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Thermochemical cycles for CO_2 capture/utilization

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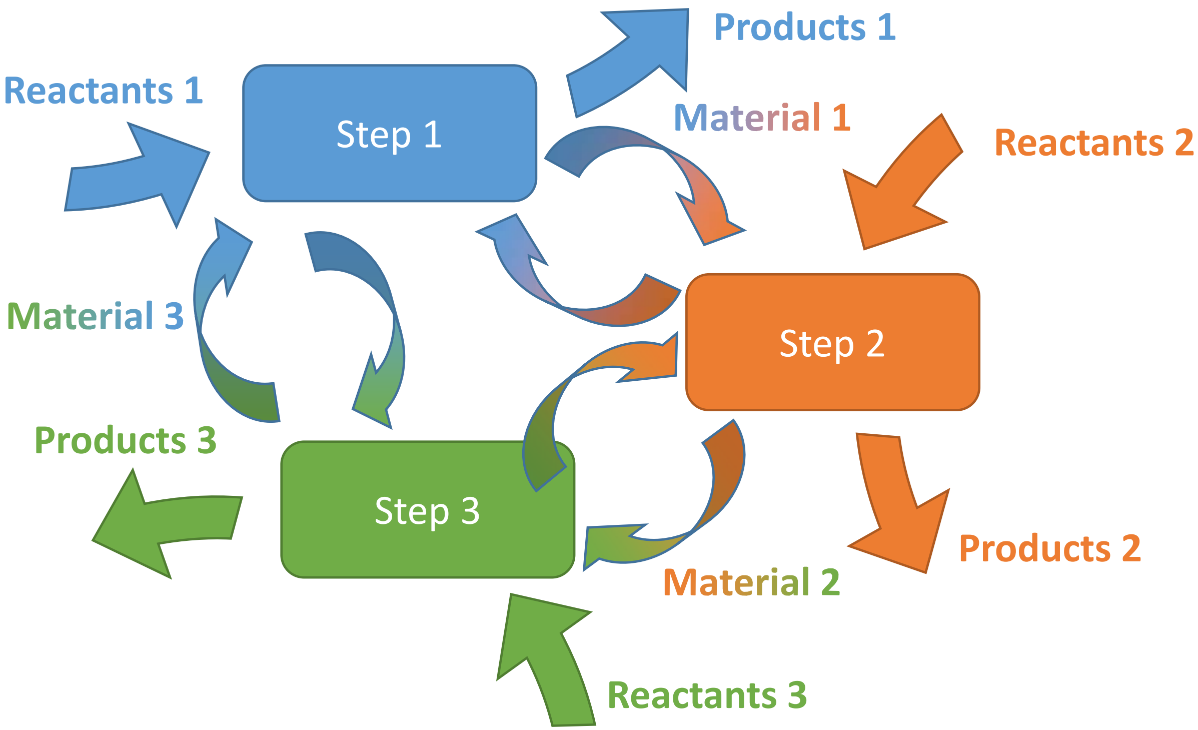
Thermochemical cycles

A thermochemical cycle (TC) is a process consisting of linked steps at varying reaction conditions



Reactants → Products

Reactants 1 → Products 1

Reactants 2 → Products 2

Reactants 3 → Products 3

Heat exchange with the surroundings

$\Delta H_{tot} = \Delta H_1 + \Delta H_2 + \Delta H_3$

One or more materials are used

- ✓ *their composition is modified during the different steps*
- ✓ *their initial state is restored at the end of the cycle*

Examples

Chemical looping combustion

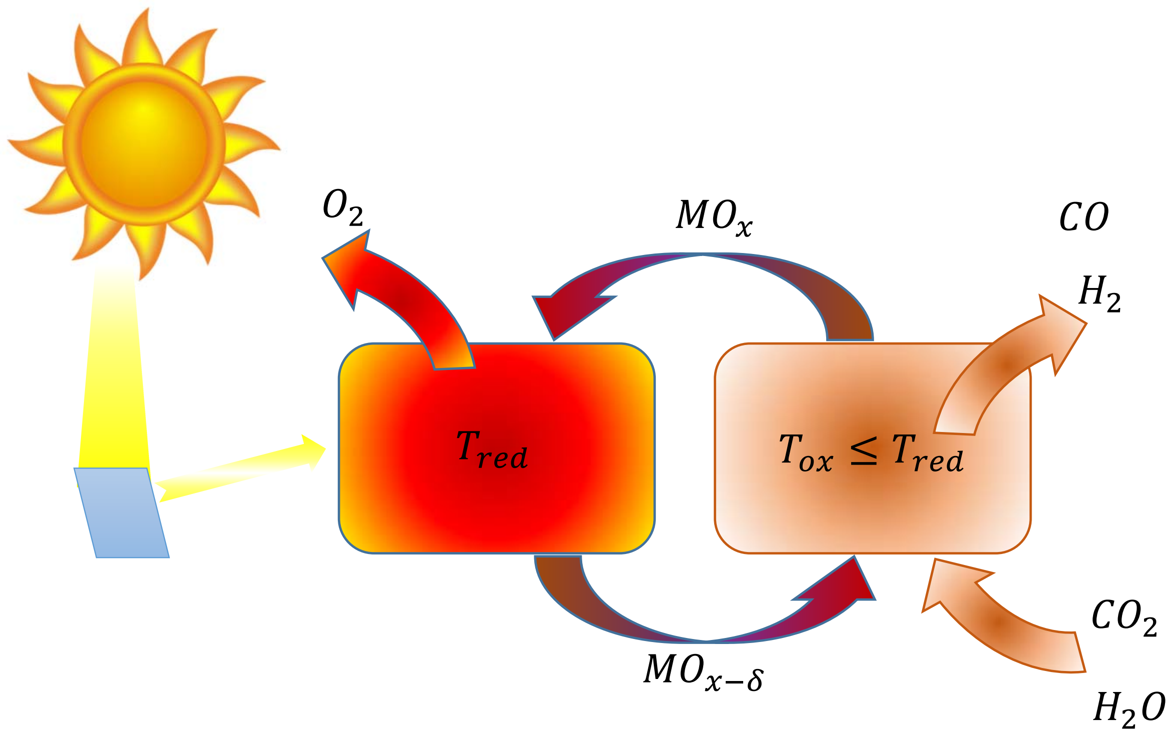
Chemical looping reforming

Chemical looping gasification

Water/Carbon dioxide splitting

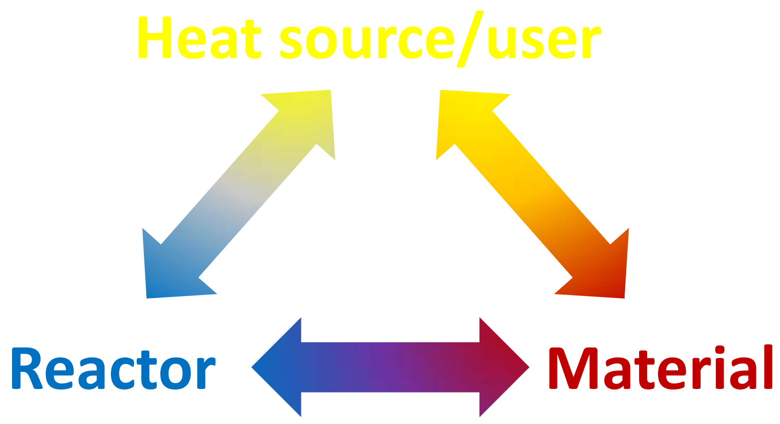
CO_2 capture and methanation

…



<u>Endothermic processes can be sustained by renewable heat sources</u>

Thermochemical cycles: a multidisciplinary issue



Materials, reactors and heat sources / users must adapt to each other in processes showing different reaction conditions, which are also different in each step.

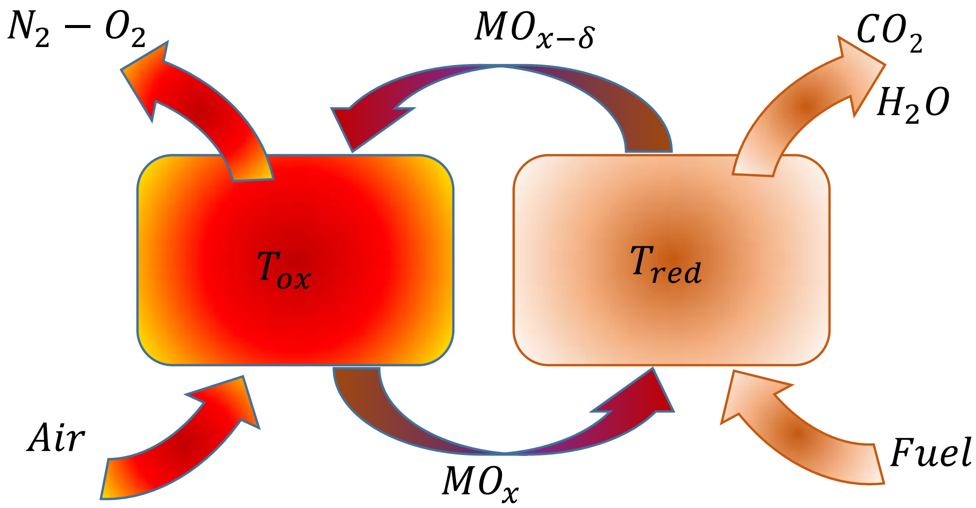
Different expertises are needed to develop a successful TC process

Materials

With respect to the overall cycle, they can be seen as catalysts (no modification). However, with respect to each step, for the most of the processes, they are reactants.

- ✓ high oxygen storage capacity
- ✓ fast reduction/oxidation kinetics
- ✓ low working temperatures
- ✓ good thermal stability
- ✓ good cyclability

Oxygen carriers for Chemical Looping Combustion



Capture ready

Oxysulphates for Chemical Looping Combustion

Lanthanum oxysulphates doped with trantion metals (Co, Mn, Cu)

$La_2O_2SO_4 + 4\ H_2 \rightarrow La_2O_2S + 4\ H_2O$ (*reduction*)

$La_2O_2S + 2\ O_2 \rightarrow La_2O_2SO_4$ (*oxidation*)

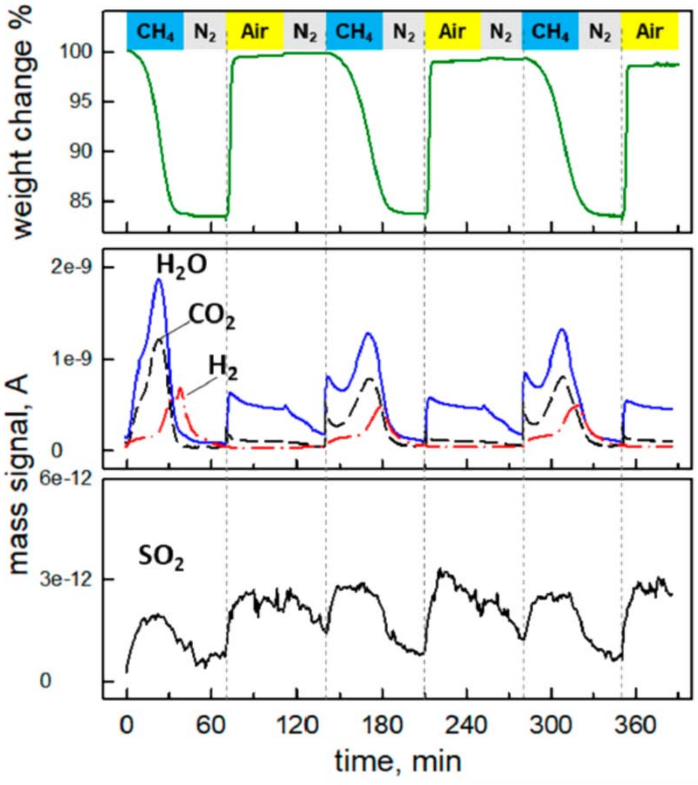
Doping with transition metals increases both performances and thermal stability of $La_2O_2SO_4$

5% CH_4/air cycles @800°C over Co-doped lanthanum oxysulphate

Repeatable cycles Stoichiometric reduction/oxidation

High selectivity to H_2O and CO_2

Negligible degradation of carrier by sulphate decomposition

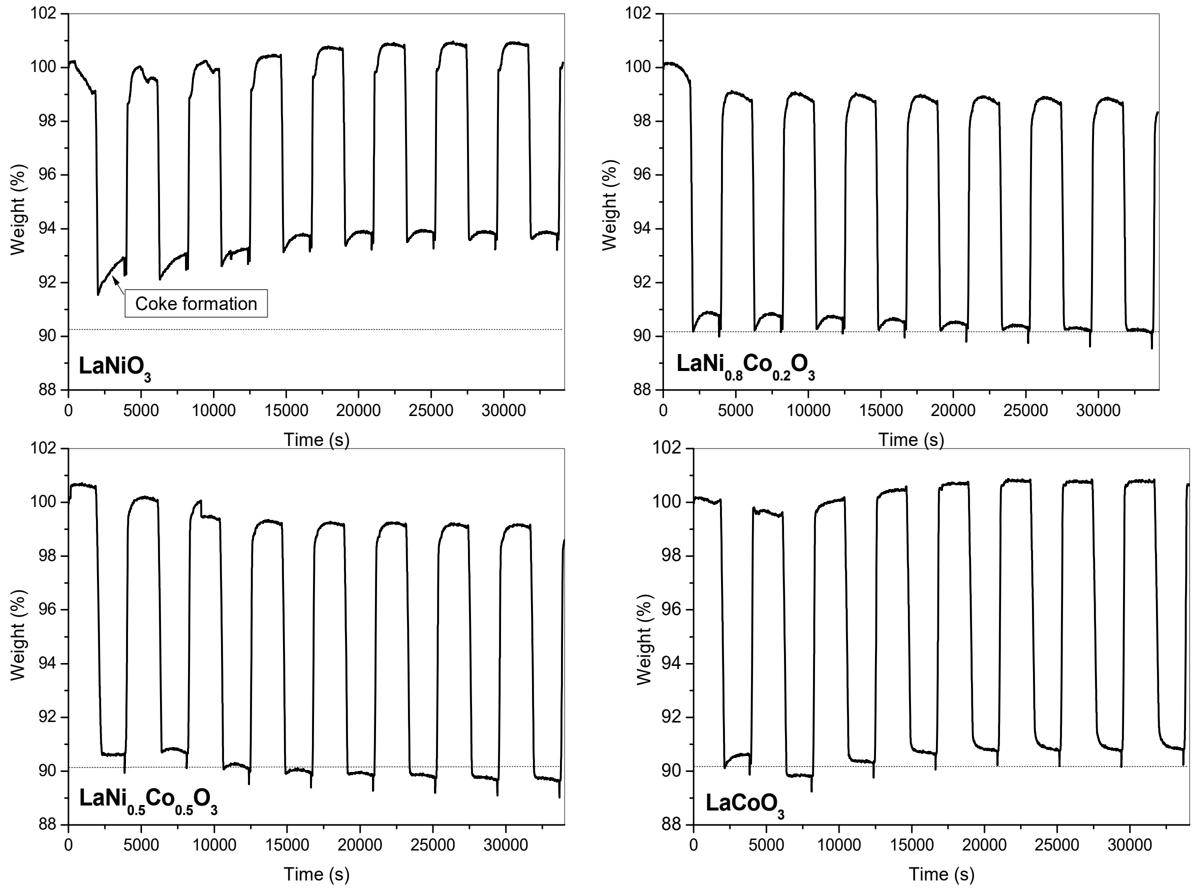


Perovskites for Chemical Looping Combustion

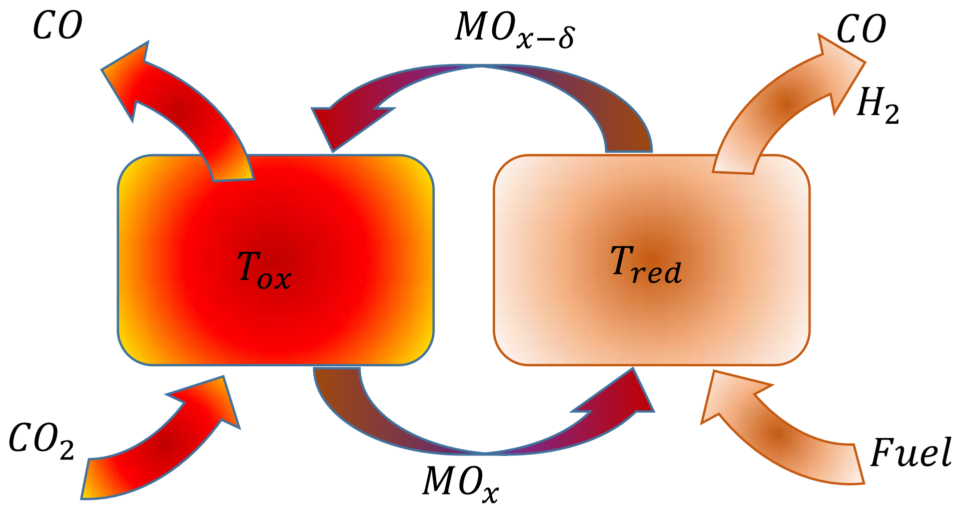
$LaNi_xCo_{1-x}O_3$

Formation of Ni^0 and Co^0 in addition to La_2O_3 during reduction step
Oxidation restores the perovskite structure almost completely for the richest nickel samples (x = 0.0 and 0.2) and fully regenerated samples with a higher cobalt content (x = 0.5 and 1.0).

CLC cycles @950°C

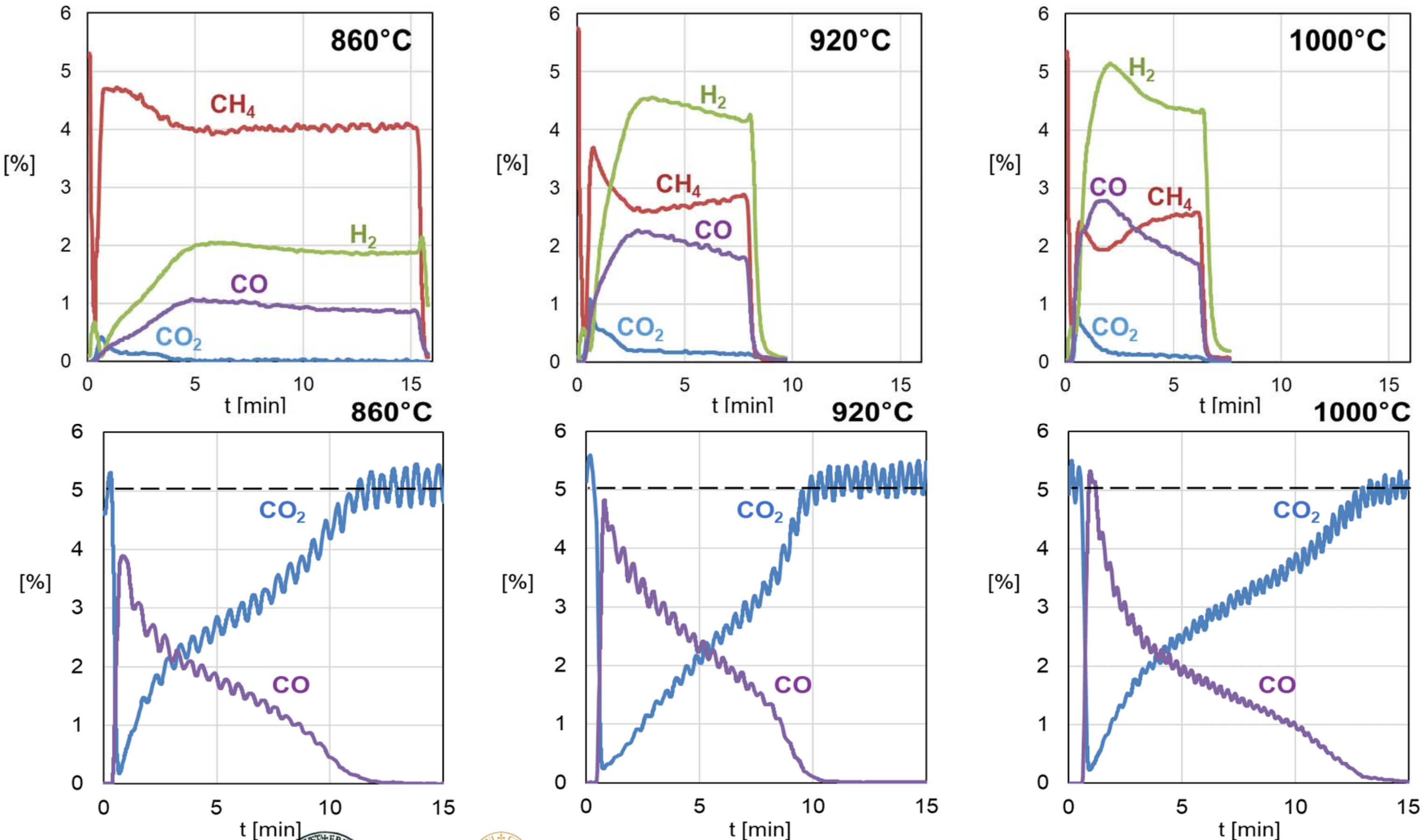


Oxygen carriers for Chemical Looping Reforming



CO_2 utilization

Perovskites for Chemical Looping Reforming

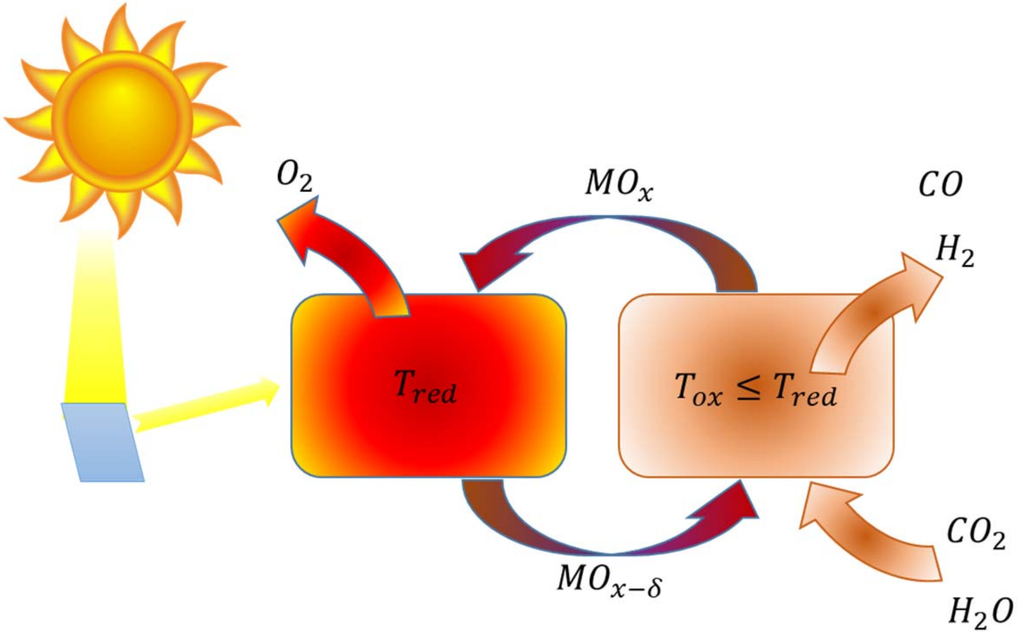


La$_{0.6}$Sr$_{0.4}$FeO$_3$

High selectivity to syngas during the reduction step

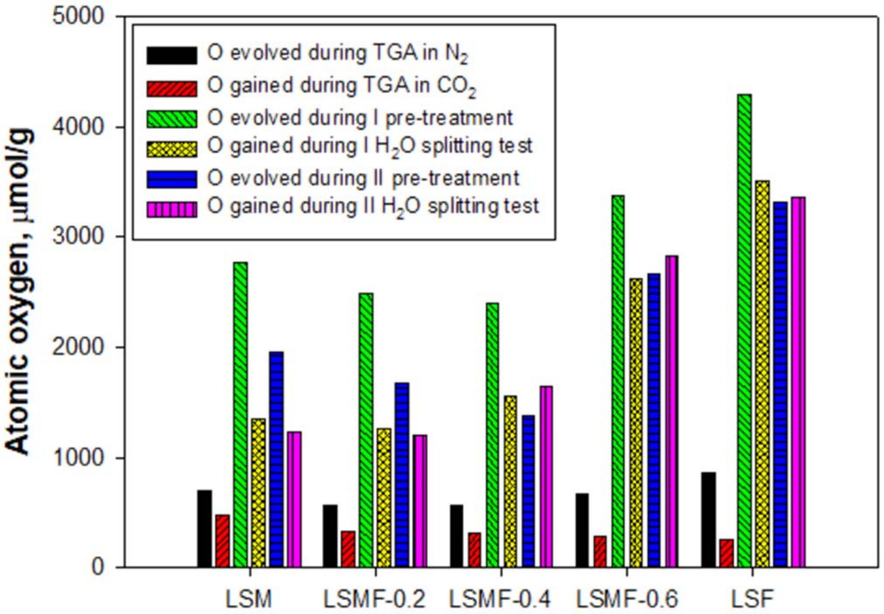
Full regeneration during the oxidation step

Oxygen carriers for Solar Thermochemical Splitting



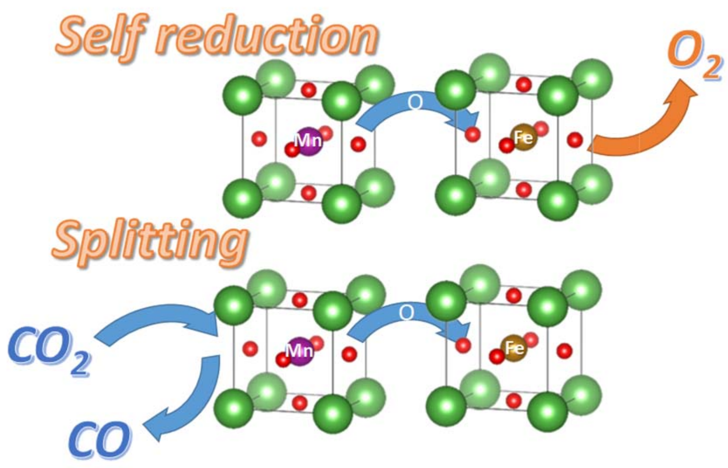
CO_2 utilization

Perovskite for CO_2/H_2O splitting

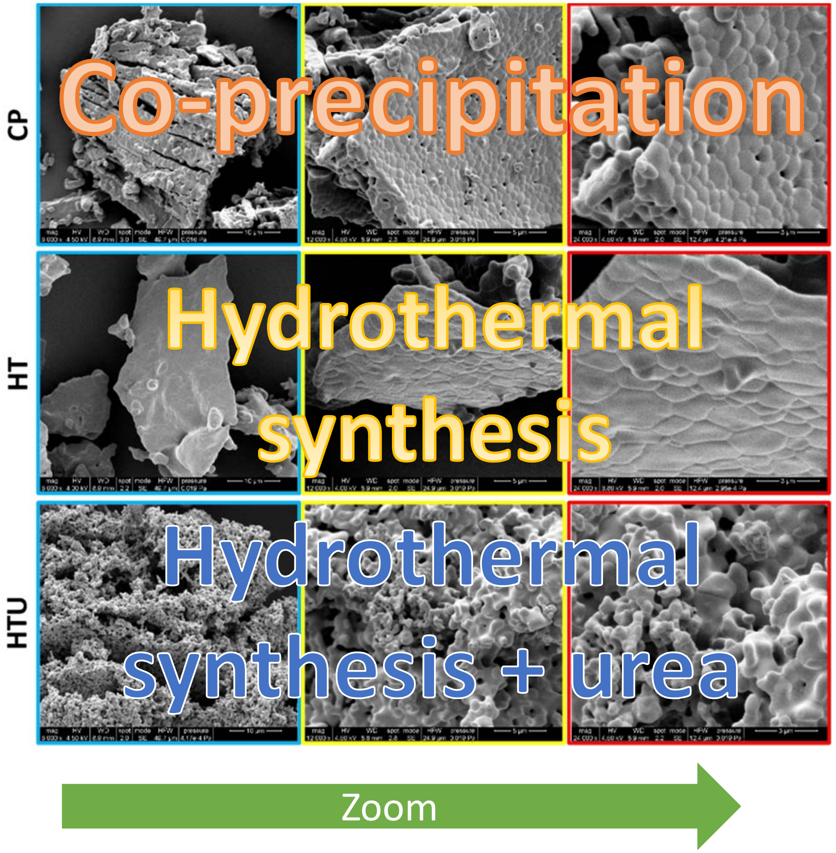


$La_{0.6}Sr_{0.4}Mn_xFe_{1-x}O_{3-\delta}$

Different B cations is an effective strategy to manage both the self-reducibility and the splitting activity



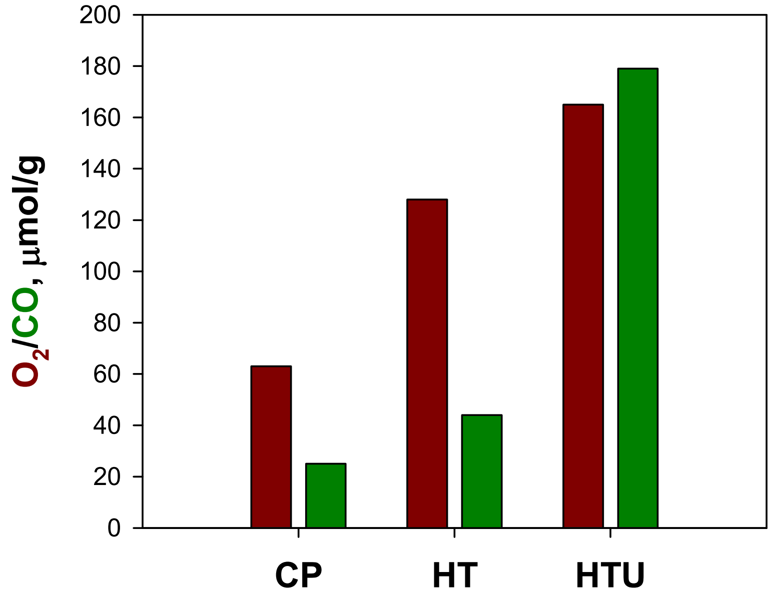
Ceria/zirconia for CO_2/H_2O splitting



$Ce_{0.75}Zr_{0.25}O_4$

Advanced preparation routes

Ceria/zirconia for CO_2/H_2O splitting



$Ce_{0.75}Zr_{0.25}O_4$

Advanced preparation routes

Positive effect of doping (K, Cu, Fe) and co-doping (K-Cu, K-Fe)

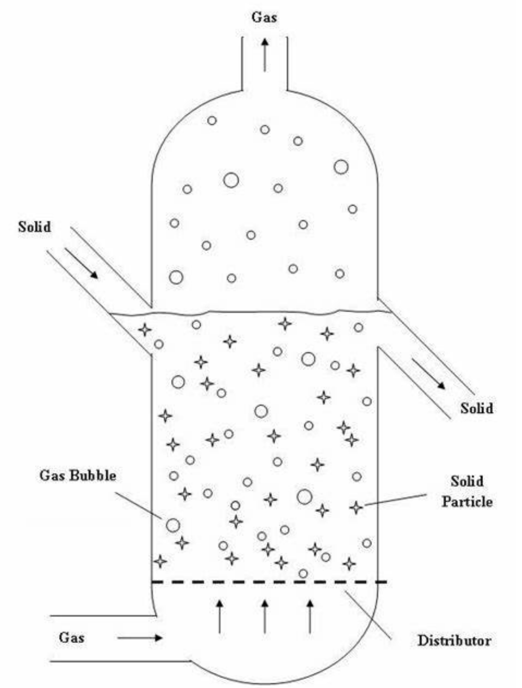
EPR and XPS analysis

- Activity related to both bulk and surface oxygen vacancies

Reactors

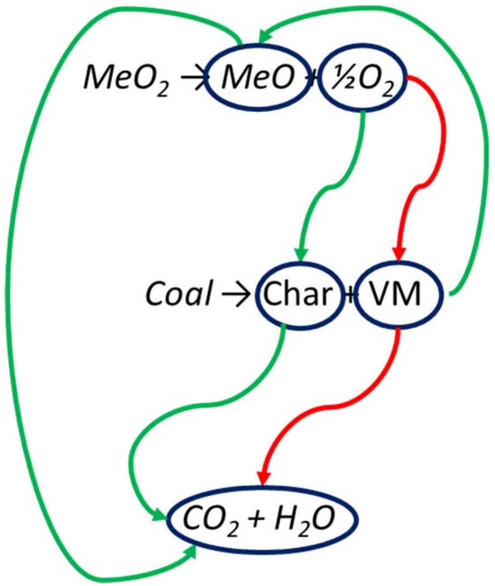
- ✓ Good heat transfer
- ✓ Good mass transfer
- ✓ Good interaction with sun radiation
- ✓ Cycling among different reaction conditions

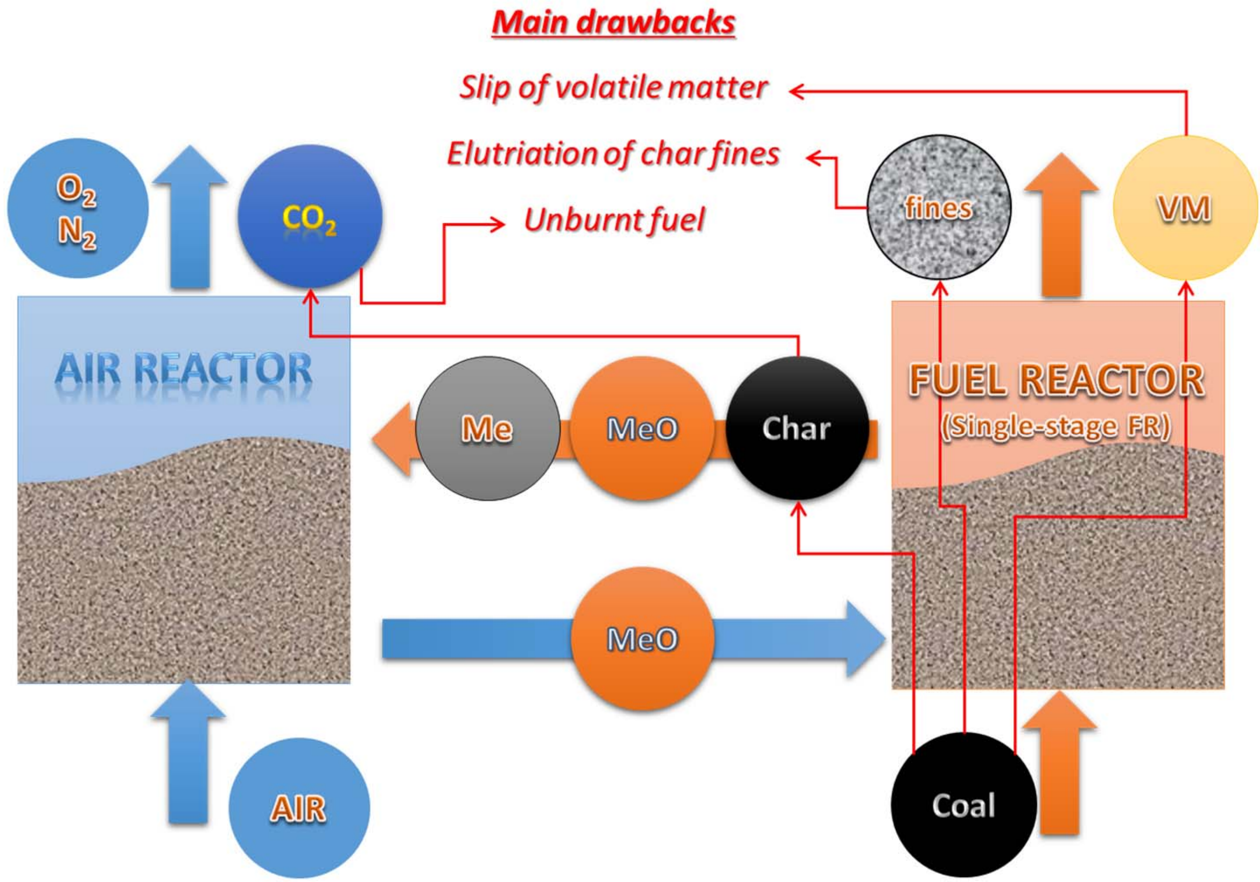
<u>Fluidized bed reactors appear the best choice</u>



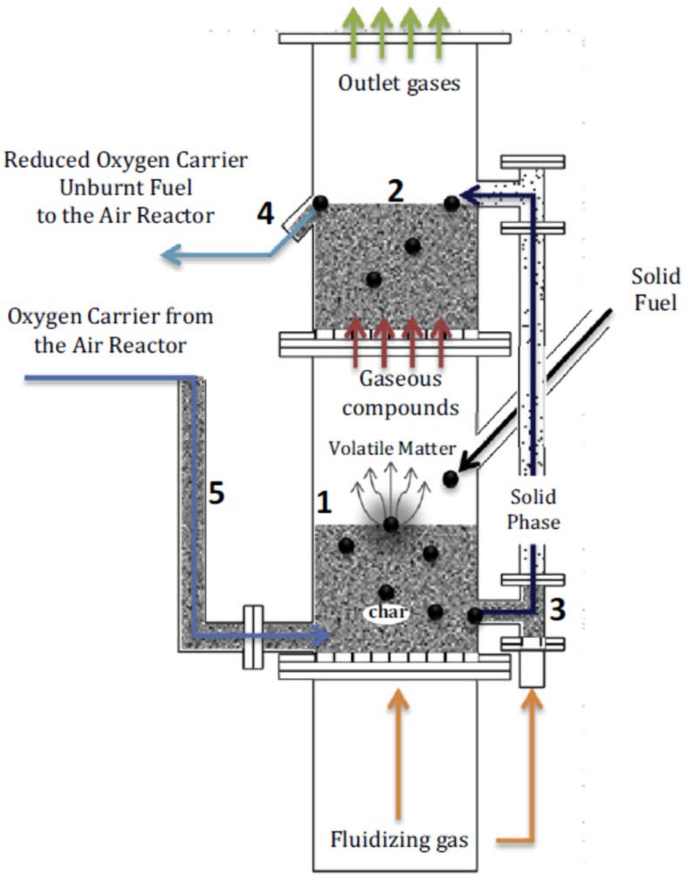
Chemical Looping with Oxygen Uncoupling - CLOU

Paradigm





The concept of the Two-stage FUEL REACTOR



Exploiting of CLOU effect for combustion of the most difficult part of the fuel: Char

Conversion of VM using the residual oxidative potential of the OC

RTD is closer to a plug flow than a single-stage FR

Two-stage FUEL REACTOR: main results

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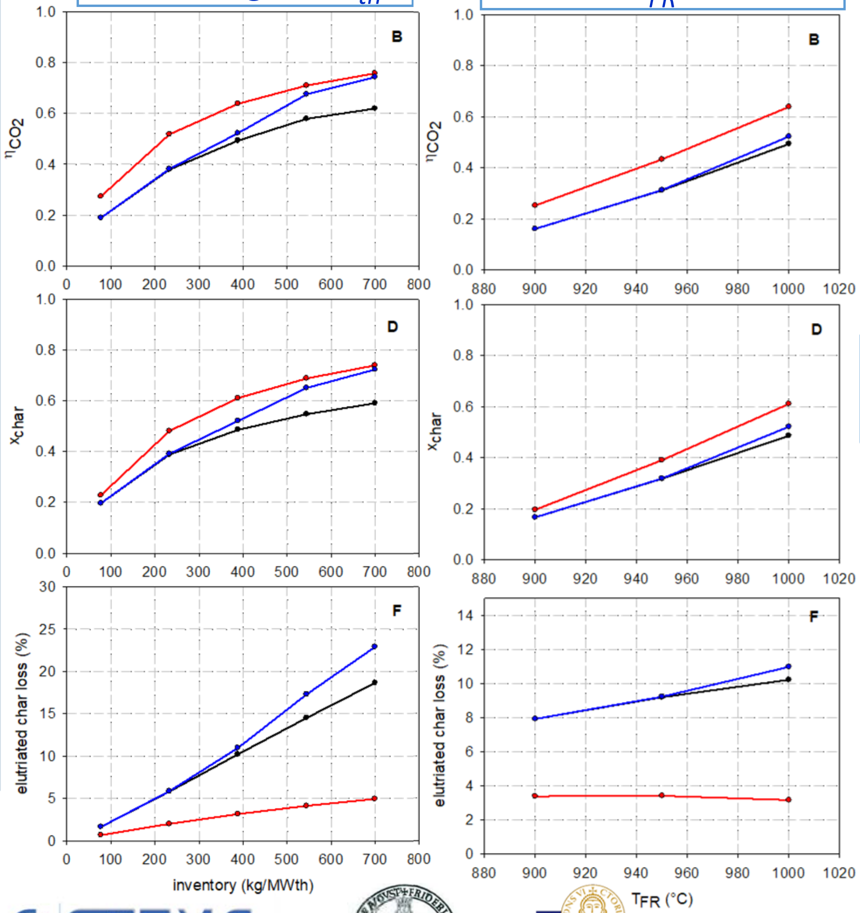
77-700kg/MW_{th}   *900°C<T_{FR}<1000°C*



Oxygen carrier: CuO (50% in mass) on ZrO_2

Fuel: bituminous South-African coal
(VM: CO CO_2 H_2 H_2O CH_4)

SS: single-stage TS: two-stage
CS: single-stage + carbon stripper

The two-stage fuel reactor shows the best performances in terms of:

combustion efficiency;

volatile matter and char conversion;

carbon-to-CO_2 conversion efficiency;

loss of elutriated carbon;

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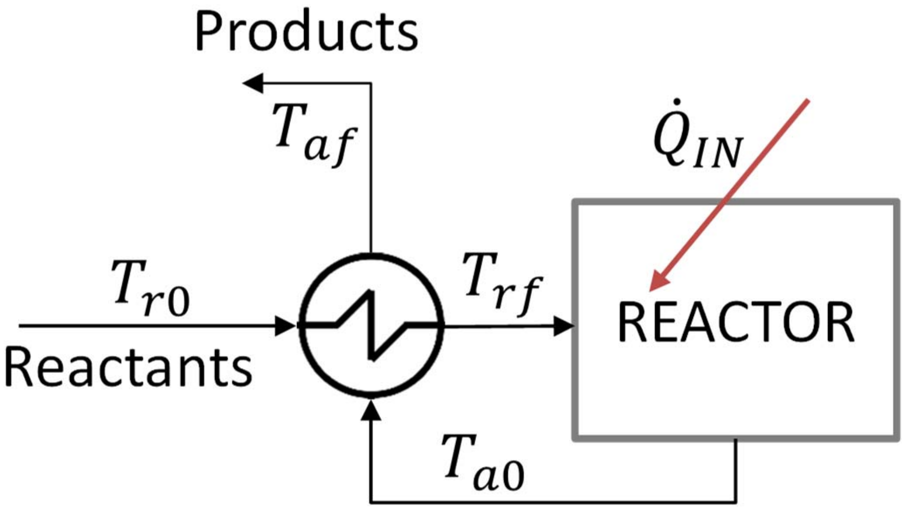
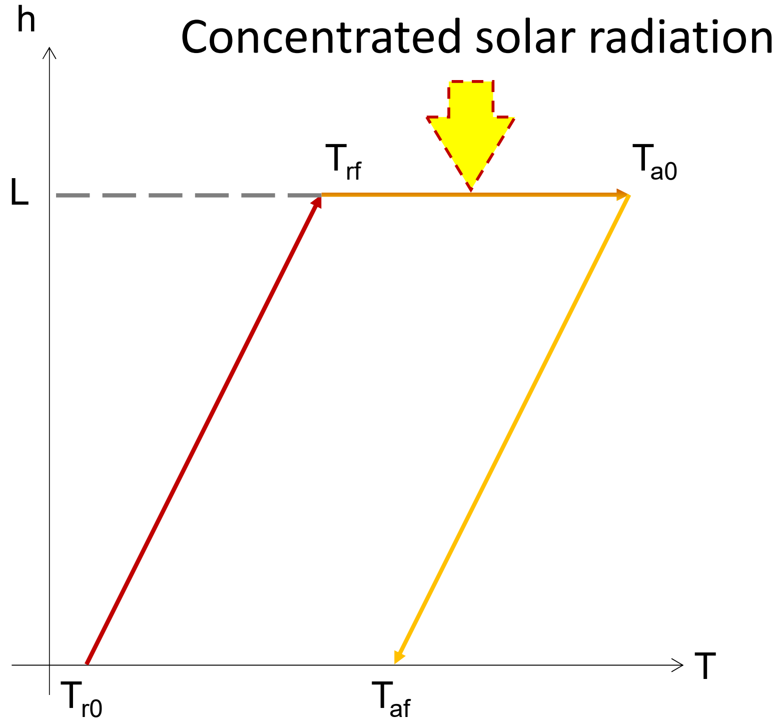
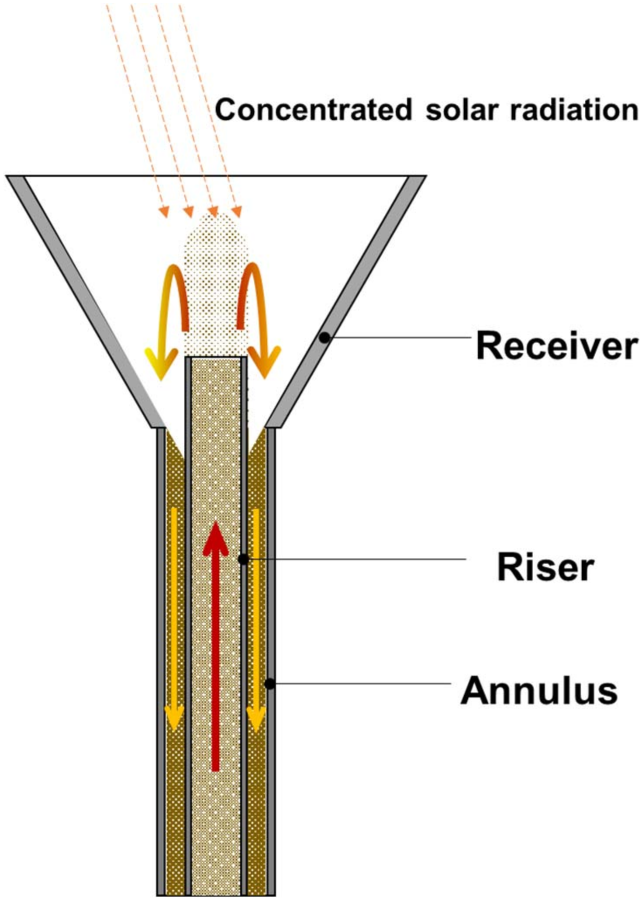
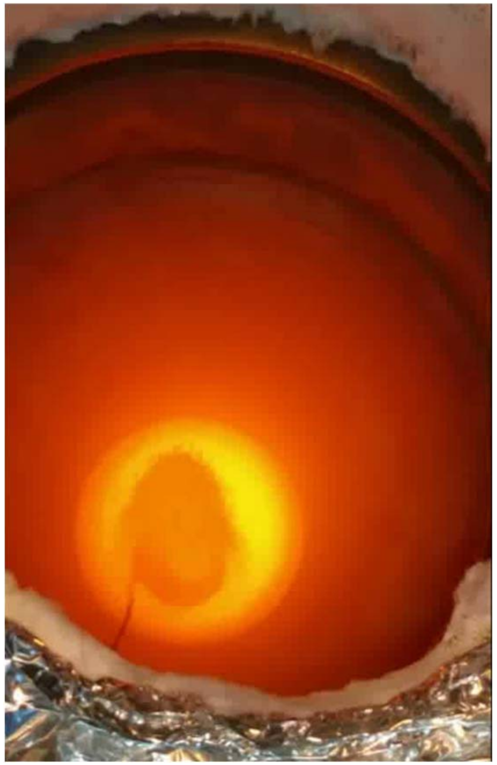
Novel reactor concept: Directly Irradiated Fluidized Bed Autothermal reactor (DIFBAR)





DIFBAR features and preliminary tests





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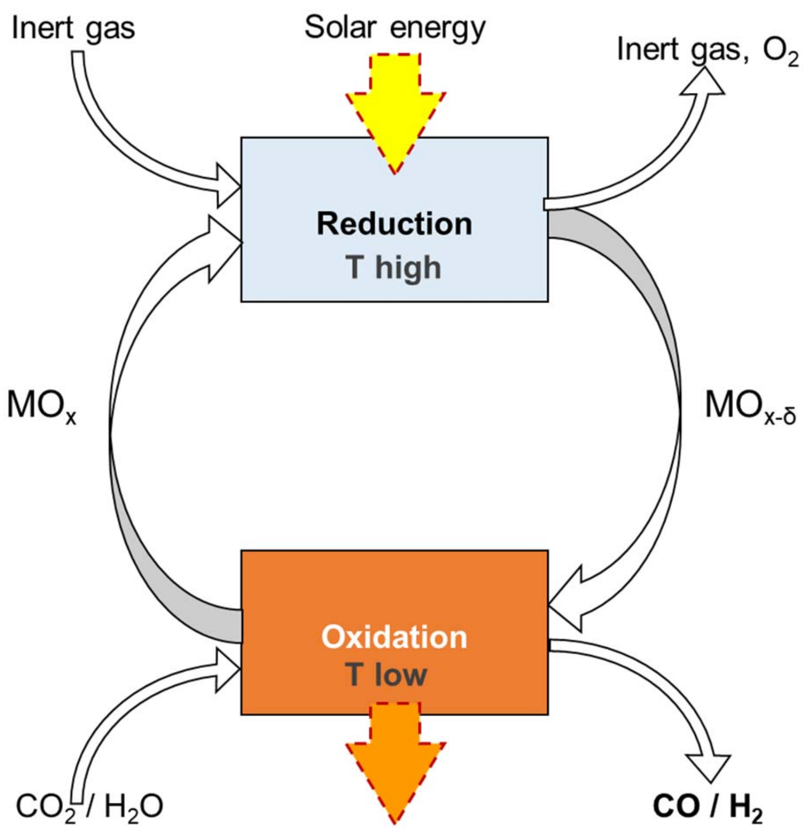
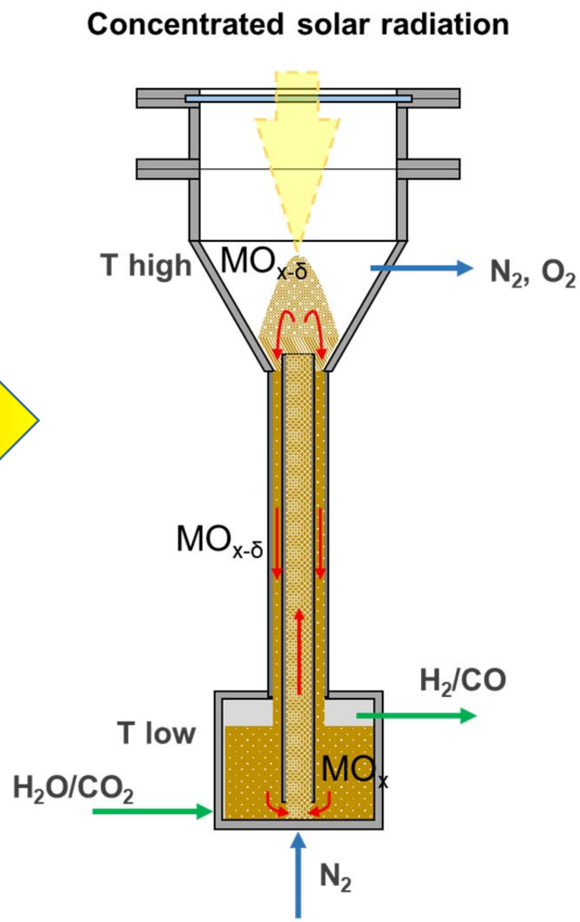
CO_2/H_2O TC splitting in solids closed loop





Conclusions

- Thermochemical cycles can be designed for CO_2 capture/utilization
- Redox materials can be adapted to the requirements of the specific process by proper formulations and preparation methods, showing
  - High oxygen storage
  - Good thermal stability and cyclability
  - Good selectivity to the desired products
- Novel reactor configurations can be designed in order to improve the overall performance of the cycle
  - Improved conversion
  - High efficiency
  - Lower emissions

Selected publications

- L. Lisi, G. Mancino, S. Cimino, *Chemical looping oxygen transfer properties of Cu-doped lanthanum oxysulphate,* Int. J. Hydrogen Energy **2015**, 40, 204
- A. Coppola, R. Solimene, P. Bareschino, P. Salatino, *Mathematical modeling of a two-stage fuel reactor for chemical looping combustion with oxygen uncoupling of solid fuels*, Appl Energy **2015**, 157, 449.
- G. Luciani, G. Landi, A. Aronne, A. Di Benedetto, *Partial substitution of B cation in $La_{0.6}Sr_{0.4}MnO_3$ perovskites: A promising strategy to improve the redox properties useful for solar thermochemical water and carbon dioxide splitting,* Sol Energy **2018,** 171, 1.
- S. Cimino, G. Mancino, L. Lisi, Performance and stability of metal (Co, Mn, Cu)-promoted $La_2O_2SO_4$ oxygen carrier for chemical looping combustion of methane, Catalysts **2019**, 9, 147
- G. Luciani, G. Landi, C. Imparato, G. Vitiello, F.A. Deorsola, A. Di Benedetto, A. Aronne, *Improvement of splitting performance of $Ce_{0.75}Zr_{0.25}O_2$ material: Tuning bulk and surface properties by hydrothermal synthesis*, Int J Hydrogen Energy **2019**, 44, 17565
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- C. Tregambi, C. Bevilacqua, M. Troiano, R. Solimene, P. Salatino, *A novel autothermal fluidized bed reactor for concentrated solar thermal applications*, Chem Eng J **2020**, 398, 125702
- M. de Santana Santos, R. Frety, L. Lisi, S. Cimino, S. Teixeira Brandão, *$LaNi_{1-x}Co_xO_3$ perovskites for methane combustion by chemical looping*, Fuel **2021**, 292, 120187

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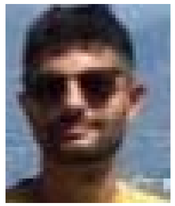
C. Tregambi

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Thank you

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