Workshop on “Carbon Capture, Storage & Utilization”

Combined CO_2 Capture & Methanation

Consiglio Nazionale delle Ricerche
STEMS
Istituto di Scienze e Tecnologie per l'Energia e la Mobilità Sostenibili

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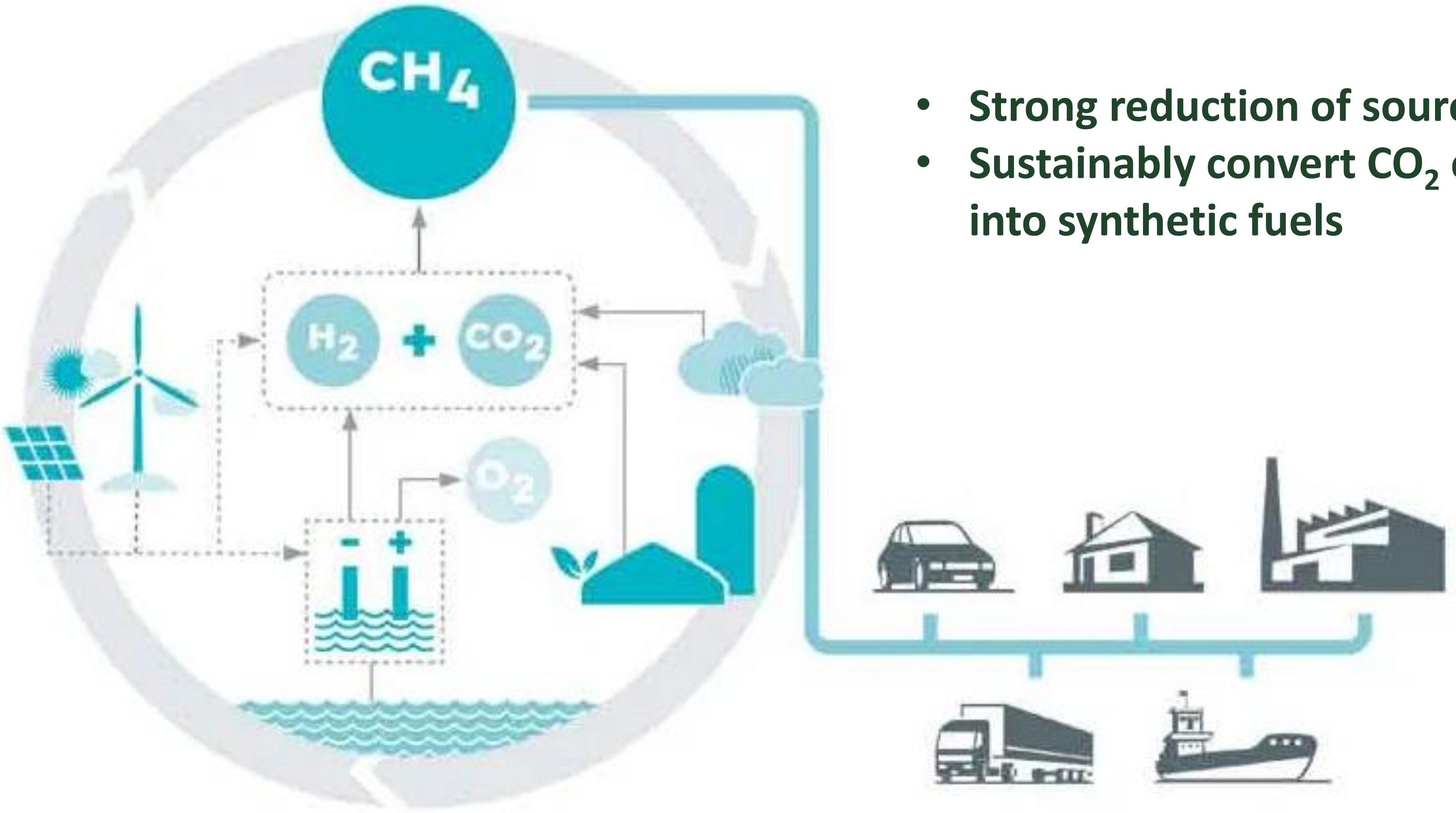
CO_2 Capture & Utilization – Power to Gas

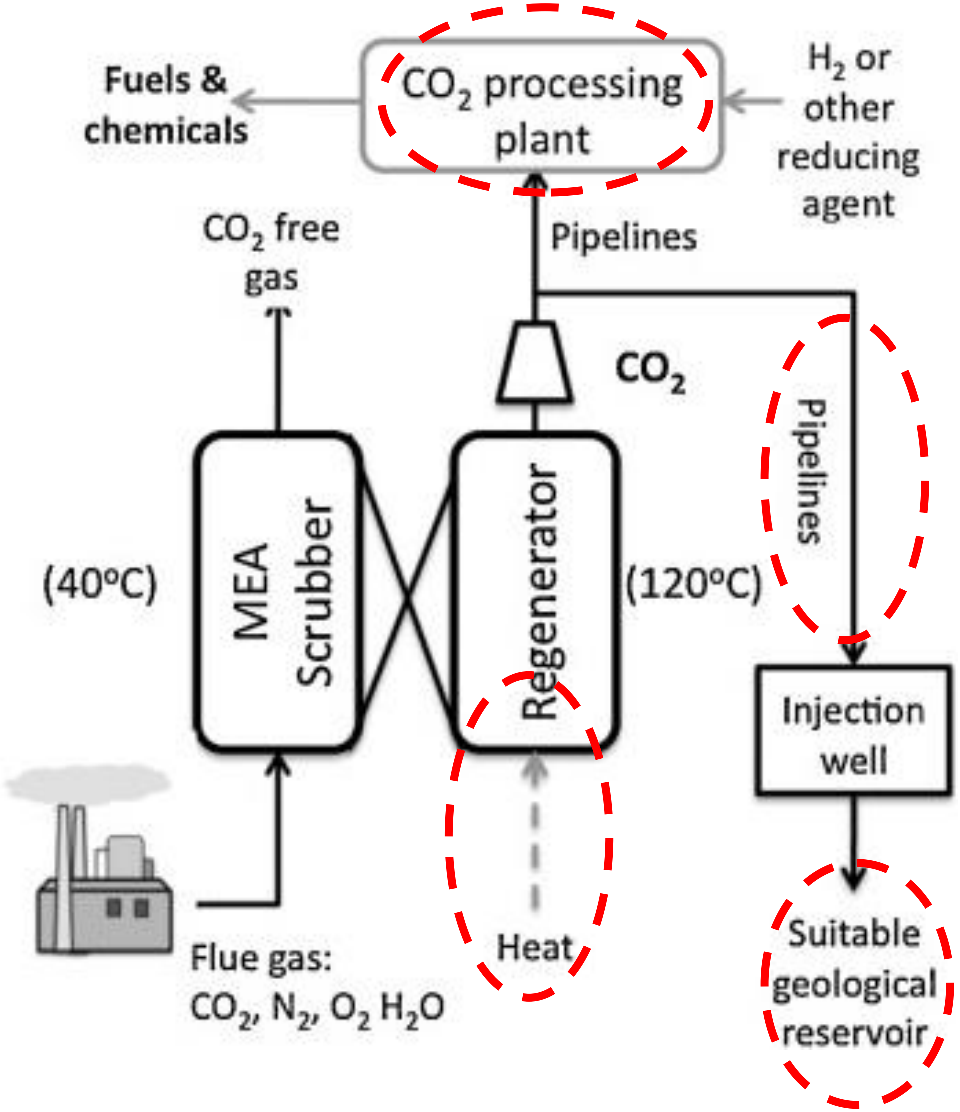


- **Strong reduction of source greenhouse gas emissions**
- **Sustainably convert CO_2 emissions from industrial processes into synthetic fuels**

- CO_2 capture from point sources or air
- H_2 from renewable energy sources
- Carbon neutral cycle
- Chemical storage of excess energy
- CH_4 (SNG) advantageous energy carrier: easily handled, existing distribution grid

Kamkeng, A.D.N.; Wang, M.; Hu, J.; Du, W.; Qian, F. Transformation technologies for CO2 utilisation: Current status, challenges and future prospects. Chem. Eng. J. 2021, 409, 128138.

Conventional CO_2 Capture, Utilization & Storage



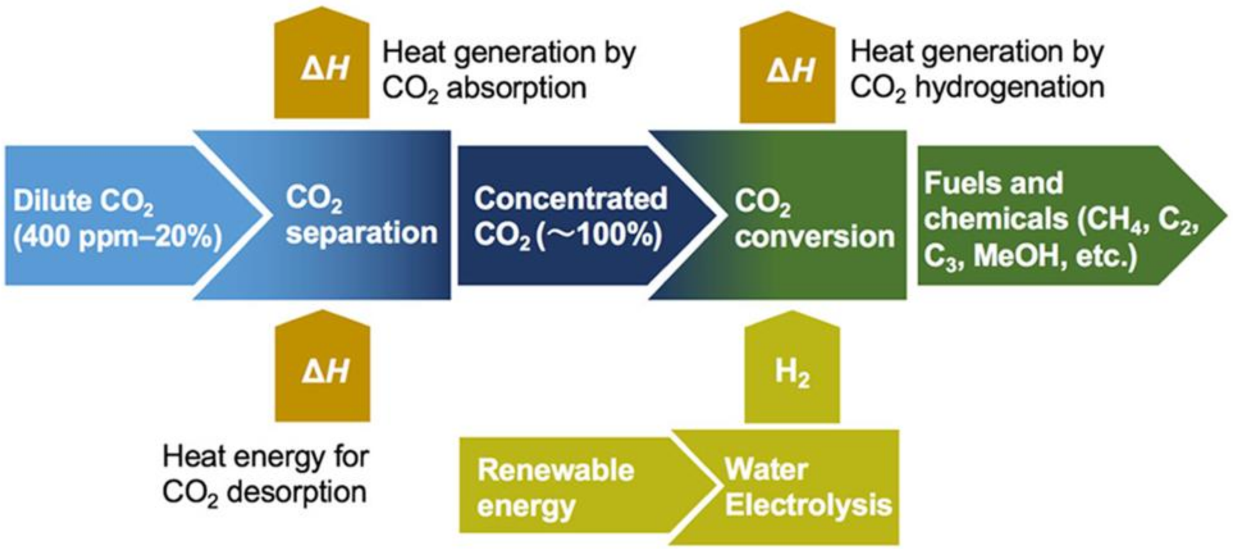
	Absorption	Adsorption	Membrane
Energy requirement	4-6 MJ/kg CO_2	2-3 MJ/kg CO_2	0.5-6 MJ/kg CO_2
Cost	expensive	expensive	expensive
CO_2 recovery	90-98%	80-95%	80-90%
Challanges	• Corrosion • Huge energy req. • Solvent degradation	• Attrition • Pressure drops • Affected by impurities	• Not suitable for high T • Low CO_2 select. • Costly membranes

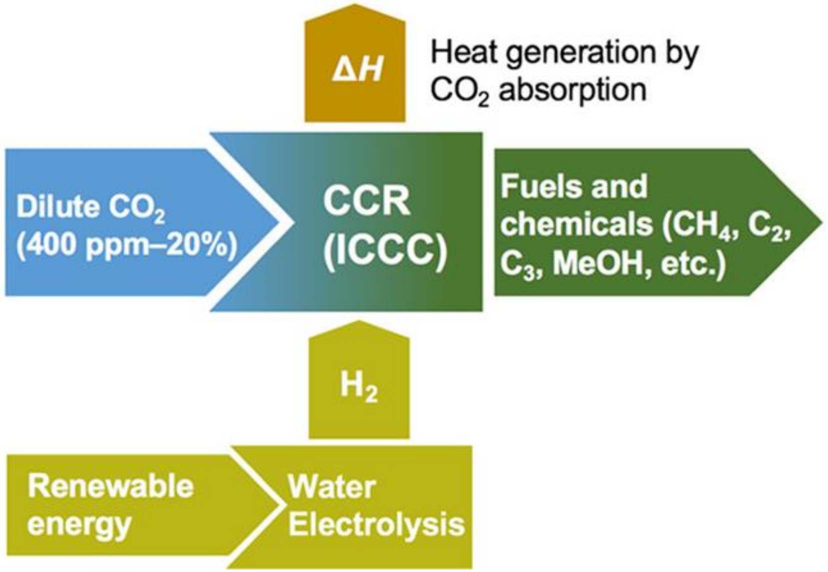
Omodolor,et al. Ind. Eng. Chem. Res. 2020, 59, 17612–17631.

- energy intensive CO_2 desorption step: high cost
- problem of transporting concentrated CO_2 to another site for storage or utilization
- Difficult thermal management of methanator

Can we make it simpler ?

Combined CO_2 Capture & Methanation

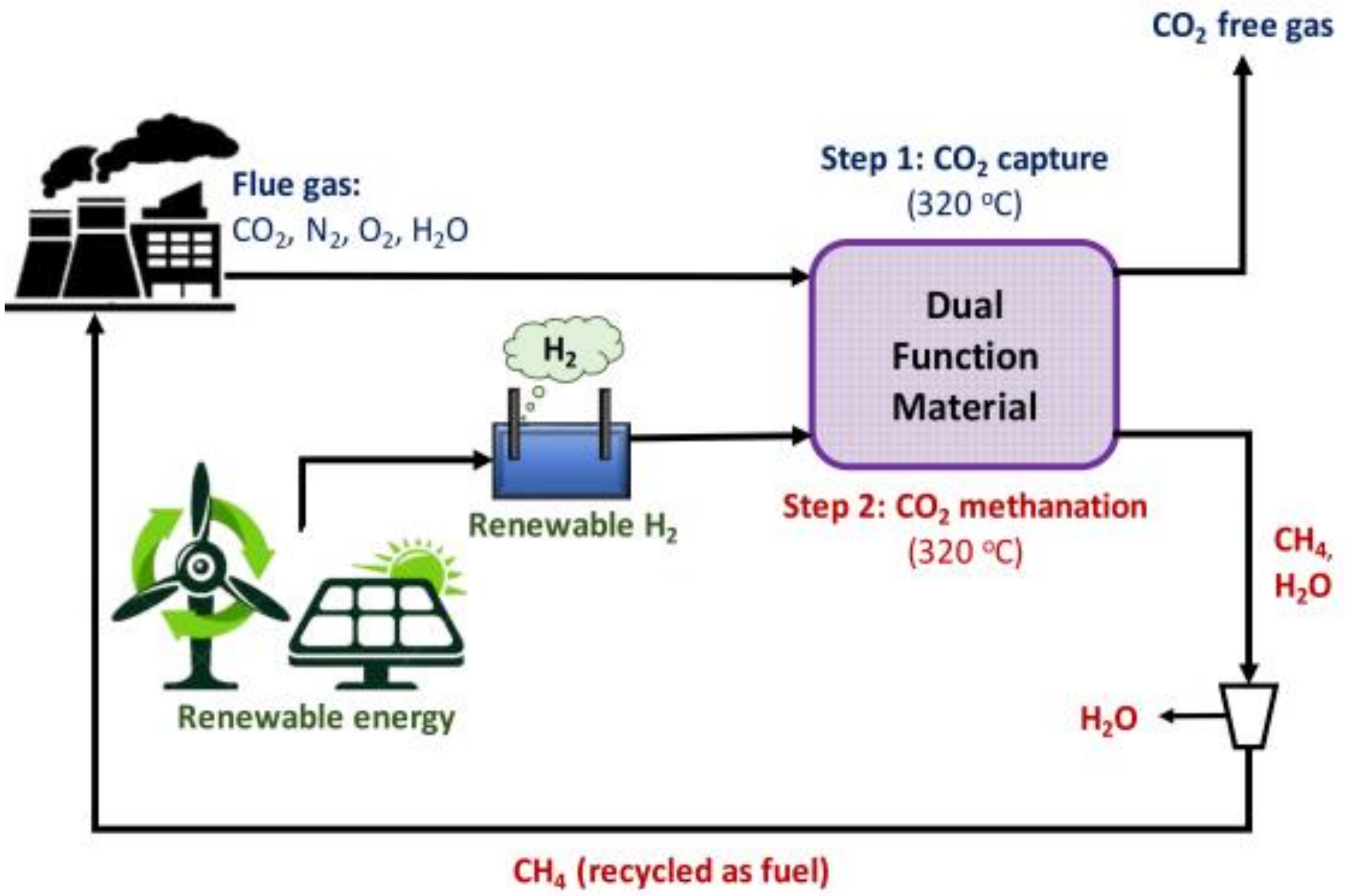




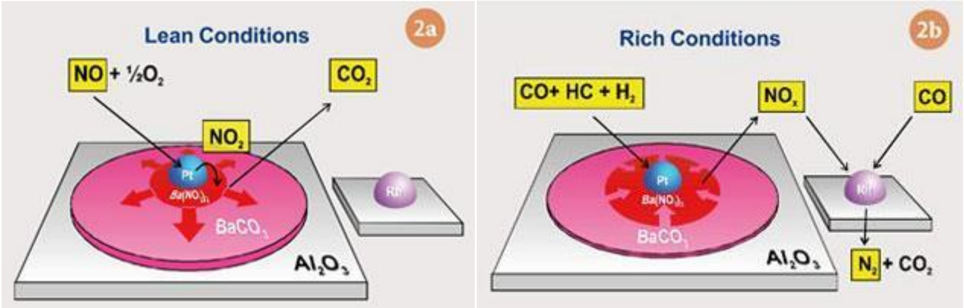
- Innovative strategy integrating both technologies
- No need for CO_2 desorption and transport

Duyar, M.S.; Treviño, M.A.A.; Farrauto, R.J. Dual function materials for CO2 capture and conversion using renewable H2. Appl. Catal. B Environ. 2015, 168–169, 370–376.

Combined CO_2 Capture & Methanation

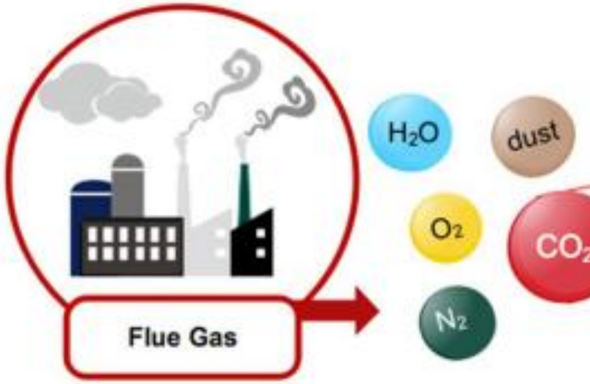


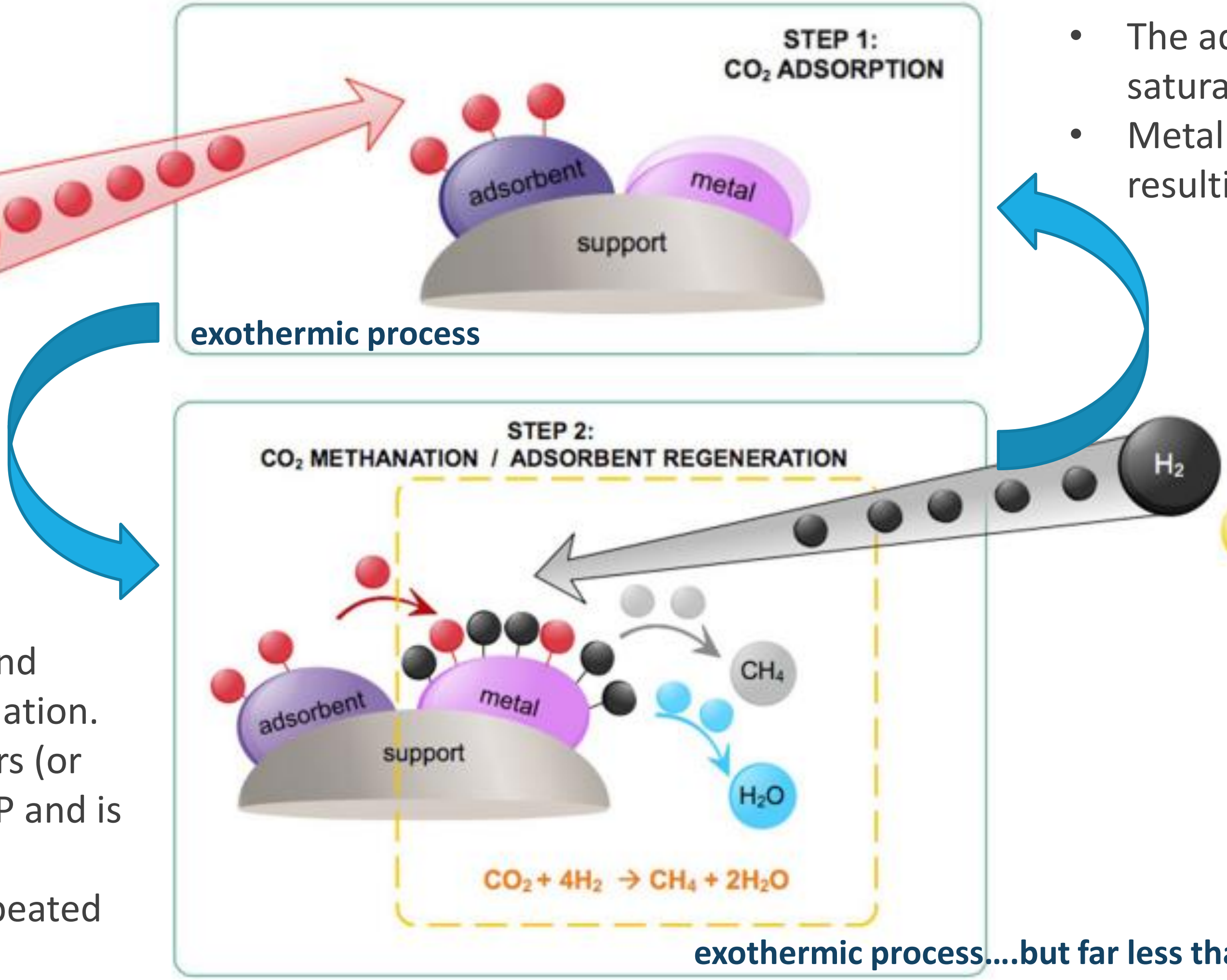
- **<u>Dual Function Materials</u>** capture CO_2 from industrial flue gases (or even air) and release it as concentrated synthetic natural gas (SNG)
- **Catalytic looping process**
- 2 half-cycles with a CO_2 sorbent/catalyst
- Requires materials / processes to switch between capture & methanation cyclically
- Analogy with LNT deNOx

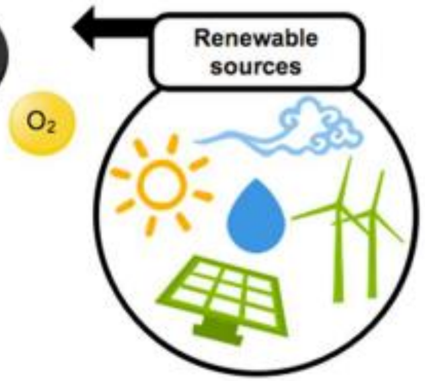


Tsiotsias, et al. Catalysts 2020, 10, 1–36; 1
Arellano-Treviño, et al. Chem. Eng. J. 2019, 375, 121953
Bermejo-López et al. Appl. Catal. B Environ. 2019, 256, 117845.

Combined CO_2 Capture & Methanation





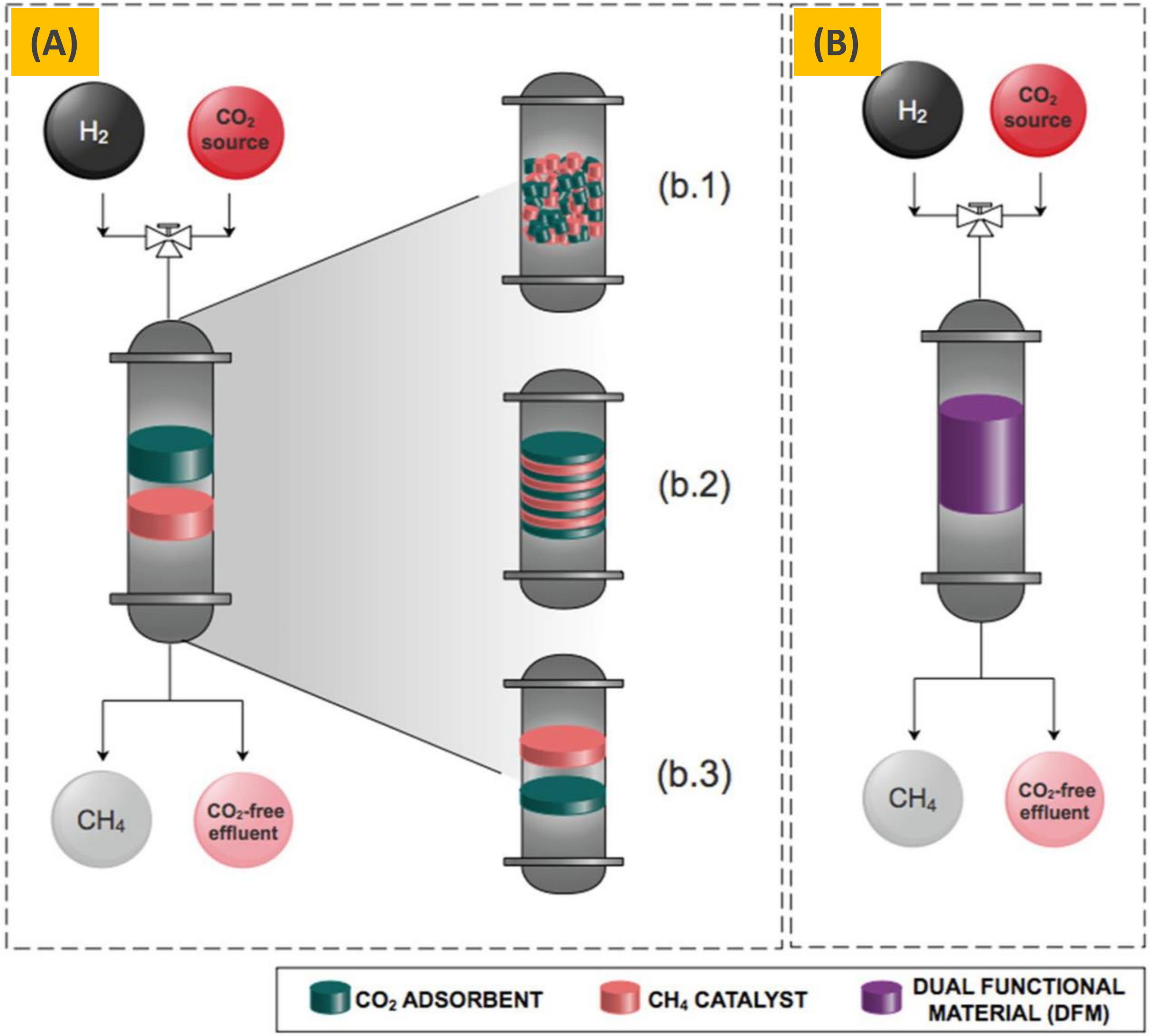


- The adsorbent is progressively saturated with CO_2
- Metal NPs may be partially oxidized, resulting a passivation layer

- Metal NPs are reduced back and become active for the methanation.
- CO_2 on the adsorbent spillovers (or desorbs) towards the metal NP and is hydrogenated to methane.
- These 2 steps are cyclically repeated

Melo Bravo, P.; Debecker, D.P..Waste Dispos. Sustain. Energy 2019, 1, 53–65.

Combined CO_2 Capture & Methanation



Proposed process configurations

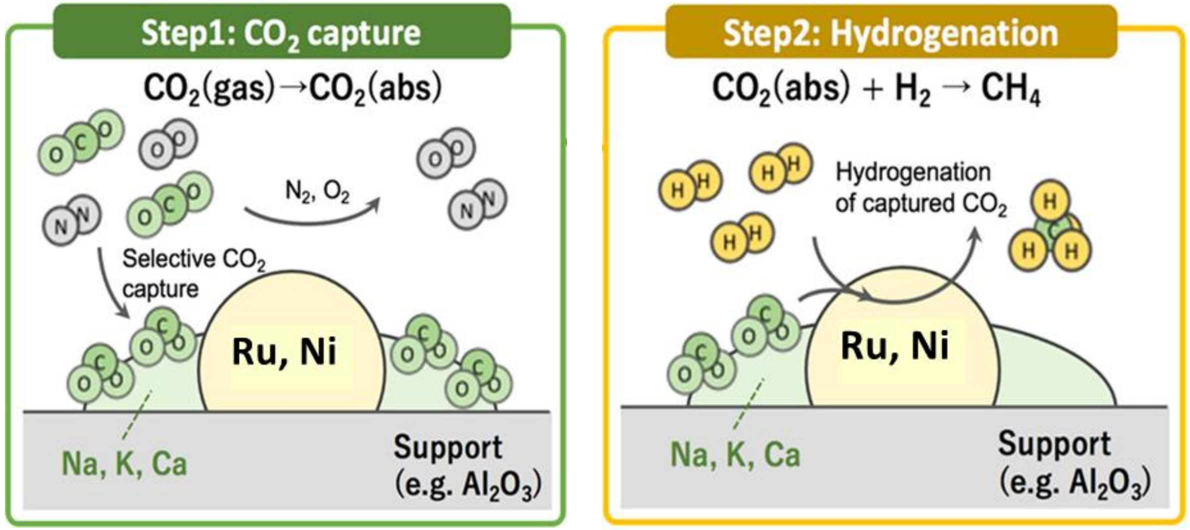
A. Mixed Beds of Sorbent + Catalyst
   - Thermal coupling: heat of methanation drives CO_2 desorption / sorbent regeneration

B. DFM: Intimate mix at nanoscale
   - ✓ Thermal + Chemical coupling via spill-over from sorbent to catalyst
   - ✓ More effective regeneration at lower temperatures
   - ✓ Higher CH_4 productivity

Key to success: development of highly effective DFMs

State of the art DFMs:

- Active phase: 5-10 % wt. Ru
- Sorbent: 5-15% Na (K, Ca)
- Support: Al_2O_3



What can we improve?

- ✓ Catalytic methanation activity (work @ lower temperature)
- ✓ CH_4 selectivity
- ✓ Cost (metal loading)
- ✓ Oxidation resistance
- ✓ Lower parasitic H_2 consumption
- ✓ Large & fast CO_2 capture capacity + selectivity
- ✓ Fast & easy regeneration @ low temperature
- ✓ Mechanical strength
- ✓ Stability / Durability / Tolerance to Poisoning

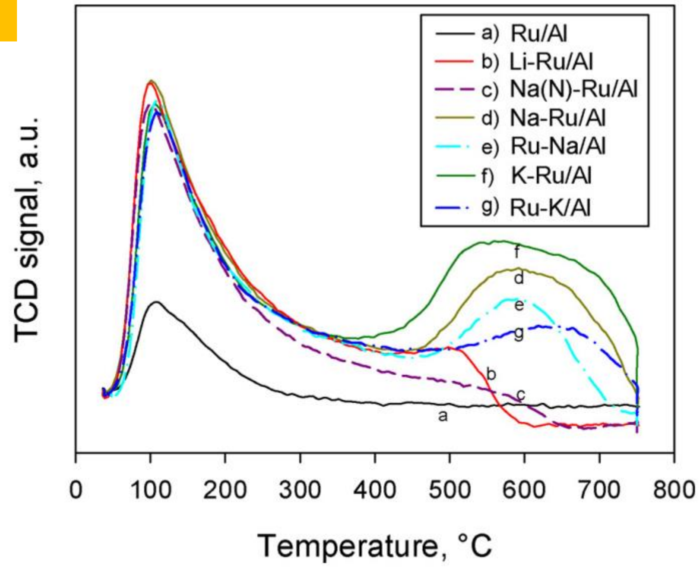
Kosaka et al. ACS Sustain. Chem. Eng. 2021, acssuschemeng.0c07162.

Key to success: DFM development

Comparative study on the effect of alkali promoters (Li, Na, K) on the performance of 1%Ru/Al_2O_3 [*Cimino et al.* J. CO_2 Utilization 37 (2020)]

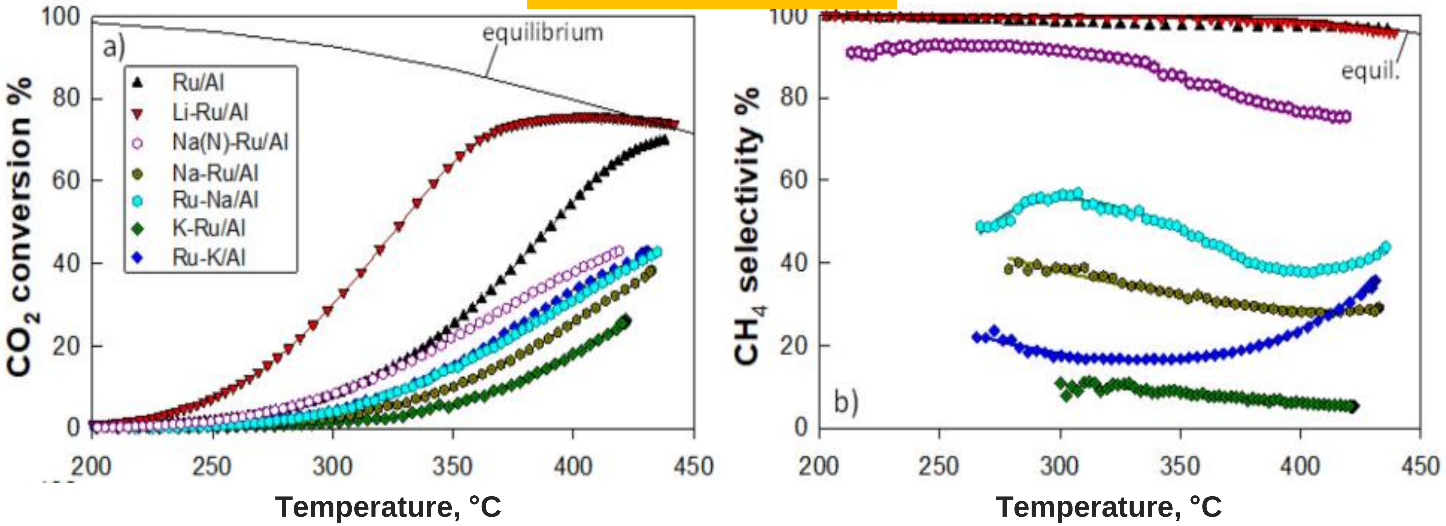
Catalyst	Alkali Precursor	Order of deposition	Alkali metal load (wt %)
Ru/Al	–	–	–
Li-Ru/Al	nitrate	1st Ru, 2nd alkali	1.73
Na(N)-Ru/Al	nitrate	1st Ru, 2nd alkali	4.34
Na-Ru/Al	carbonate	1st Ru, 2nd alkali	4.34
Ru-Na/Al	carbonate	1st alkali, 2nd Ru	4.34
K-Ru/Al	carbonate	1st Ru, 2nd alkali	5.66
Ru-K/Al	carbonate	1st alkali, 2nd Ru	5.66

CO_2 TPD



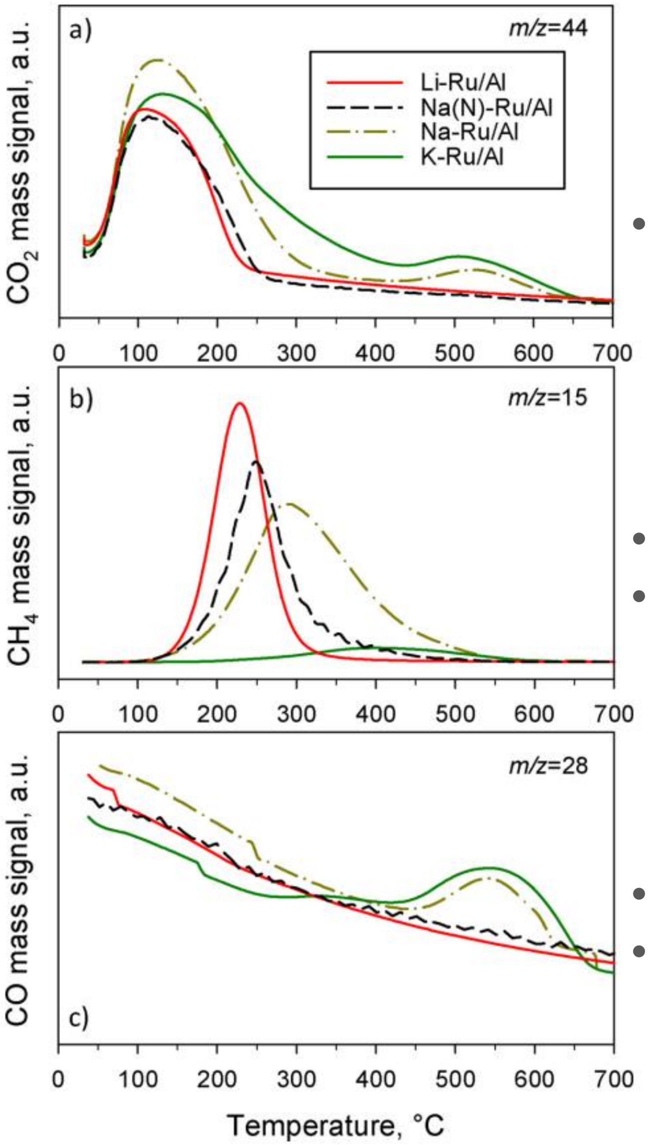
Lithium: high CO_2 storage capacity,
no formation of highly stable carbonates

Catalytic activity



Li - Ru synergy enhances Methanation Activity & Selectivity of Ru/Al_2O_3

Key to success: DFM development



H_2-TPRx of pre-adsorbed CO_2

- Pre-adsorbed CO_2 converted to CH_4 for T≥130 °C
- Li-Ru has largest CH_4 formation at lowest T
- No residual CO_2 (full regeneration) @300°C
- No CO formation with Li-Ru and Na(N)-Ru
- Absence of refractory carbonates

Formation of **Li-Al mixed phases** lowers the stability of carbonates

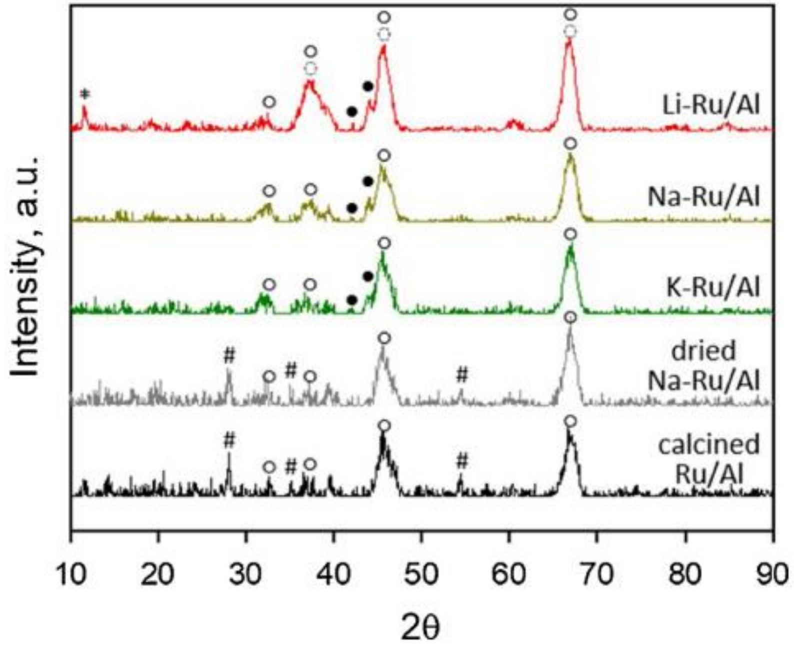
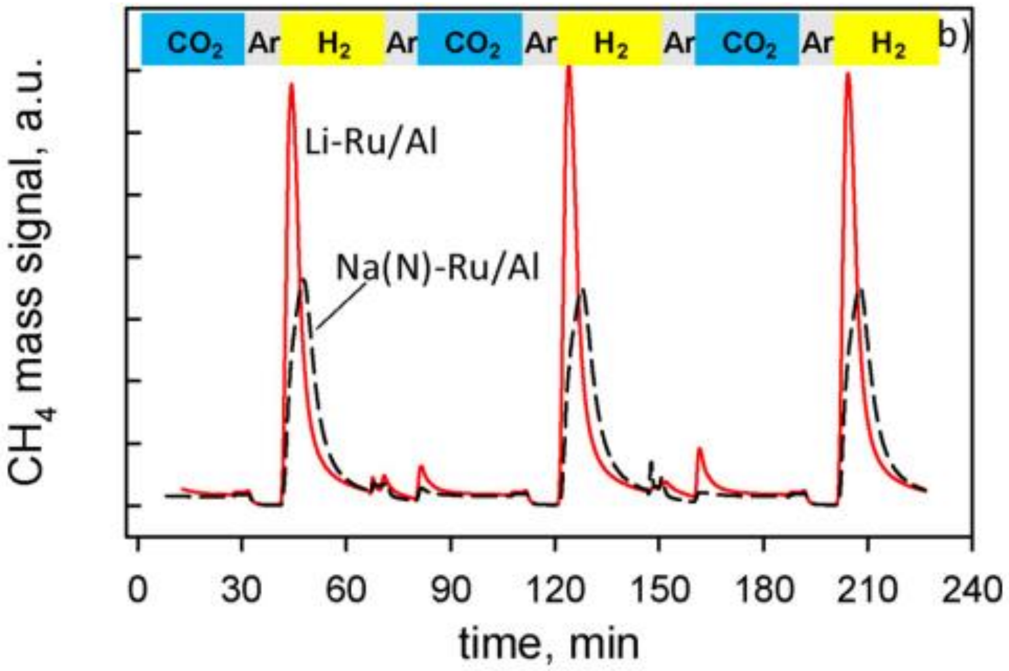
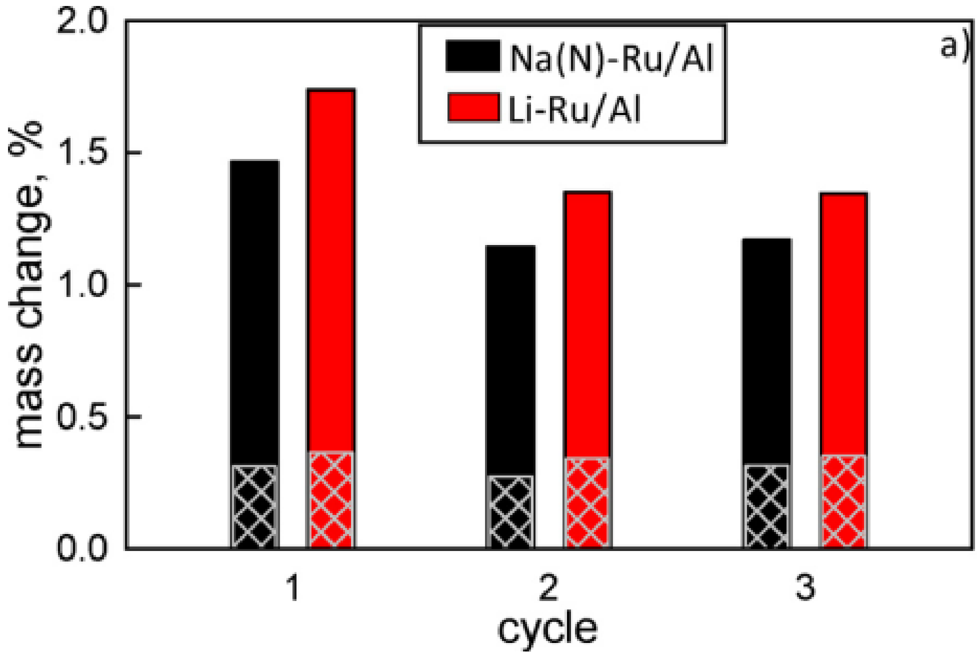


Fig. 2. XRD patterns of Li-Ru/Al, Na-Ru/Al and K-Ru/Al catalysts after testing in the CO_2 hydrogenation reaction. The spectra of dried Ru-/Al and Na-Ru/Al samples (before pre-reduction) are also reported for reference. Legend: ○ = γ-Al_2O_3 (PDF 29-63); ○ = $LiAl_5O_8$ (PDF 3-911); * = $Li_2Al_4(CO_3)(OH)$ (PDF 37-185); ● = Ru (PDF 6-663); # = RuO_2 (PDF 43-1027).

Key to success: DFM development

Cyclic CO_2 capture and methanation (TG-MS @230 °C)

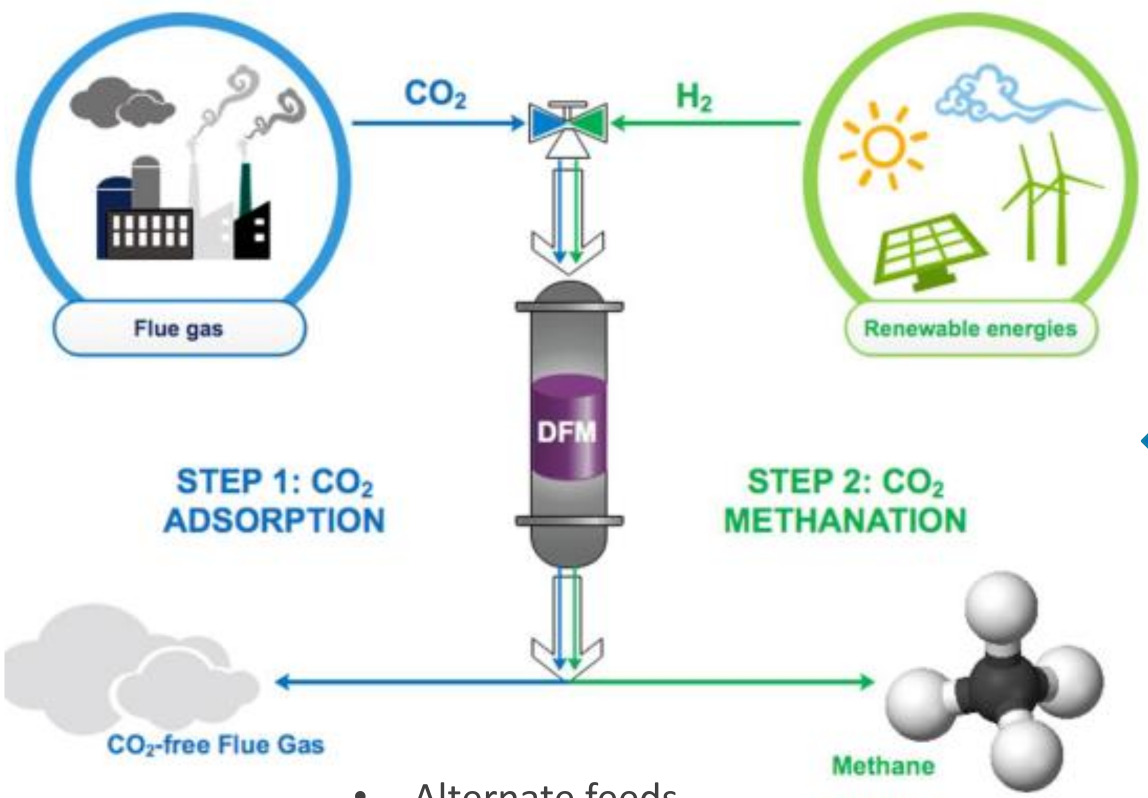




- **Stable, repeatable CH_4 production already @ 230 °C**
- **Repeatable CO_2 capture (regeneration)**
- **Faster & larger CH_4 production over Li-Ru vs. Na-Ru**
- **Low Ru loading: remarkable CH_4 turnover (mol CH_4 / mol Ru)**

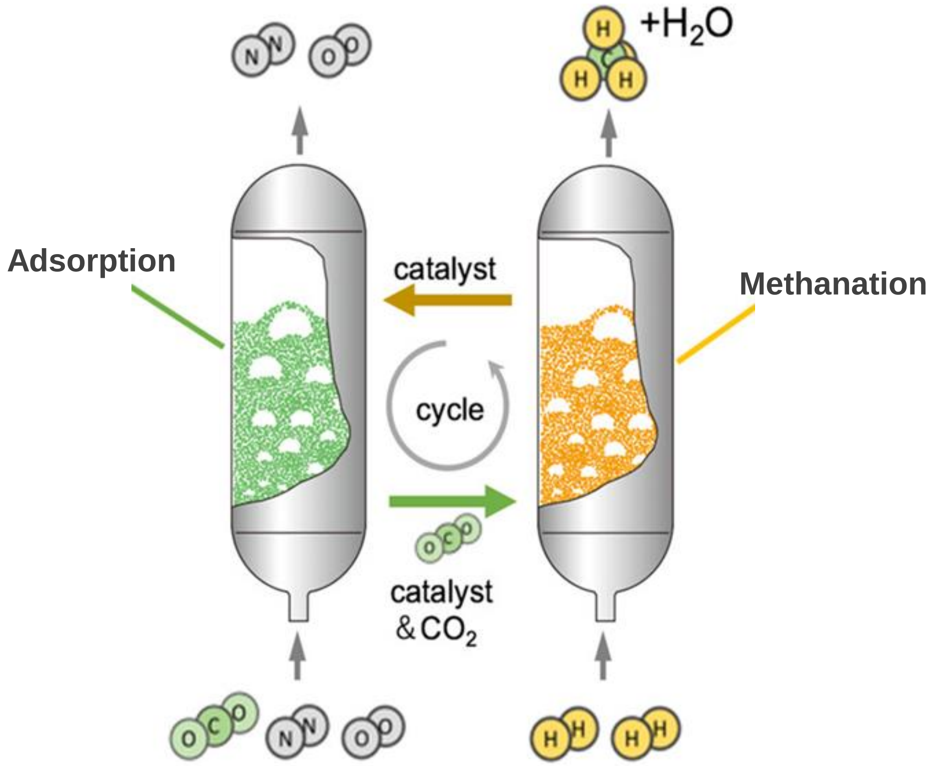
Process intensification

Single Fixed Bed Reactor



- Alternate feeds
- Intermediate purging
- Parallel reactors
- Isothermal operation
- Heat removal?

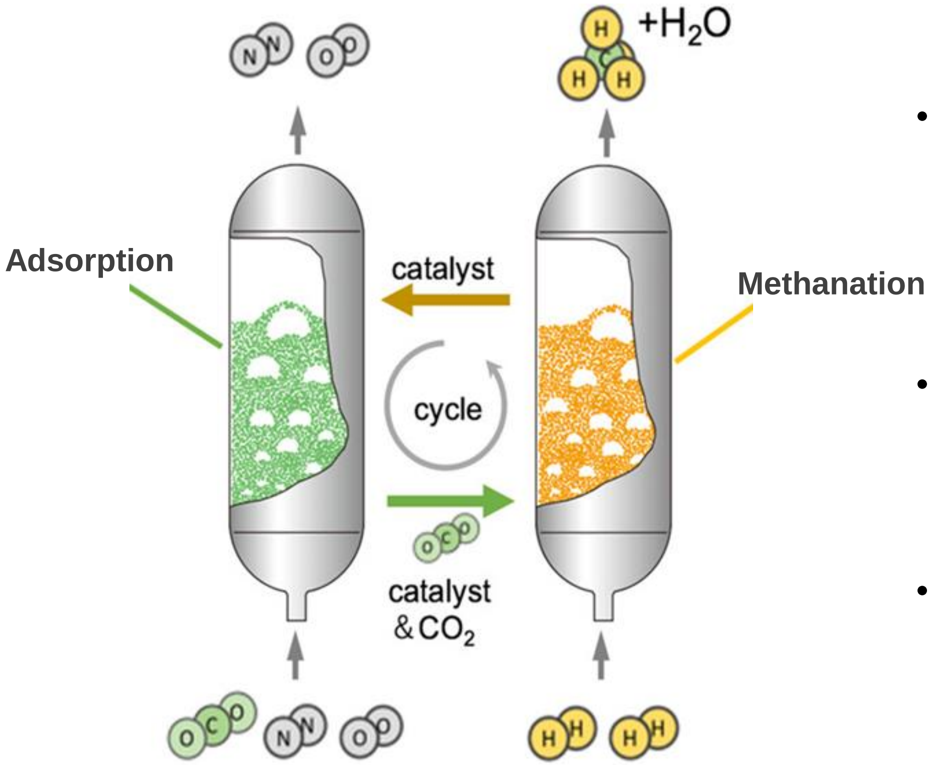
Dual Interconnected Fluidized Bed Reactors



- Continuous operation
- Circulating DFM
- 2 reactors, optimized individually (i.e. different T)
- High heat transfer
- Mechanical stability / Attrition/ Fragmentation

Project: ECO_2Me

Efficient **CO_2** capture and **Me**thanation



- Develop highly innovative dual function catalytic materials to facilitate the production of methane from industrial flue gas emissions aiming at a significant increase in the overall efficiency compared to the State-of-the-Art: **Advanced Lithium Ceramics + Ru**
- Develop innovative, renewable energy driven, catalytic looping processes, to produce synthetic CH_4 demonstrating effectiveness and reduction of GHG emissions: **Dual Interconnected Fluidized Beds Technology**
- Address economic, regulatory, environmental and (critical) raw material constraints, as well as public acceptance issues and socio-economic impact related to the proposed technological pathway: Techno-Economic Evaluation (**TEE**), Life Cycle Assessment (**LCA**), Social Impact Assessment (**SIA**)