Sorption enhanced steam methane reforming coupled with chemical looping: Novel technology for high purity hydrogen production with low energy demand and carbon footprint

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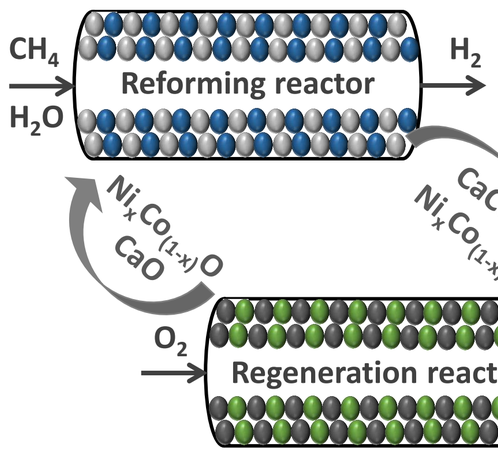
Priority topic area: Clean Energy and Climate Action

1 – Problem definition and objective

- H_2 is a major industrial gas and promising energy vector, but the conventional steam reforming of natural gas synthesis is characterised by high CO_2 emissions and energy demand.
- Introducing a CaO-based sorbent enables *in situ* CO_2 removal and high-purity H_2 production in a single autothermal stage at a milder reforming temperature of 650°C. However, the formed $CaCO_3$ must be regenerated in a second reactor.
- Energy demand of endothermic regeneration can be supplied by the exothermic oxidation of a suitable oxygen carrier (OC).
- **Objective:** Investigate Ni-Co OCs to experimentally prove the SE-CL-SMR concept and unravel the effect Co addition.

Sorption Enhanced Chemical Looping Steam Methane Reforming (SE-CL-SMR)



Reforming stage

$CH_4 + H_2O \rightarrow 3H_2 + CO$, $\Delta H = 206$ kJ/mol

Q $CO + H_2O \rightarrow H_2 + CO_2$ $\Delta H = -41$ kJ/mol

$CaO + CO_2 \rightarrow CaCO_3$ $\Delta H = -179$ kJ/mol

$4Ni_xCo_{(1-x)}O + CH_4 \rightarrow 4Ni_xCo_{(1-x)} + 2H_2O + CO_2$ $\Delta H > 0$

$Ni_xCo_{(1-x)}O + H_2 \rightarrow Ni_xCo_{(1-x)} + H_2O$ $\Delta H \leq 0$

Regeneration stage

$CaCO_3 \rightarrow CaO + CO_2$ $\Delta H = 179$ kJ/mol

Q $Ni_xCo_{(1-x)} + \frac{1}{2}O_2 \rightarrow Ni_xCo_{(1-x)}O$ $\Delta H < 0$

2 – Methodology

SE-CL-SMR experiments in a fixed bed reactor

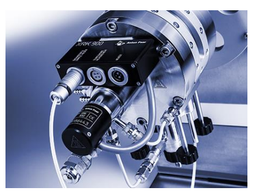
Loading reactor with mixture:
Sorbent: 66wt%CaO/$CaZrO_3$
OC: 40wt%$Ni_xCo_{(1-X)}O/ZrO_2$
$(Ni_xCo_{(1-x)}O)/CaO = 0.5$

Reforming stage:
T = 650°C
H_2O/CH_4=3, GHSV=215 h^{-1}

Reforming stage:
T = 650→800°C
Air flow, GHSV=500 h^{-1}

In situ X-ray diffraction (XRD)

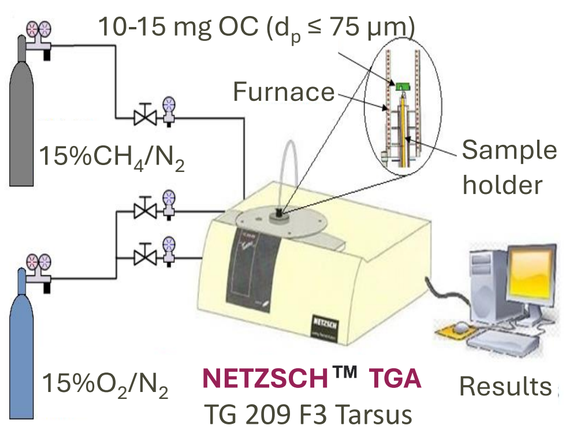
Bruker™ D8 Advance



Anton Paar™ XRK-900

Comparison of structure alterations of pre-reduced OCs during oxidation:
Step 1: T = 25→650°C, N_2 flow
Step 2: T = 650°C, air flow

Kinetic analysis of redox steps using thermogravimetric analysis (TGA)



Reduction stage:
T = 650°C, 20 min, 15%CH_4/N_2

Oxidation stage:
T = 800°C, 20 min, 15%O_2/N_2

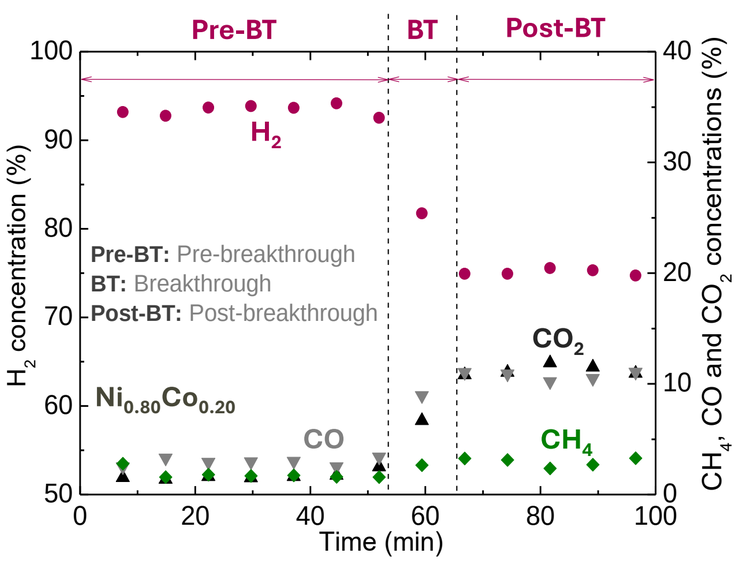
Solid-state kinetic modelling:

$$\frac{dX}{dt} = k(T) \times f(X) \times g\left(p_{red.oxid/gas}\right)$$

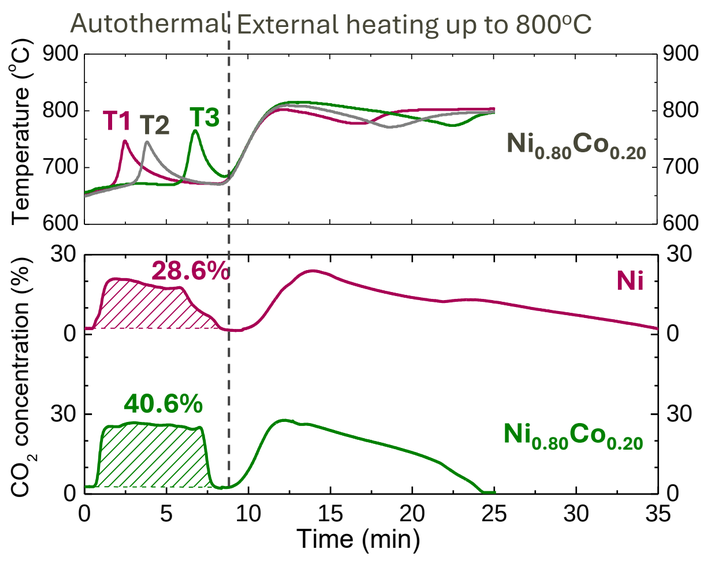
Avrami-Erofeev model (n=3):

$$f(X) = n \times (1-X) \times [-ln(1-X)]^{\frac{n-1}{n}}$$

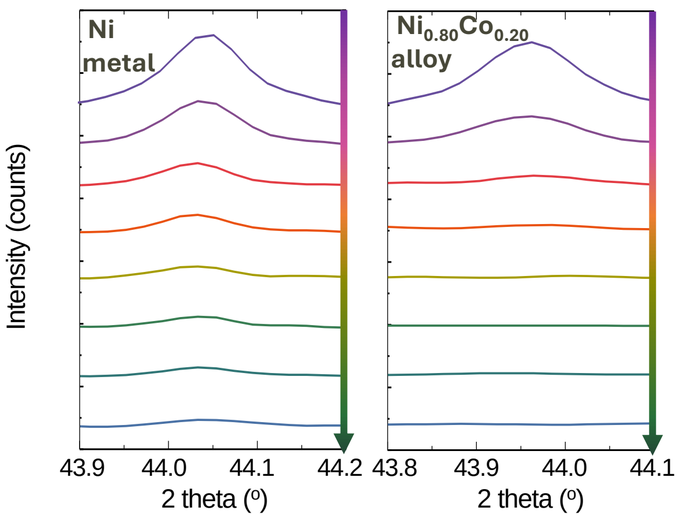
Reforming stage performance



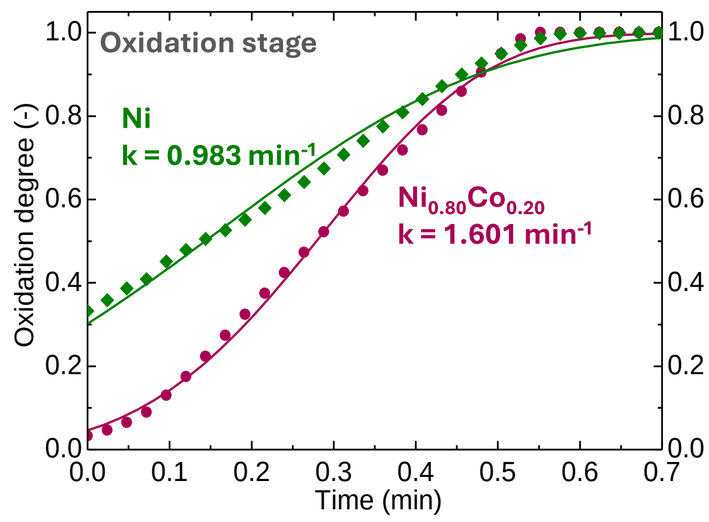
Regeneration stage performance



Advanced *in situ* XRD characterisation



Kinetic analysis results



3 – Results and findings

- **Reforming stage:** The OC is reduced from CH_4 and the formed metal/alloy acts as catalyst for reforming and water gas shift. In the Pre-BT regime, where CO_2 is captured by CaO, CH_4 undergoes 95% conversion to produce H_2 with 91% yield and 94% purity.
- Entering the BT regime signifies that the sorbent has been saturated and thus the gas feed is switched to air.
- **Regeneration stage:** The OC oxidation leads to a rapid temperature increase (indicated by thermocouples T1, T2 and T3 in the reactor) and the autothermal partial release of captured CO_2. Once oxidation concludes, external heat is supplied to release all captured CO_2 and to quantify the fraction released autothermally.
- The Ni-Co OC resulted in 42% higher autothermal CO_2 release compared to the monometallic Ni OC.
- **Role of Co**: Bimetallic OCs display different oxidation mechanism, linked with improved kinetics.
- ***In situ* XRD**: Faster reduction of alloy peak in bimetallic OC than metal peak in monometallic OC proves faster kinetics.
- **Kinetic experiments:** Bimetallic OC displays higher Arrhenius rate constant than monometallic OC.

4 – Conclusions and benefit to society

- SE-CL-SMR produces pure blue H_2 (94vol%) with 90% CO_2 capture in a single step with lower energy demand than the incumbent process, while bimetallic OCs boost the energy efficiency.
- Blue H_2 acts as bridge for smooth energy transition, with the proposed novel technology having the potential to redefine and decarbonise global H_2 production, while helping to meet regulatory sustainability goals and to contribute to climate change mitigation.

5 – Next steps

- Evaluation of the feasibility of the technology through a detailed technoeconomic analysis and comparison to the conventional natural gas reforming.
- Apply for funding to demonstrate and optimise the SE-CL-SMR operation in a pilot-scale (TRL: 5-6) unit.

References

[1] T. Papalas, A. N. Antzaras, A. A. Lemonidou, Chem. Eng. J., **2020**; 382, 122993
[2] T. Papalas, E. Palamas, A. N. Antzaras, A. A. Lemonidou, Fuel, **2024**; 359, 130272
[3] T. Papalas, A. N. Antzaras, A. A. Lemonidou, Appl. Catal. B Environ. Energy, **2024**, 347, 123777

Short CV of applicant