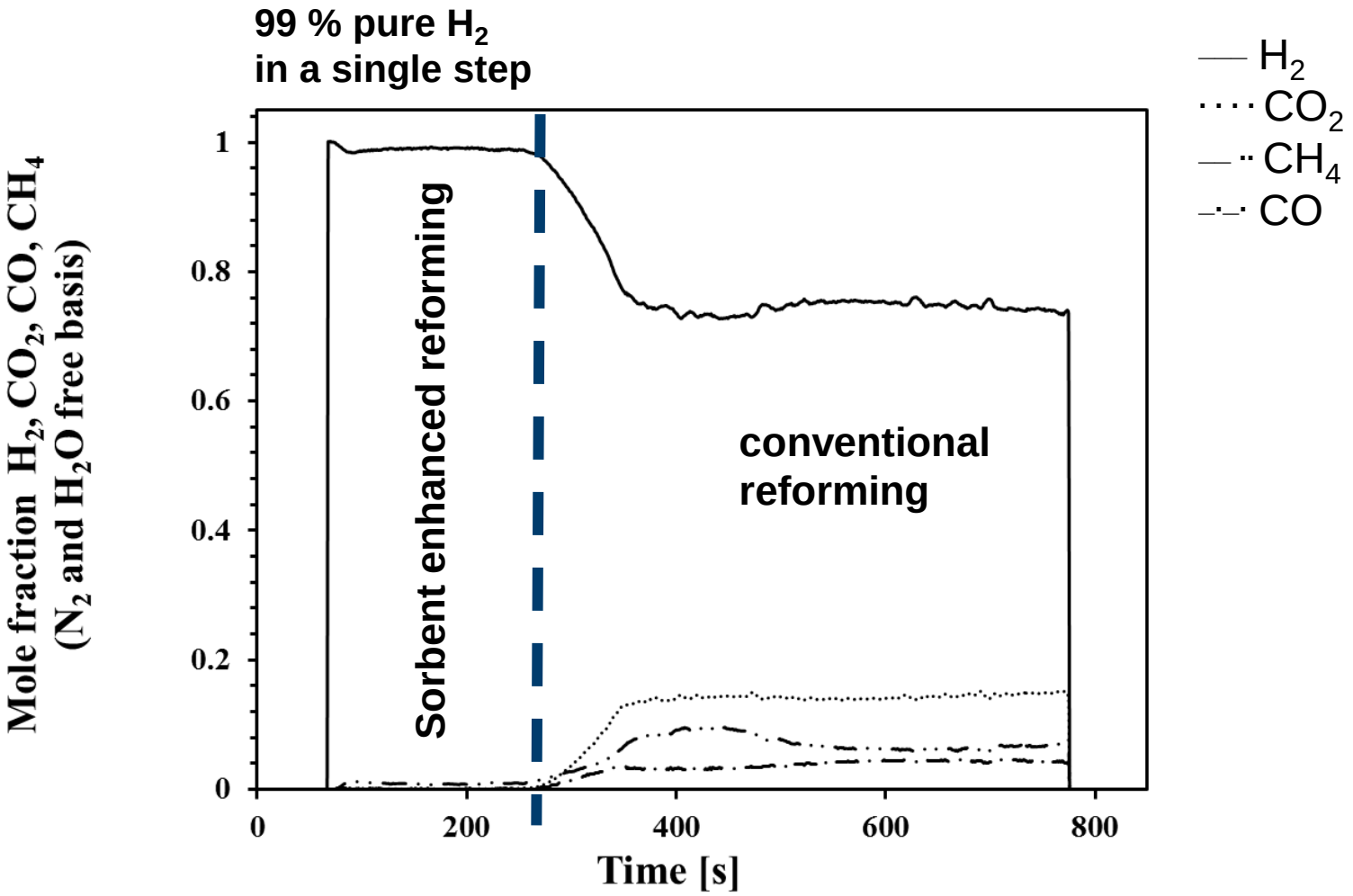
46 wt.% Ni
21 wt.% CaO

Reference materials

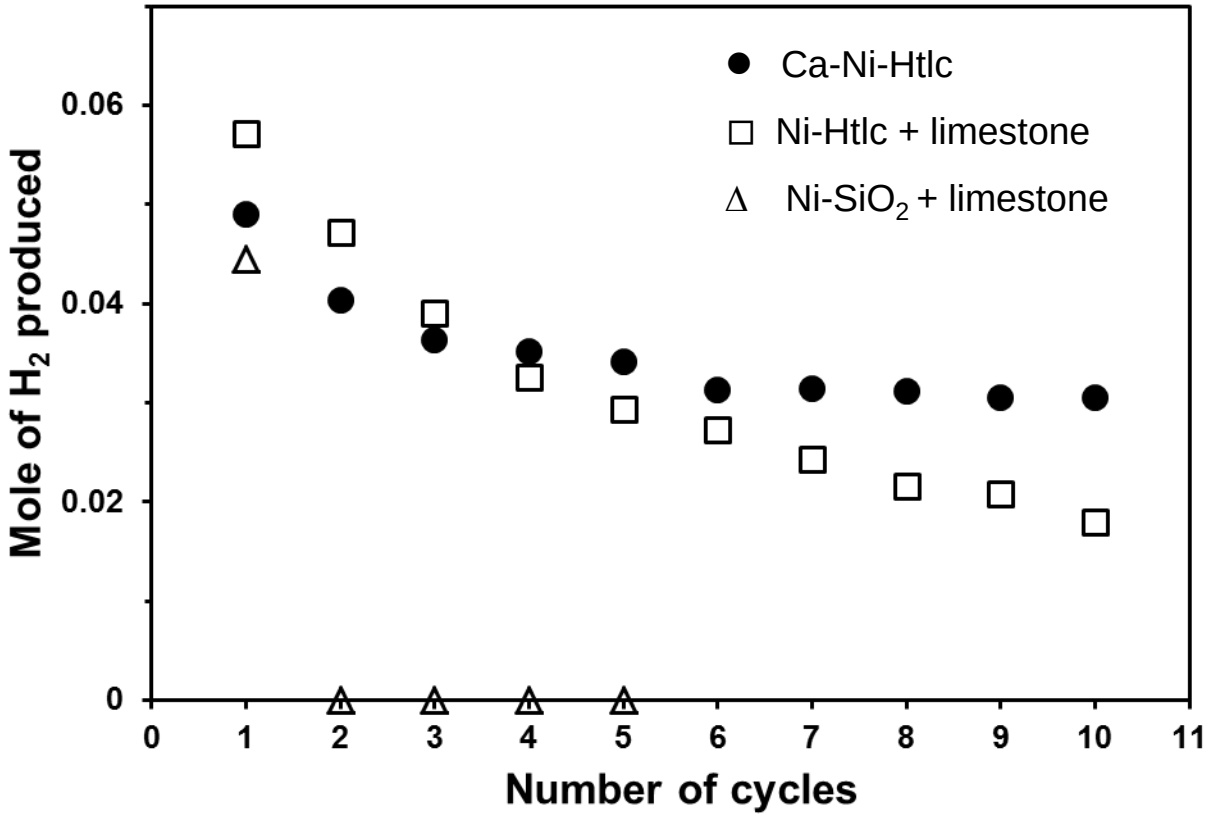
Ni-Htlc (47 wt.% Ni) + limestone
Ni-SiO_2 (Sigma Aldrich, 52 wt. % Ni) + limestone

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

SE-SMR performance (Ca-Ni-Htlc)



High-purity H_2 production



- **Ca-Ni-Htlc shows a stable pre-breakthrough production of H_2 after the 6th cycle.**
- **Continuous deactivation of Ni-Htlc + limestone**
- **For Ni-SiO_2 + limestone total loss of activity from the 2nd cycle**

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