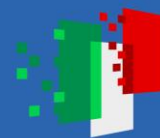




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DI RIPRESA E RESILIENZA



Turning Waste into Solutions: Silica-Based Sorbents for CO₂ Control

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di Milano Bicocca, Milano

⁴Dipartimento di Ingegneria Civile, Chimica e Ambientale
(DICCA), Università di Genova, Genova

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L. Castoldi², B. Di Credico³, R. Scotti³, L. Lietti²,
C. Cristiani¹, E. Finocchio⁴



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SILCO PRIN 2022 PNRR project: waste-derived SILica-based porous solids for Carbon diOxide capture, storage and re-use



Cinzia Cristiani
(PI)



Elisabetta Finocchio
(Co-PI)



Lidia Castoldi



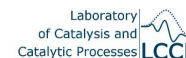
Luca Lietti



Barbara Di Credico



Roberto Scotti



Sergio Molina-Ramírez



Matteo Di Virgilio



Lorenzo Viganò



Giuseppe Nava

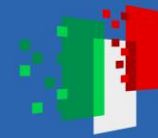




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1. General Overview and Objectives



Matteo Di Virgilio

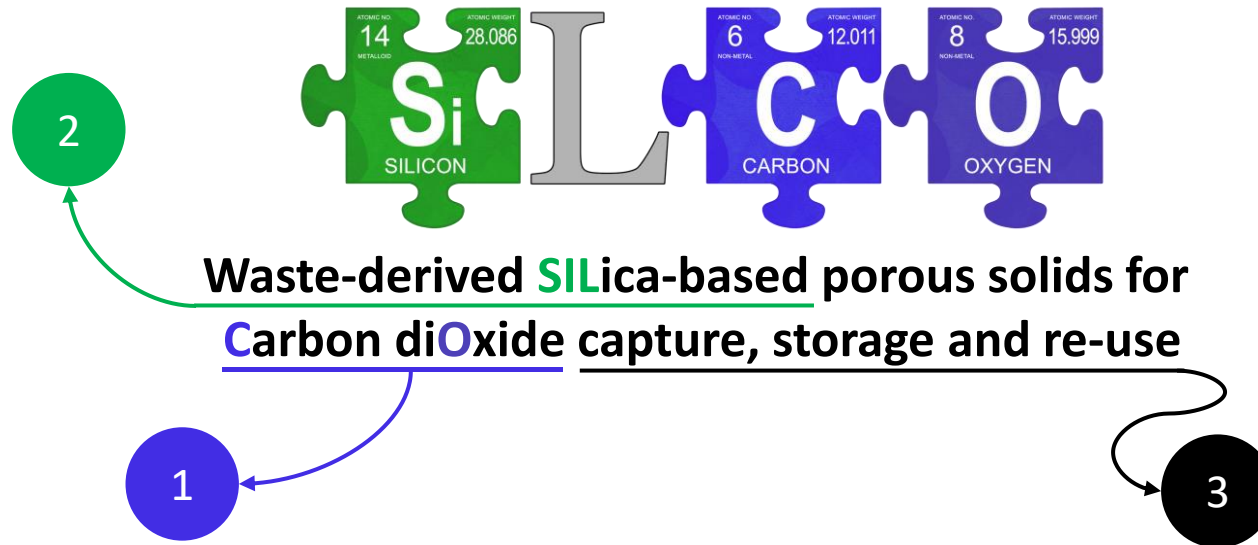


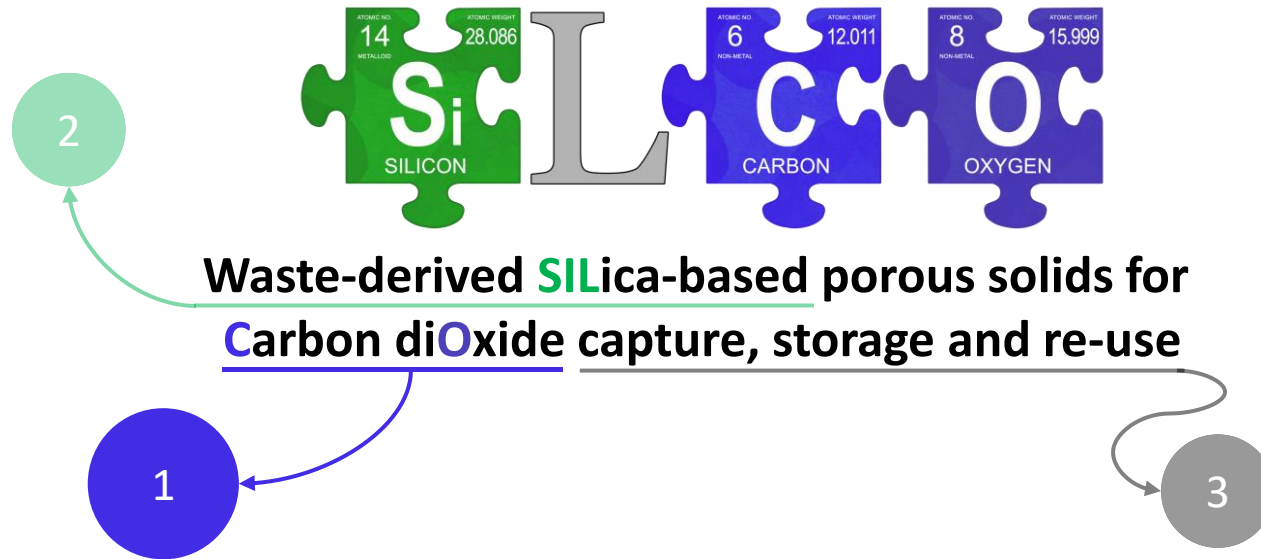
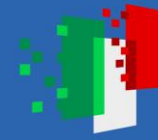
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MATERIALI E INGEGNERIA CHIMICA
GIULIO NATTA



MATERIALS FOR ENERGY AND ENVIRONMENT







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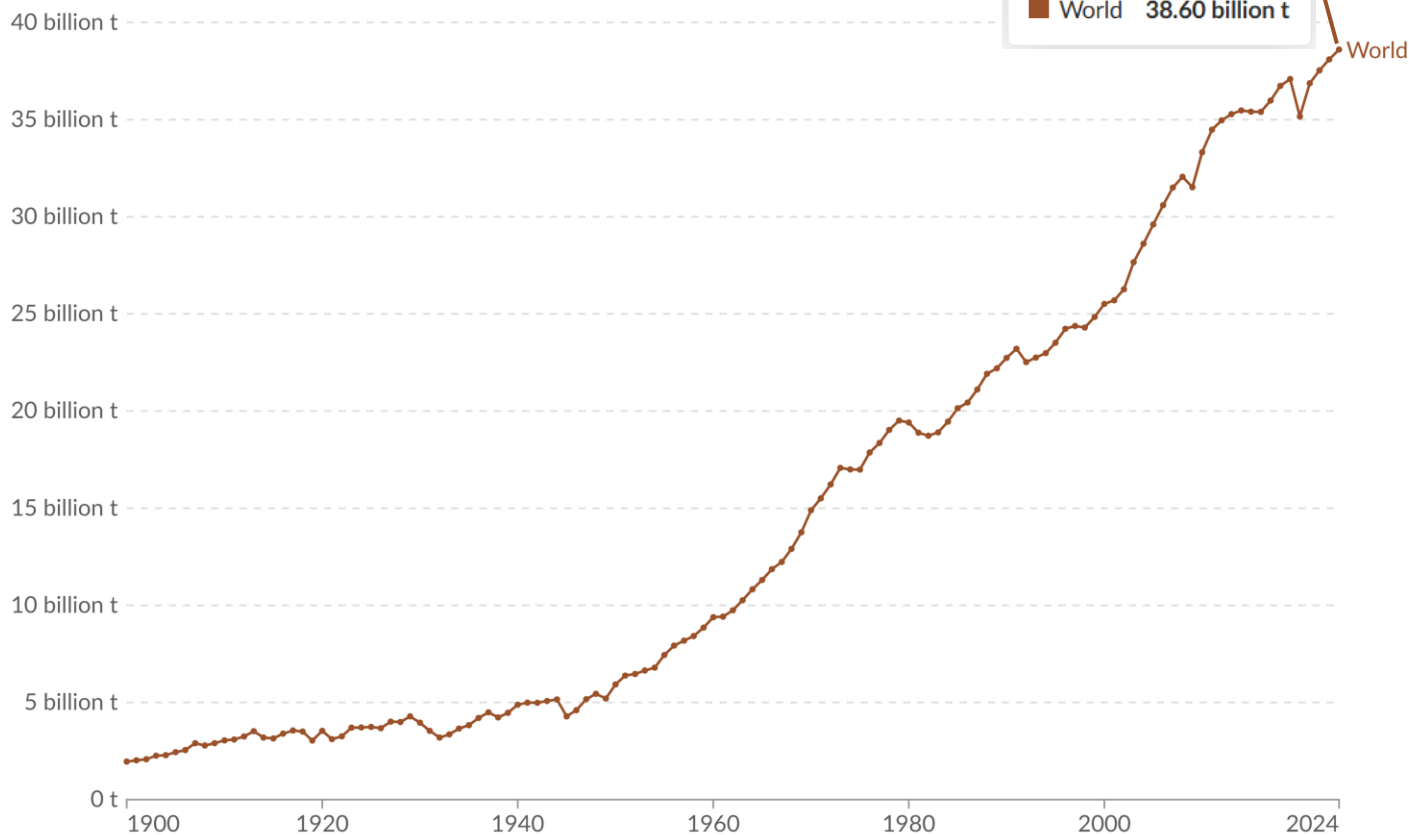
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Università di Genova

Annual CO₂ emissions

Carbon dioxide (CO₂) emissions from fossil fuels and industry.



Data source: Global Carbon Budget (2025)

OurWorldinData.org/co2-and-greenhouse-gas-emissions | CC BY



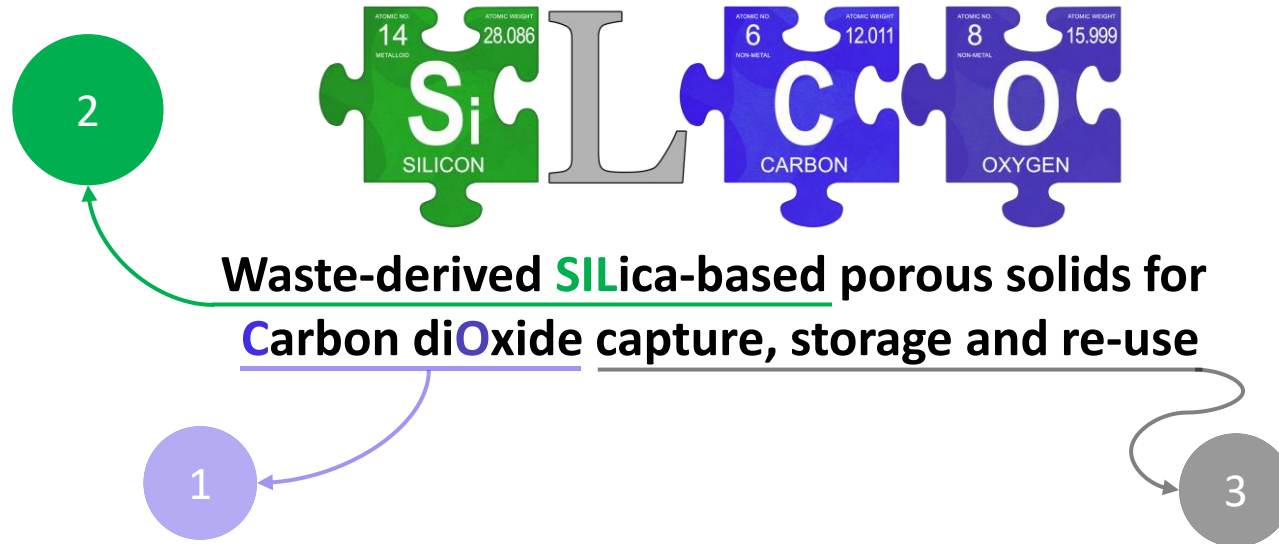
CO₂ emissions from combustion and industry processes is constantly increasing over time



Need for robust strategies to invert the trend



DECARBONIZATION PROCESSES



2 Solid waste-derived materials



The use of **silica-containing solid wastes** for synthesizing silica-based materials is becoming of **broad interest**

Silica (SiO₂) commercial production is expensive and environmentally severe

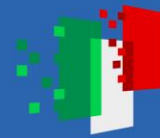


Cleaner production and circularity concepts

Waste pollution reduction

Promising CO₂ sorbents

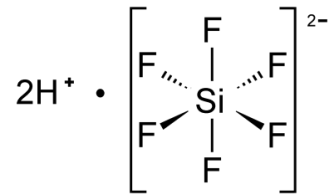
Solid waste-derived materials could provide technology with **competitive processing costs**



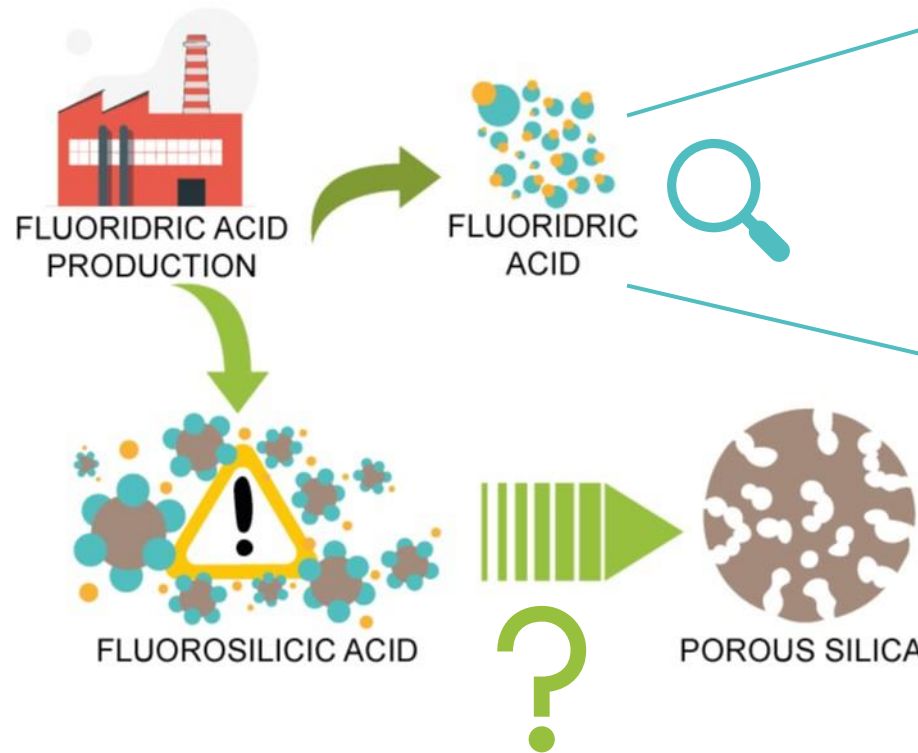
2

Hexafluorosilicic acid (FSA)

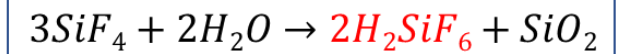
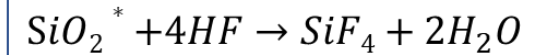
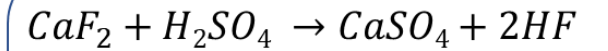
A hazardous and corrosive by-product of HF



Production of more than $2 \cdot 10^6$ tons per year



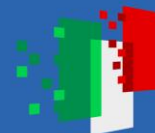
HF industrial production:



* compound as impurity in CaF_2



SiO_2 is the **major impurity (0.5–1.5 wt.%)** of acid-grade fluorspar (CaF_2)



2

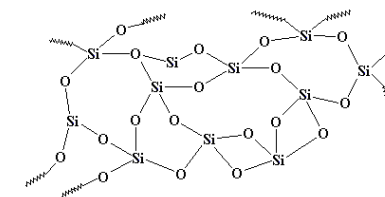
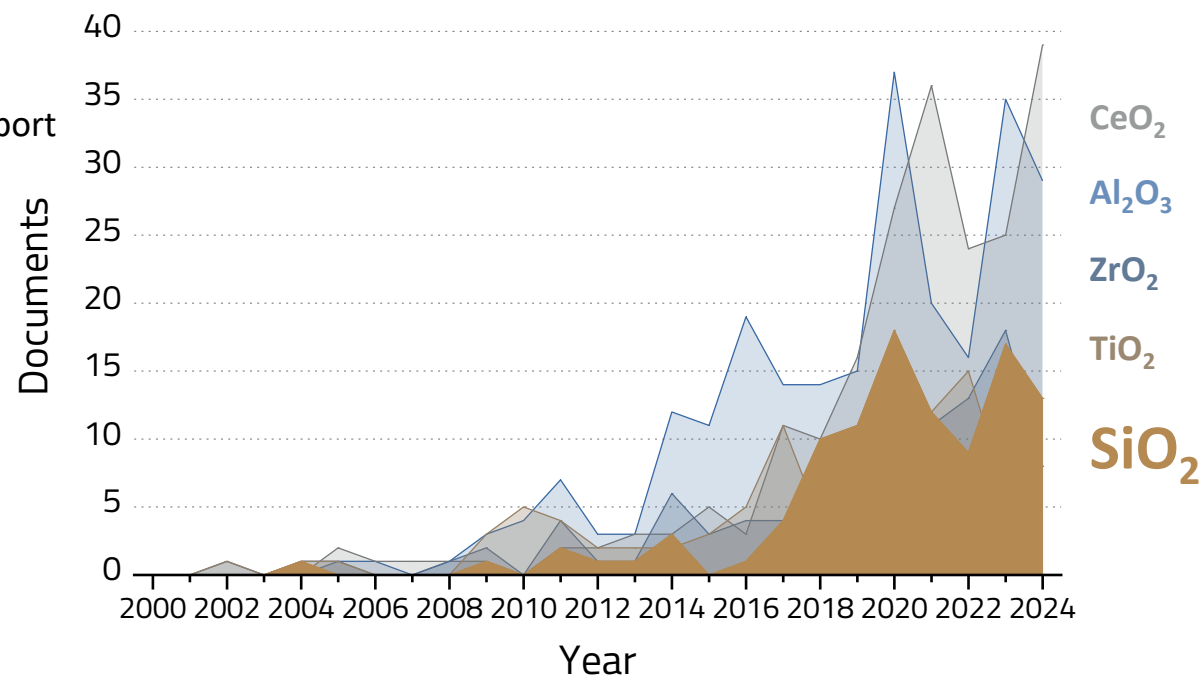
Mesoporous silica: a promising material for CO₂ adsorption and as a support for methanation catalysts

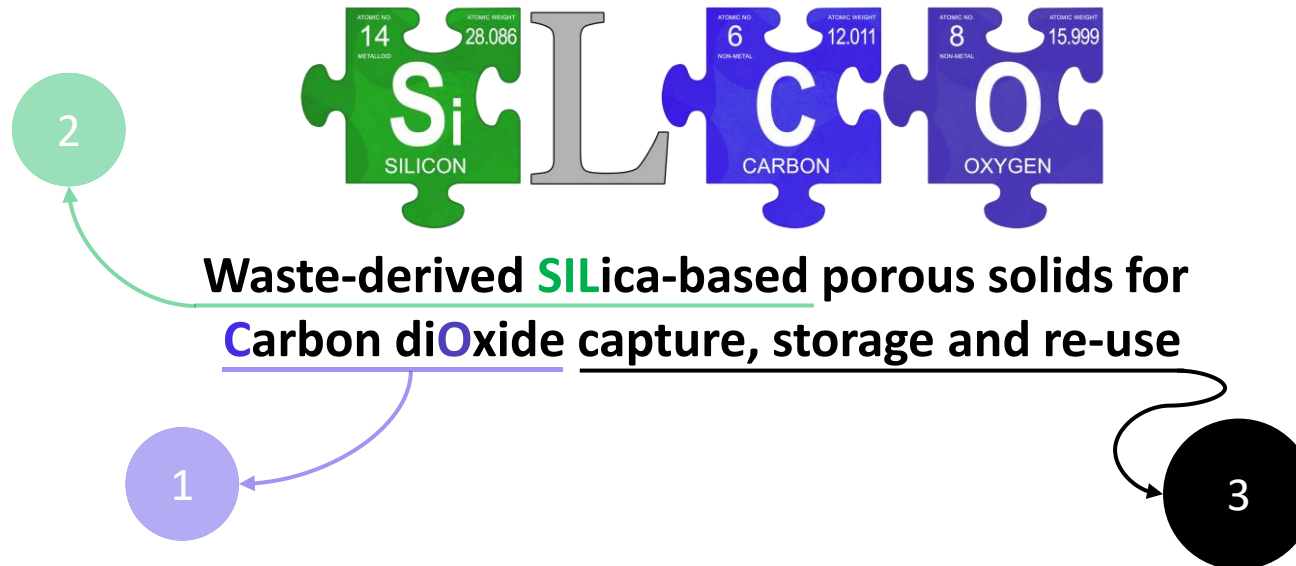
✓ High surface area

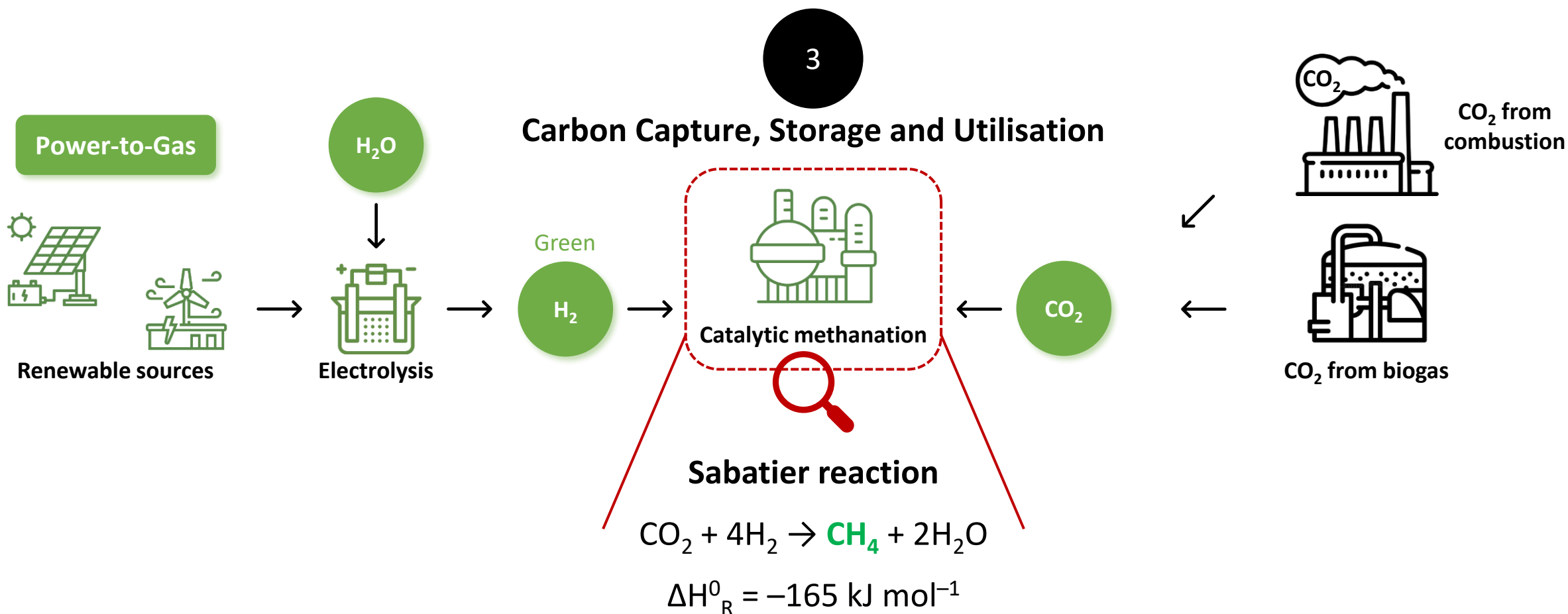
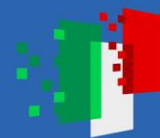
✓ Adjustable pore structure

✓ Particular surface chemistry

Scopus Database:
CO₂ + methanation + catalysis + support

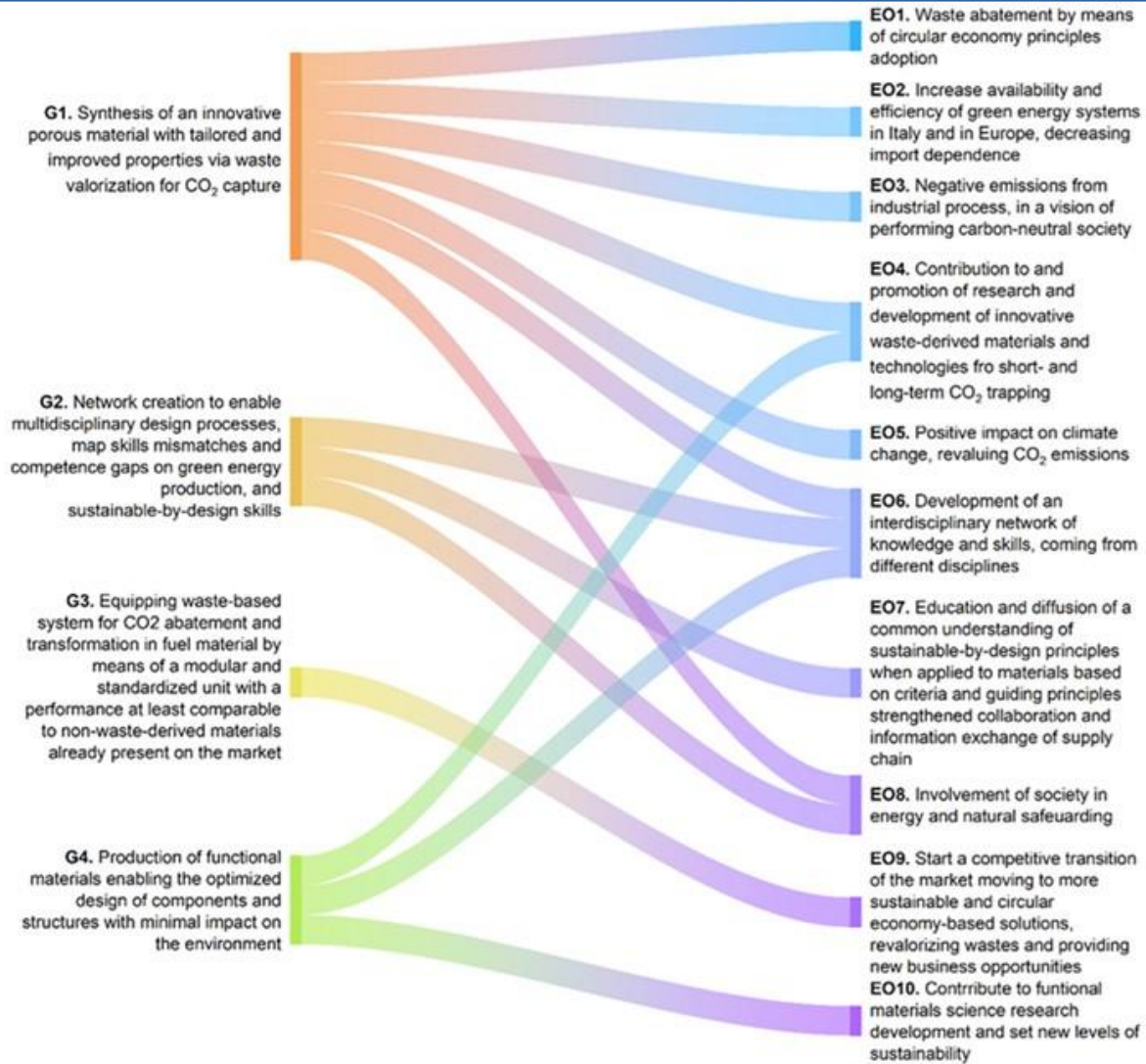




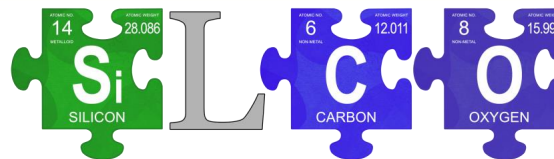




GOALS



E O
X U
P T
E C
C O
T M
E E
D S



Essential objectives of the project



Development of Waste-derived Sorbent Matrixes (WSM) based on **silica** and/or **modified silica**



Strategic and efficient **CO₂ capture, storage and re-use**

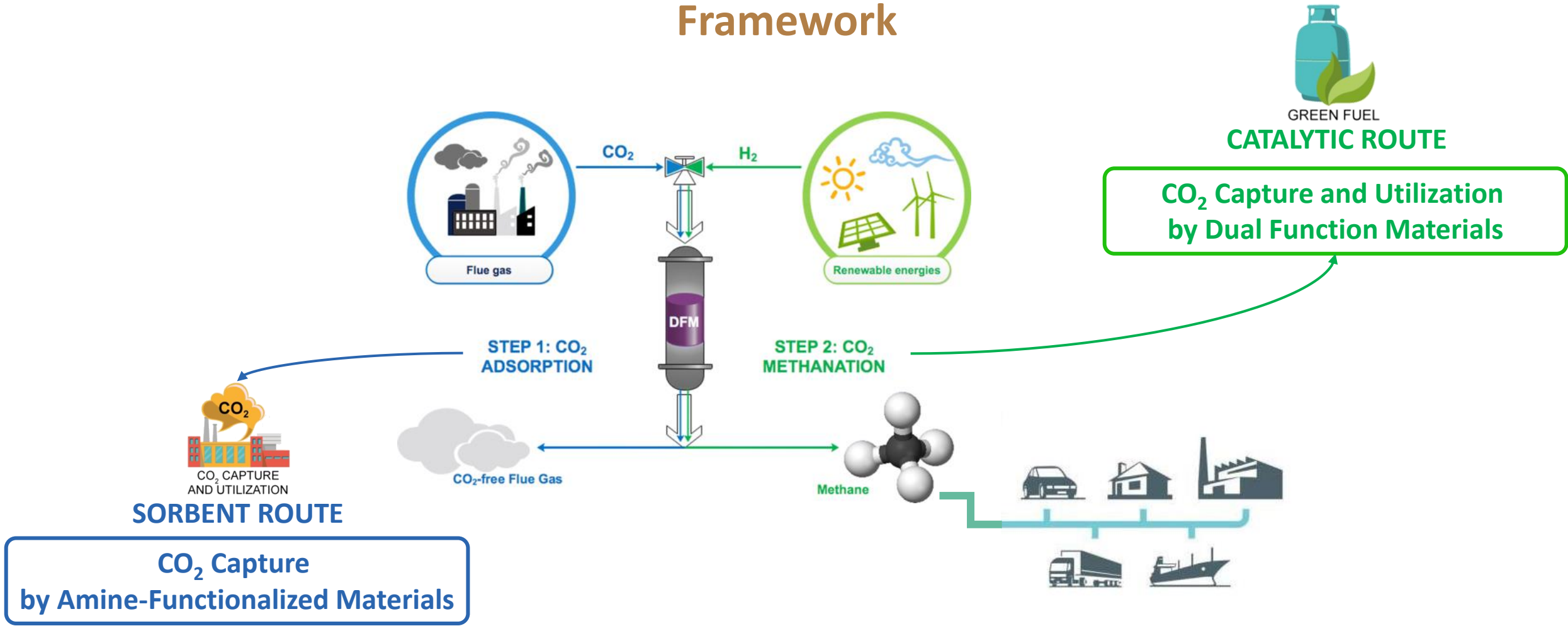


High yield and selective **e-fuel production**





Framework





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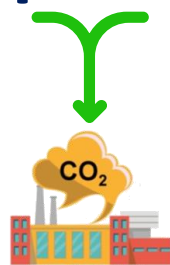
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2. Design of waste-derived silica and CO₂ Capture Application



CO₂ CAPTURE
AND UTILIZATION

SORBENT ROUTE

**CO₂ Capture
by Amine-Functionalized Materials**



Lorenzo Viganò



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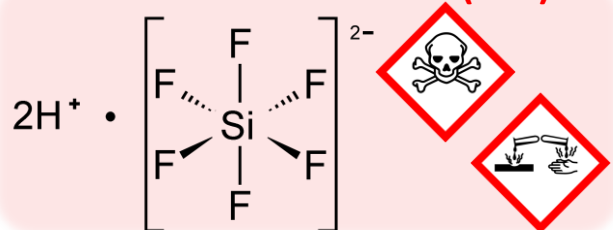
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MATERIALI E INGEGNERIA CHIMICA
GIULIO NATTA



Hexafluorosilicic acid production and valorization

HF production from CaF_2

Hexafluorosilicic acid (FSA)



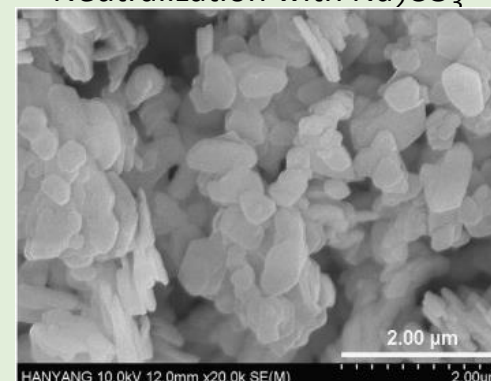
Phosphate ores Leaching for fertilizers

Neutralization in sea

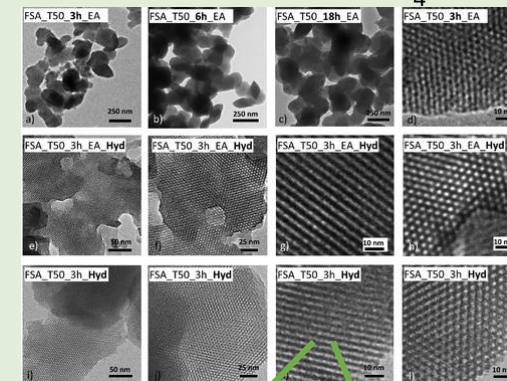
Limited applications • Water fluorination • AlF_3 synthesis • Metal surface treatment

Conversion of FSA into SiO_2

Neutralization with Na_2CO_3



Neutralization with NH_4OH

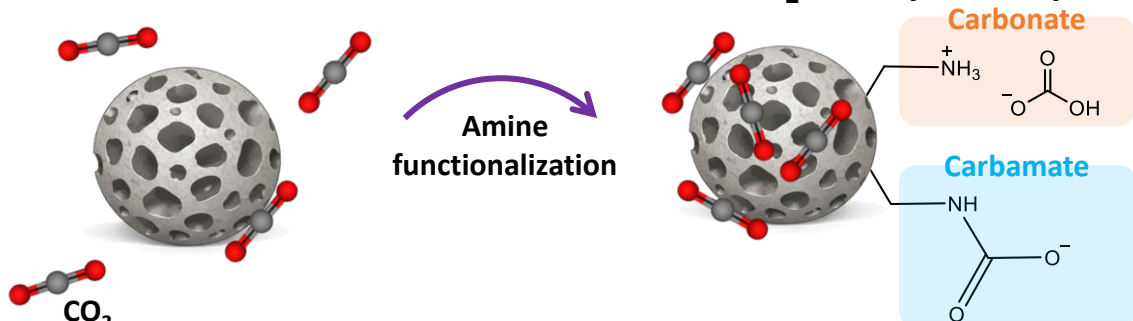


✓ Low-cost ✓ Easy-process ✓ Sustainable

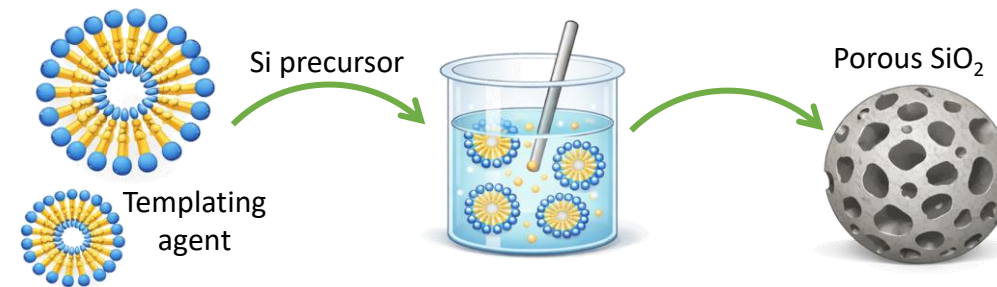


What is needed for catalytic and CO_2 adsorption applications?

2. Amine functionalization enhances CO_2 adsorption capacity

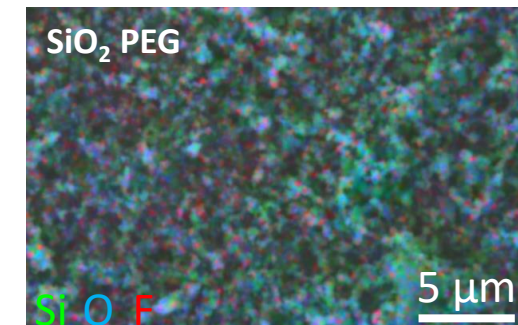
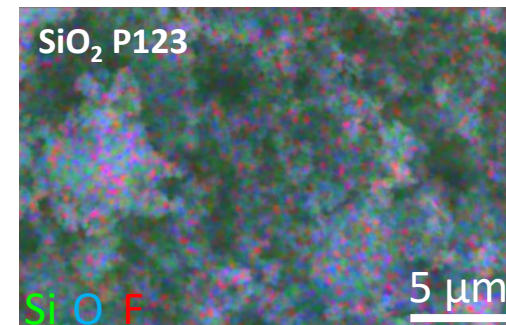
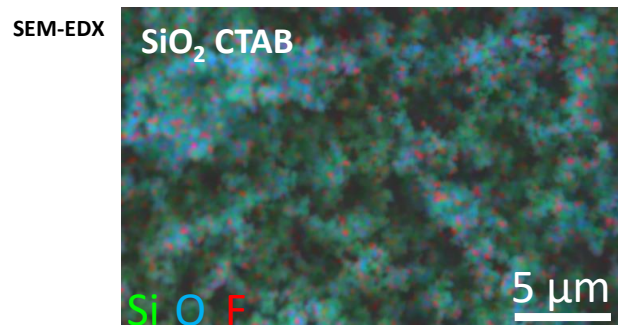
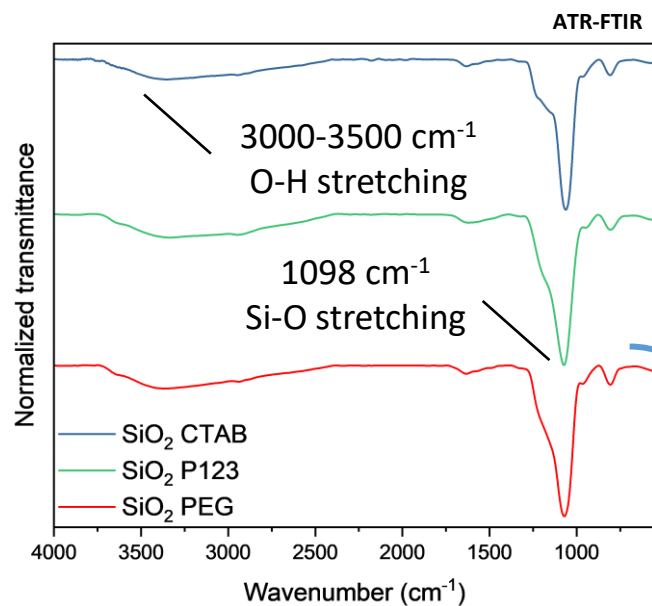
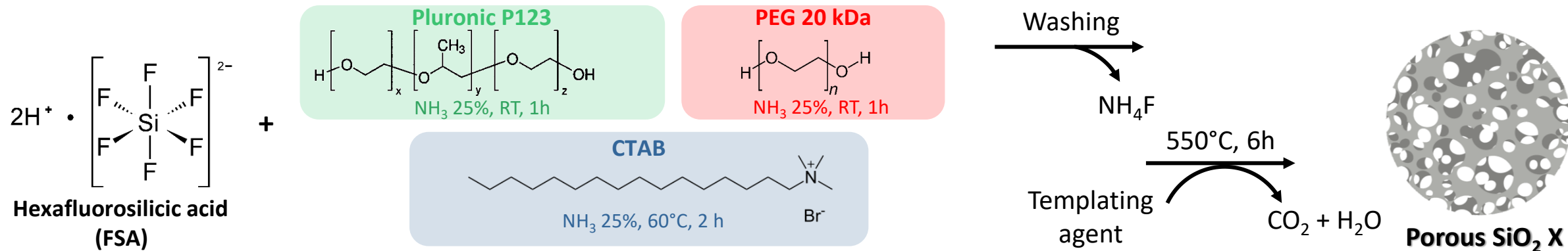


1. Higher surface area through soft templated synthesis



[1] Montini, D., et al. *Materials*, 16 (2023) [2] Sarawade, P. B. et al. *J. Hazard. Mater.*, 173 (2010), 576–580 [3] Vacca, M. A., et al. *ACS Sustain. Chem. Eng.*, 8 (2020), 14286–14300

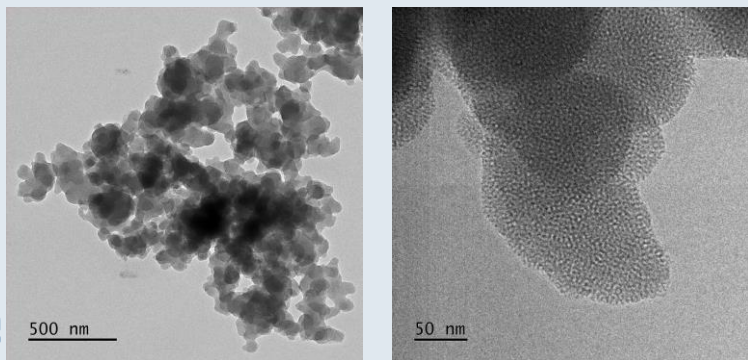
Synthesis and characterization of porous SiO₂ from FSA



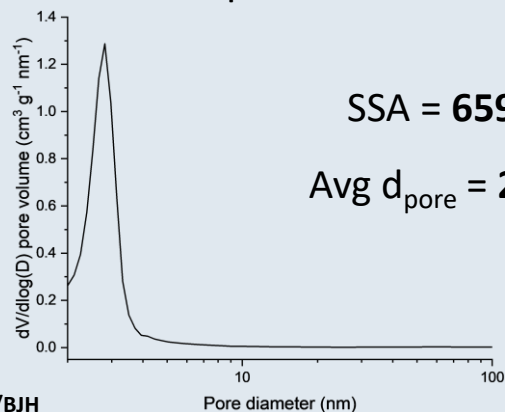
ATR-FTIR
All samples show the main SiO₂ IR signals
and no traces of templates or NH₄F

SEM-EDX + XRF
Fluorine is efficiently removed, with a [F] ≤ 0.33 %

Characterization of porous SiO₂: morphology

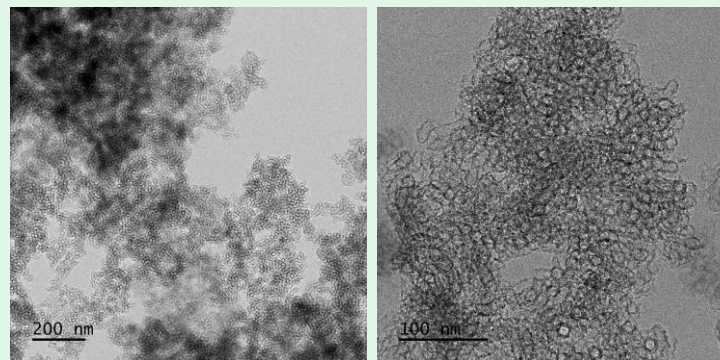


Aggregates of >100 nm primary particles
Avg. $d_{\text{pore}} = 2.7 (\pm 0.3)$ nm

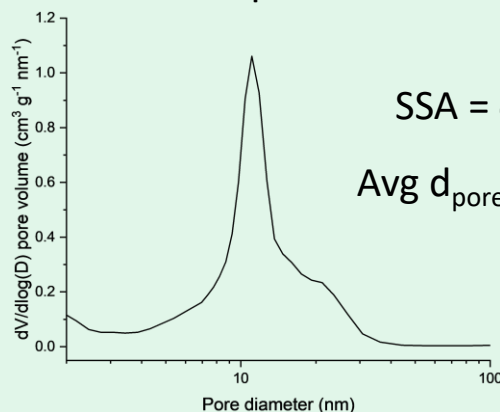


SSA = 659 m²/g
Avg $d_{\text{pore}} = 2.81$ nm

SiO₂ P123

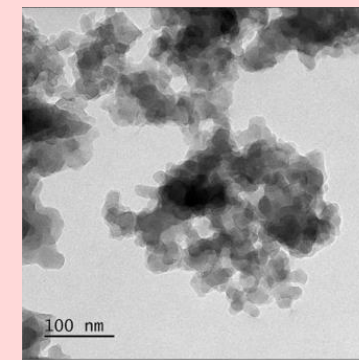


Particles with sheet-like shape
Avg. $d_{\text{pore}} = 10.0 (\pm 0.7)$ nm

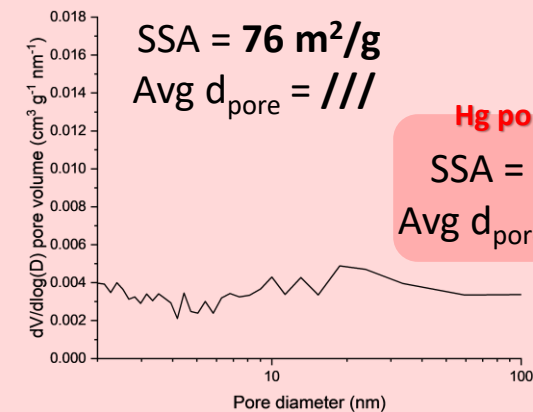


SSA = 487 m²/g
Avg $d_{\text{pore}} = 10.6$ nm

SiO₂ PEG



Aggregates of 20-25 nm primary particles



SSA = 76 m²/g
Avg $d_{\text{pore}} = ///$

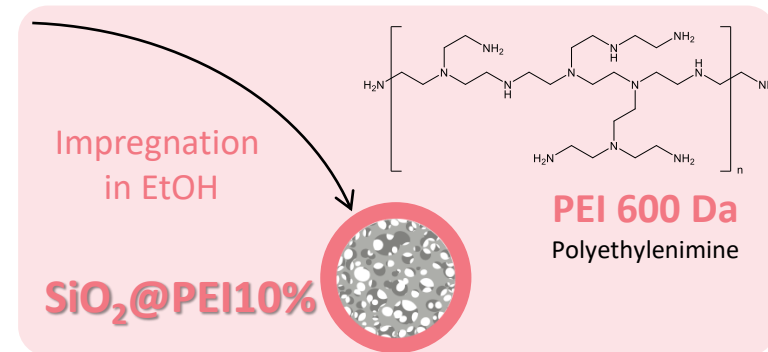
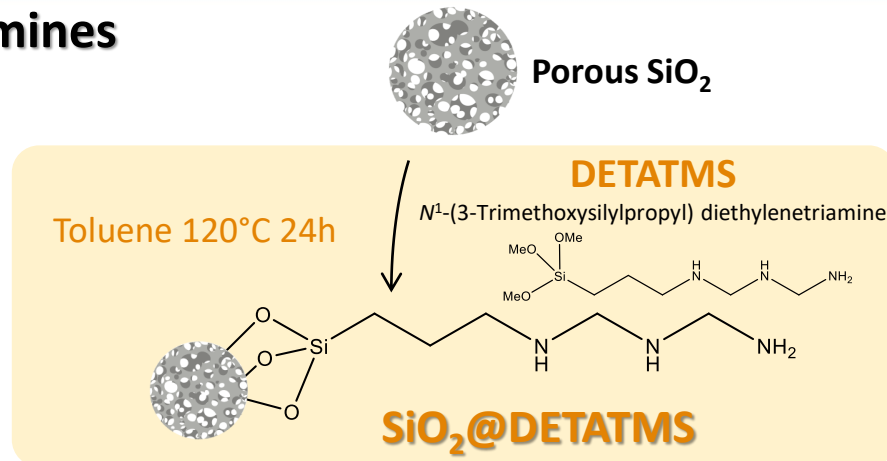
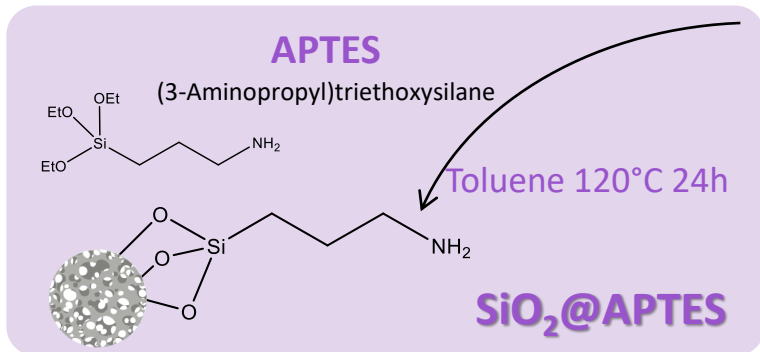
Hg porosimetry
SSA = 104 m²/g
Avg $d_{\text{pore}} = 346$ nm

Distinct particles morphologies with different mesopores sizes

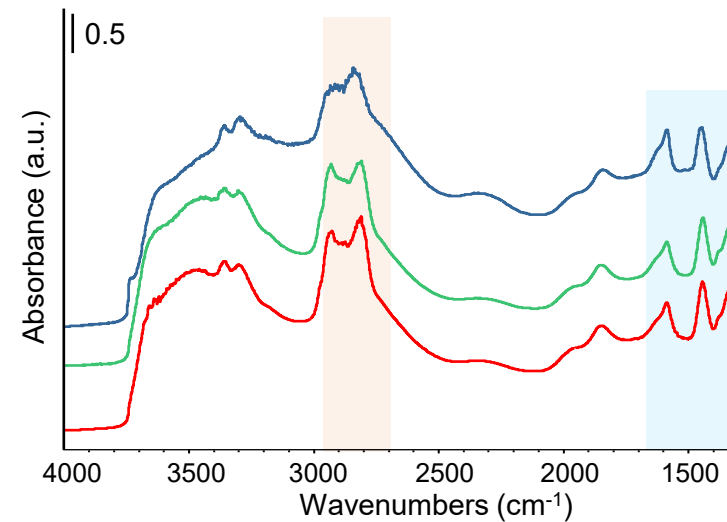
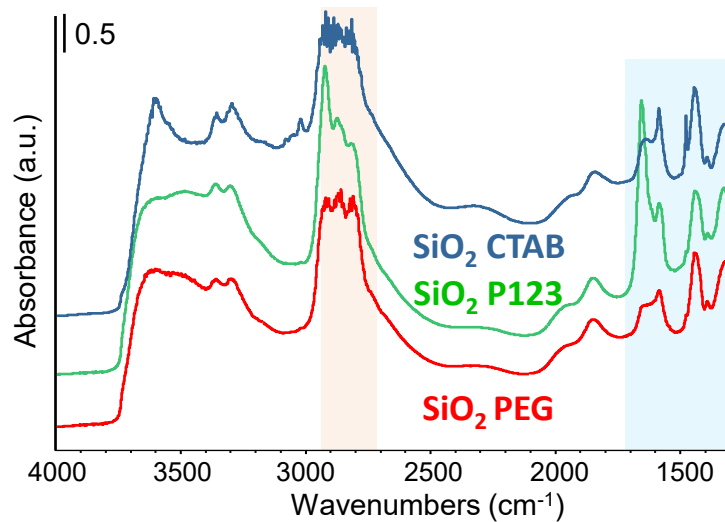
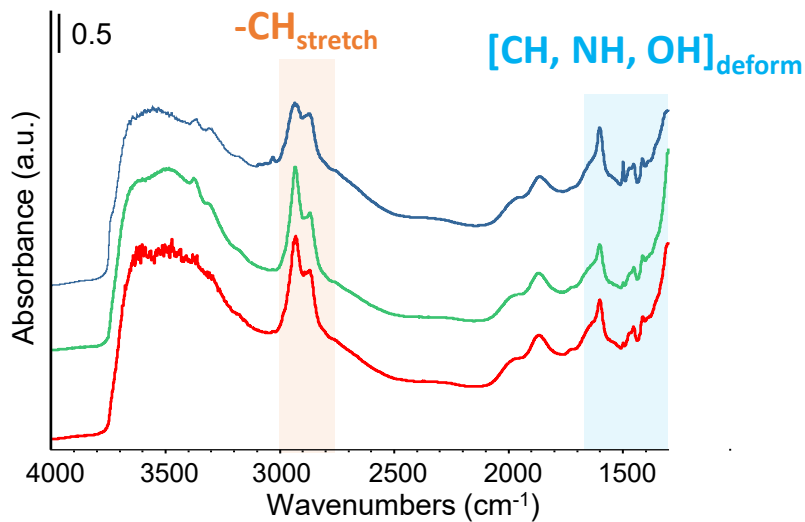
Aggregated NPs forming a macroporous structure



Porous SiO₂ functionalization with amines



*In situ FTIR spectra : activation in vacuum (10⁻³ Pa), 100°C, 1h



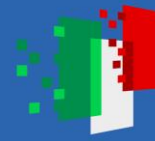
Infrared (IR) spectra confirm the successful incorporation of aminated organic moieties onto SiO₂ surface



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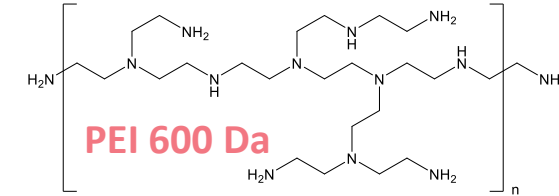
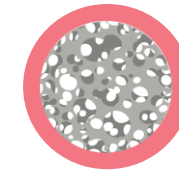
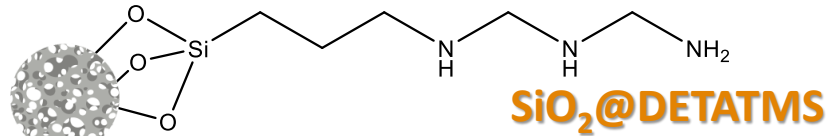
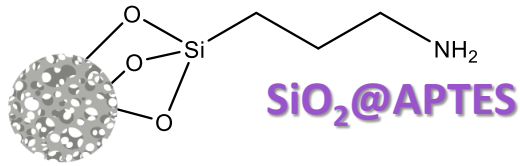
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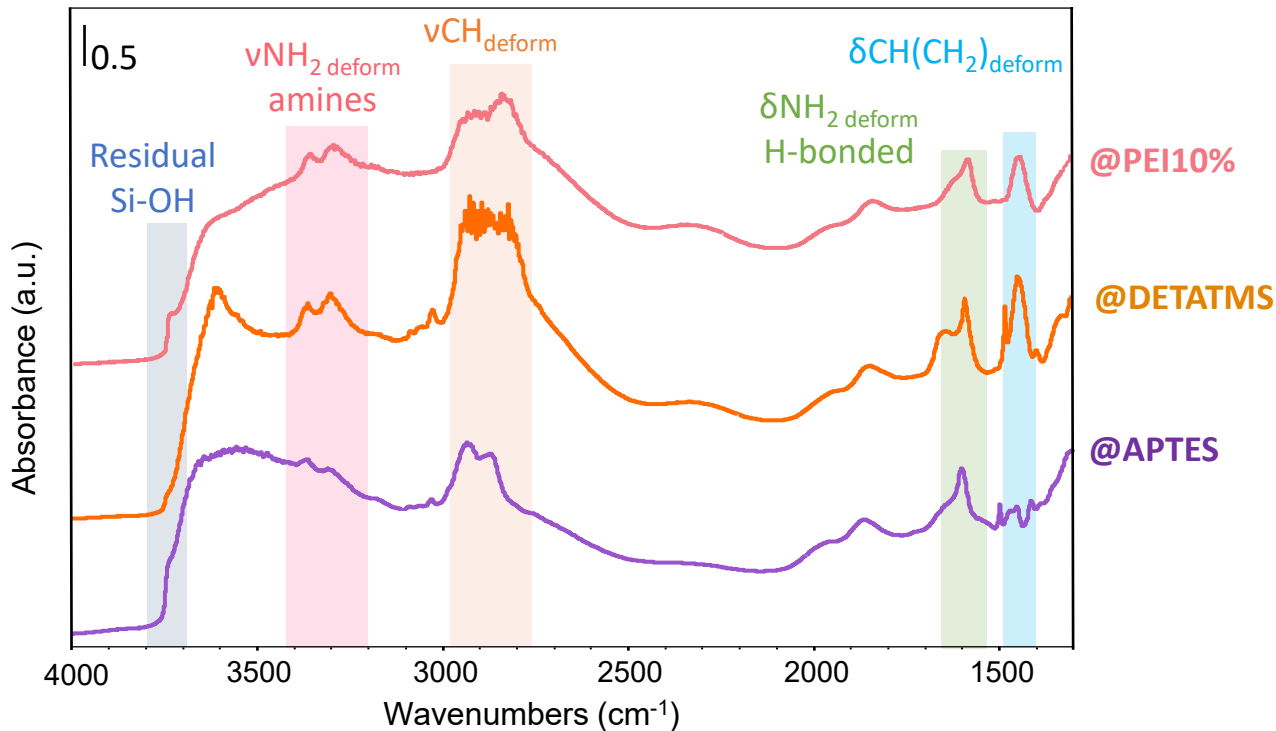
Porous SiO₂ functionalization with amines



SiO₂@PEI10%

*In situ FTIR spectra: activation in vacuum (10⁻³ Pa), 100°C, 1h

SiO₂ CTAB



After activation, characteristic **CH/CH₂** and **NH** bands **persist**, demonstrating the stability of grafted amines



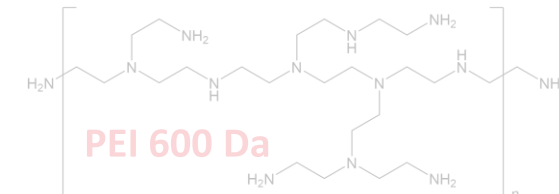
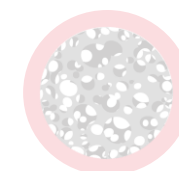
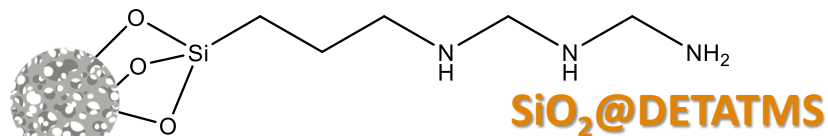
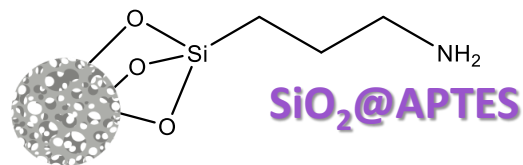
Free **NH** groups (amine species) bands were observed



Free -NH groups are available to interact with CO₂

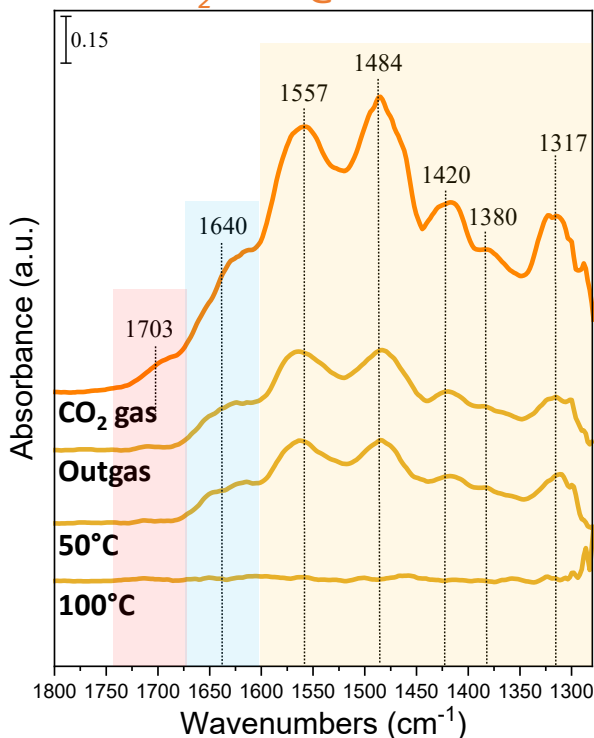
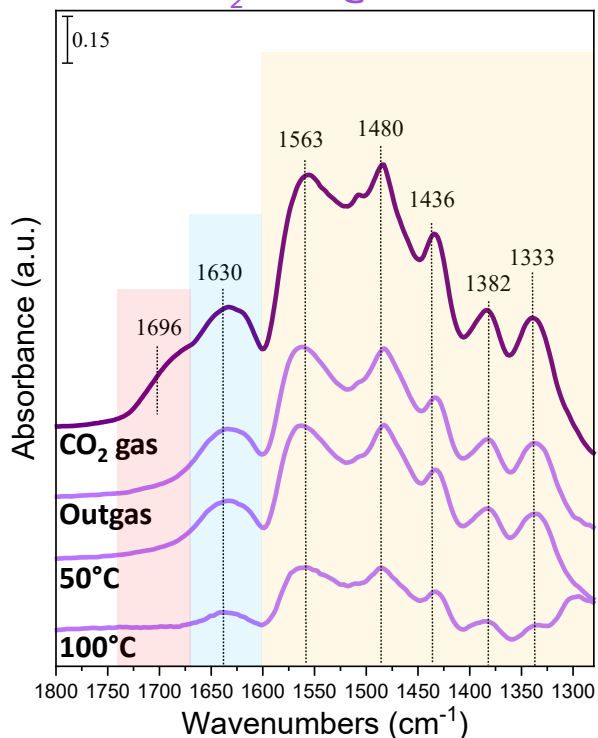
[1] Bacsik, Z. *et al. Langmuir*, 27 (2011), 11118-11128

Amine functionalized SiO₂: CO₂ interaction



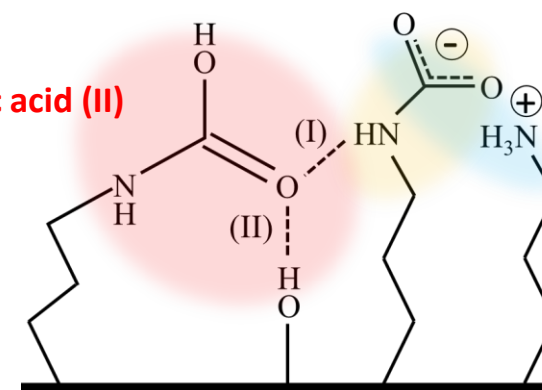
SiO₂ CTAB@APTES

SiO₂ CTAB@DETATMS



1696 cm⁻¹
H-bonded carbamic acid (II)

1310-1560 cm⁻¹
carbamate species



1630 cm⁻¹
NH₄⁺-carbamate salt

Only carbamate species are **stable** after outgassing at R.T.

No remarkable intensity changes detected by outgassing up to 50 °C

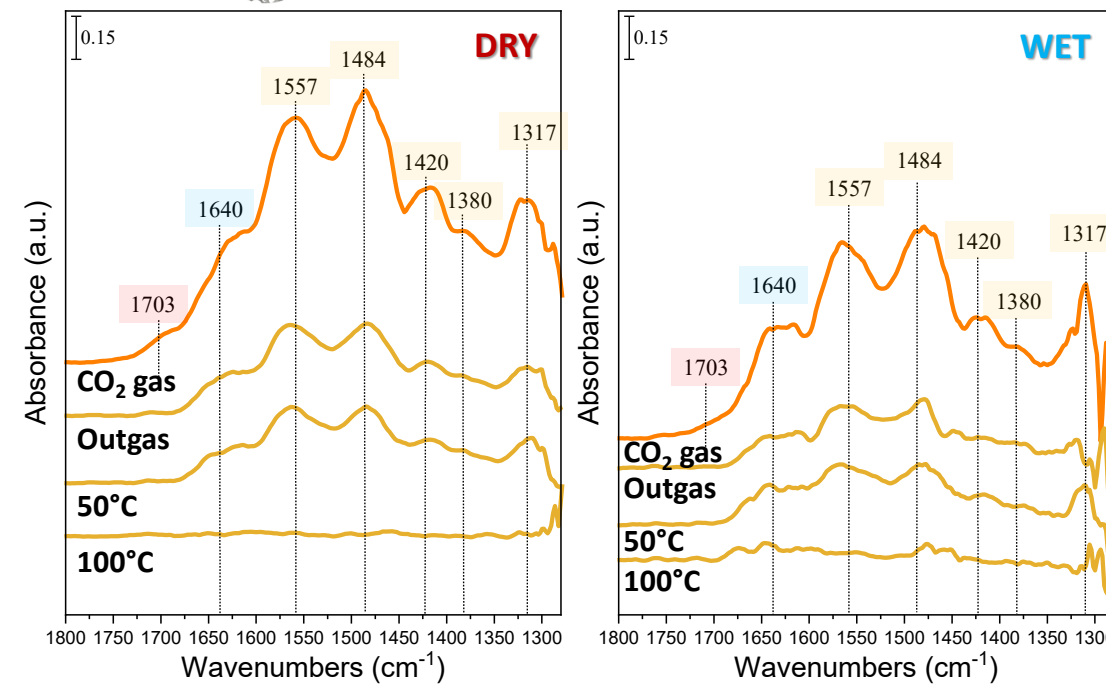
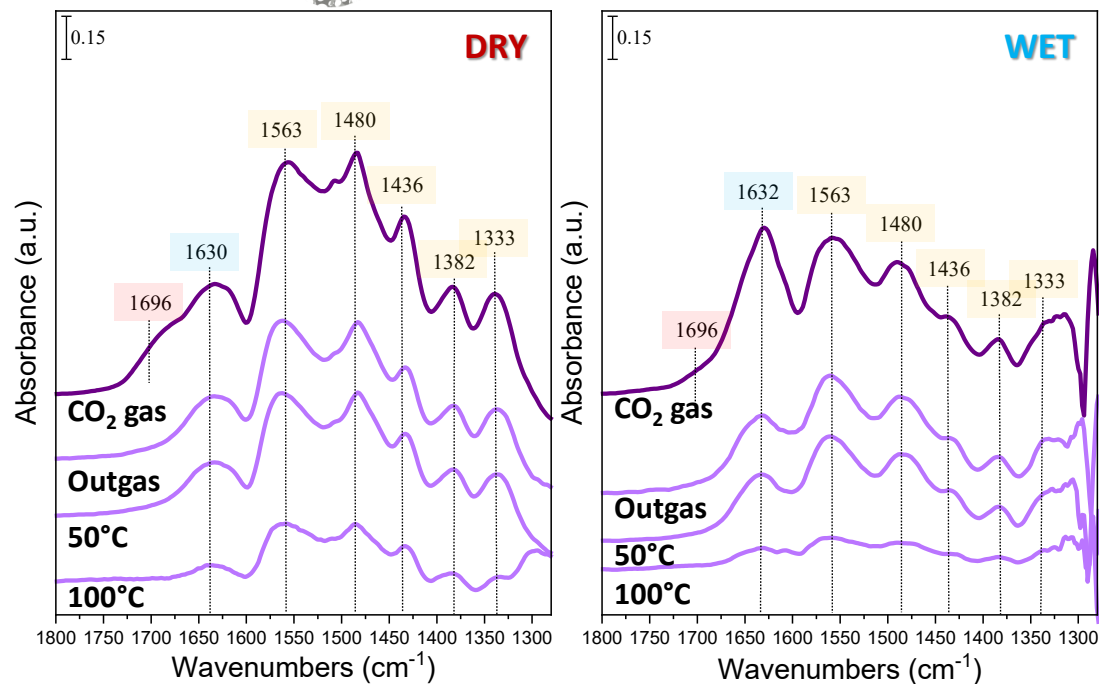
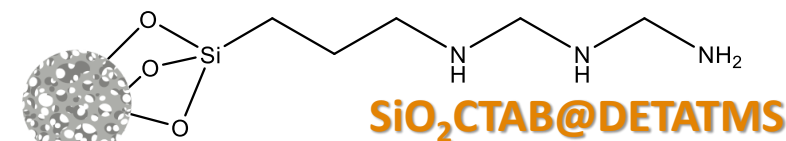
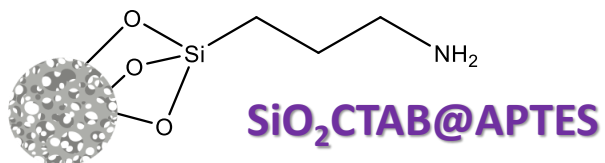
Heating to 100 °C induces CO₂ desorption

*After activation, 16 Torr CO₂, R.T.; outgassing R.T-100°C. Activated spectrum at 100 °C subtracted

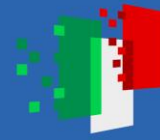
[1] Hedin, N. et al. *Curr. Opin. Green Sustain. Chem.*, 16 (2019), 13-19 [2] Hiyoshi, N. et al. *Micropor. Mesopor. Mat.*, 84 (2005), 357-365

Amine functionalized SiO₂: CO₂ interaction

*After activation, 16 Torr CO₂ R.T.; outgassing R.T-100°C. Activated spectrum at 100 °C subtracted

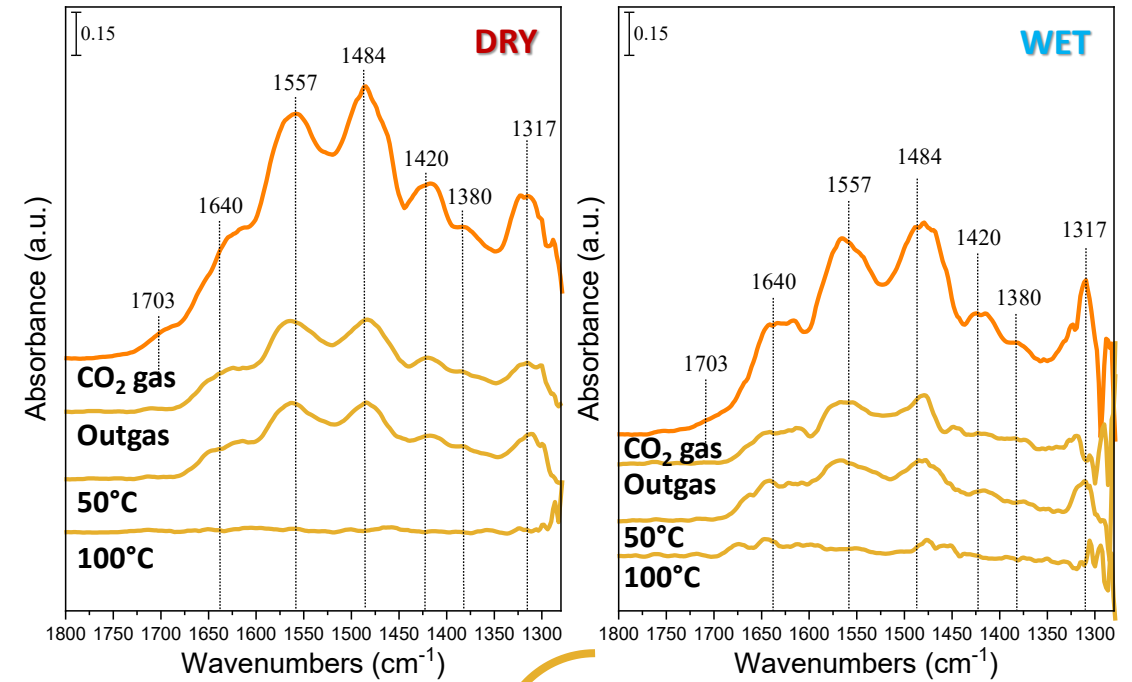
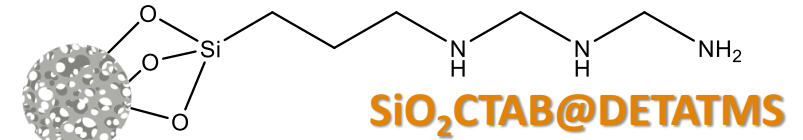
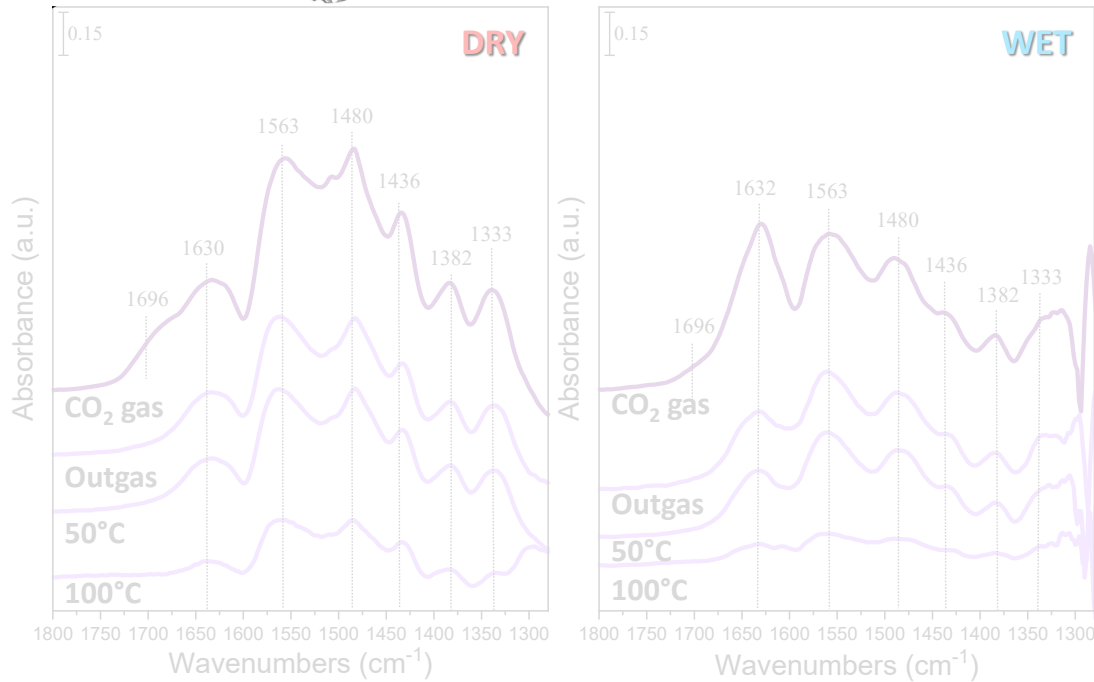
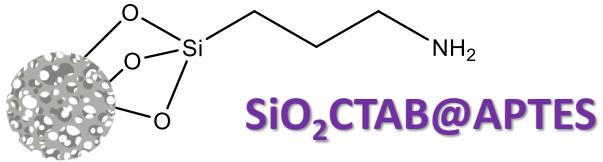


! No differences in the species generated after CO₂ exposition, with dry and wet condition



Amine functionalized SiO₂: CO₂ interaction

*After activation, 16 Torr CO₂ R.T.; outgassing R.T-100°C. Activated spectrum at 100 °C subtracted



✓ SiO₂ CTAB@DETATMS presents remarkable regeneration capacity

← Flat subtraction spectrum after outgassing at 100°C



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3. FTIR surface analysis of silica-based DFMs



GREEN FUEL

CATALYTIC ROUTE

CO₂ Capture and Utilization
by Dual Function Materials



Sergio Molina-Ramírez

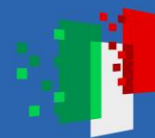


POLITECNICO MILANO 1863

DIPARTIMENTO DI CHIMICA, MATERIALI E INGEGNERIA CHIMICA GIULIO NATTA

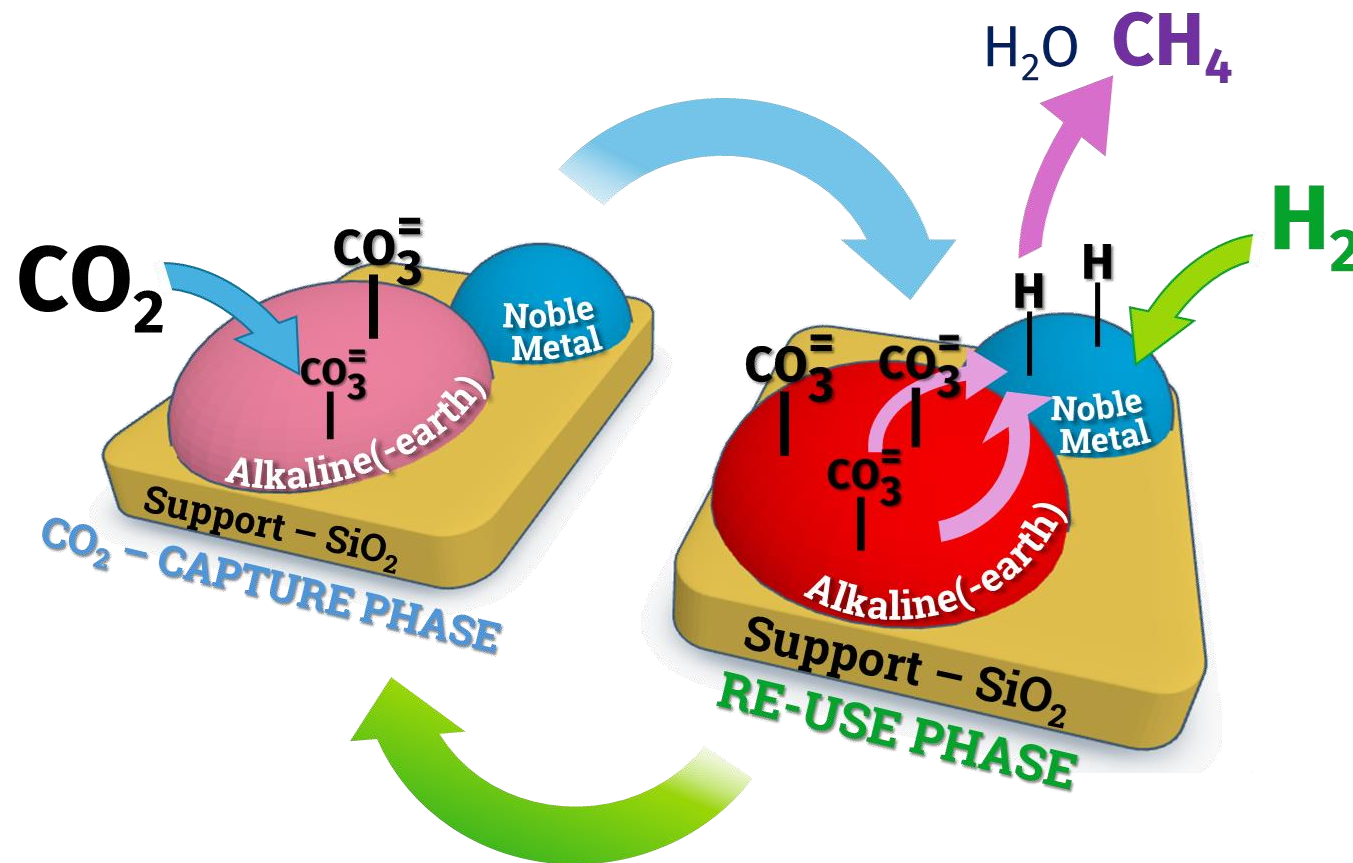


Università di Genova



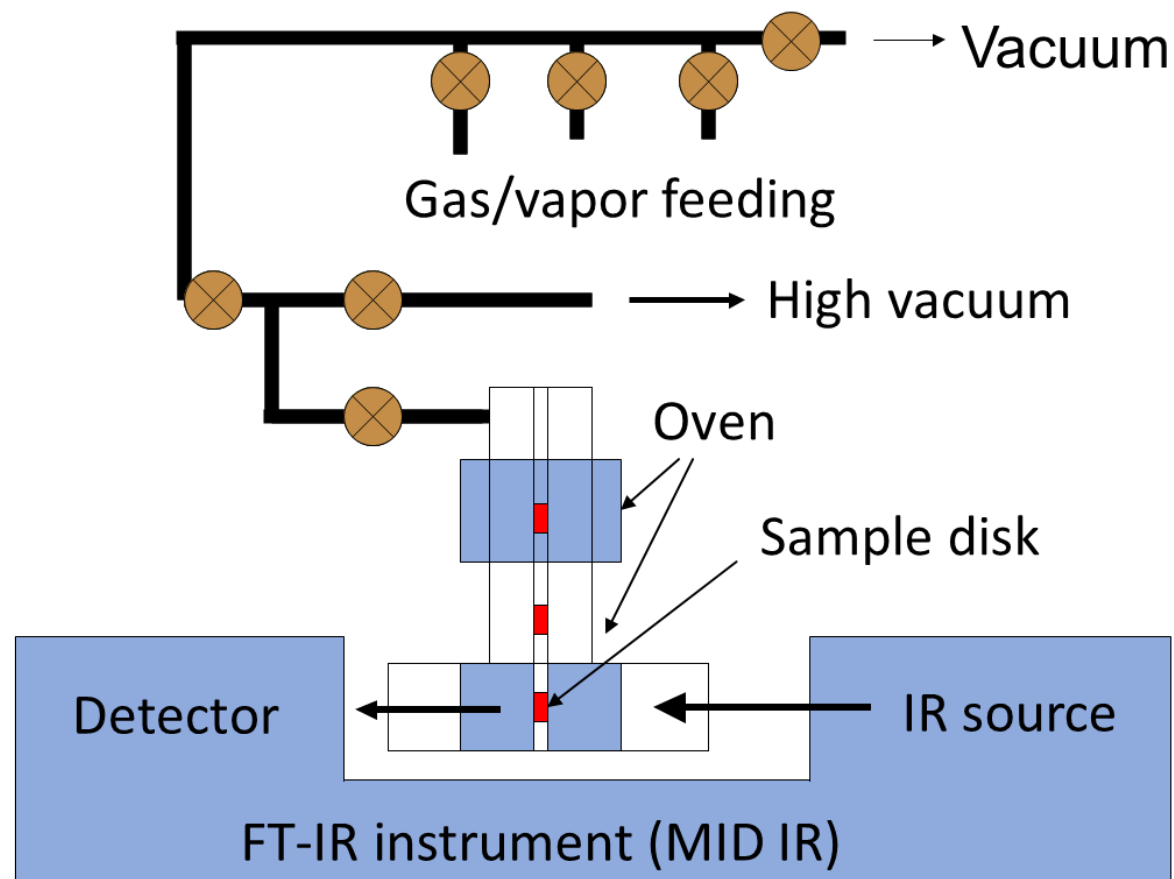
Dual Function Materials (DFMs)

Mechanistic scheme



Surface characterization by *in situ* FT-IR spectroscopy

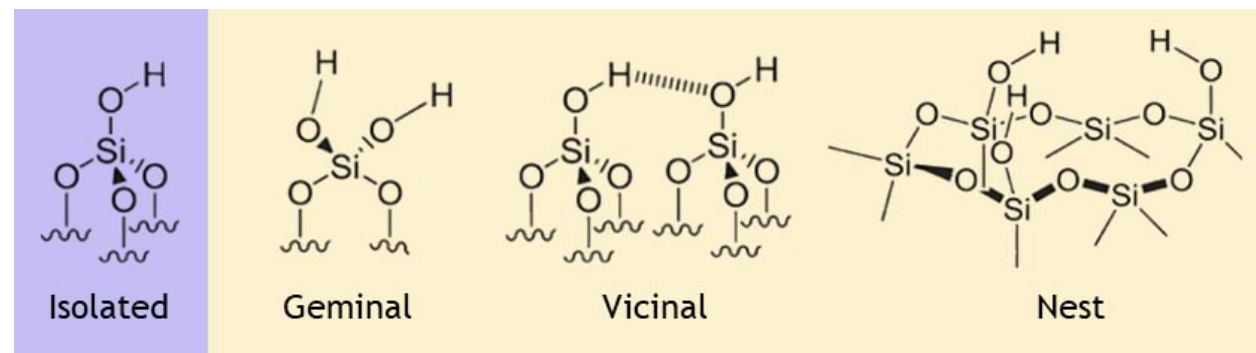
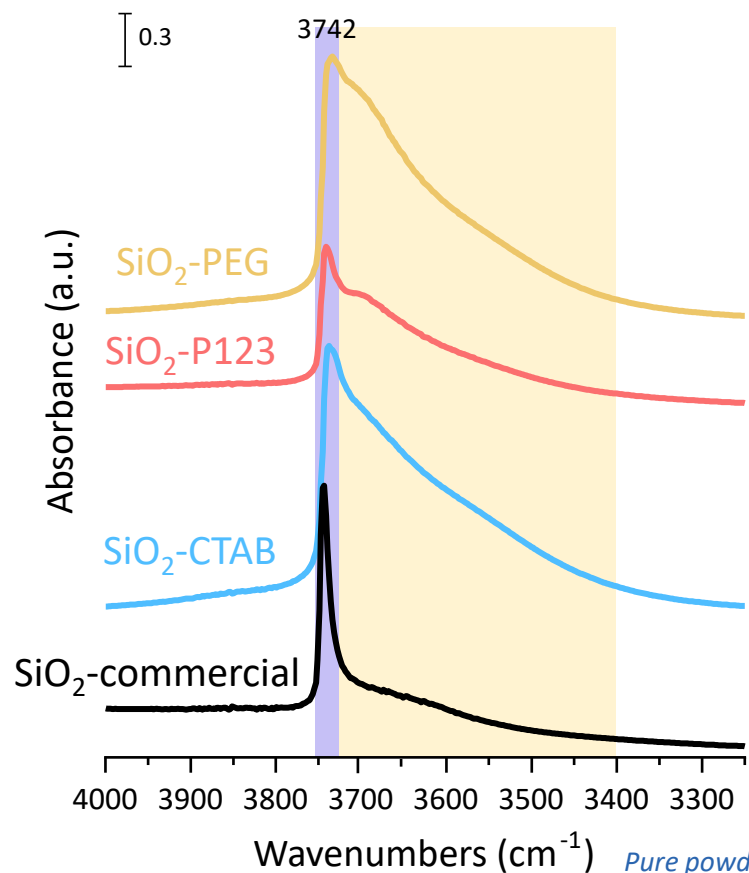
- Activation in vacuum in T
- Activation in H₂ in T
- PY and PN adsorption
- CO adsorption low-T and R.T.
- CO₂-TPD (O₂, wet conditions)
- H₂-TPSR
- Co-feeding
- Cycling conditions CO₂-H₂





Waste-Derived Silica Supports

OHs stretching region



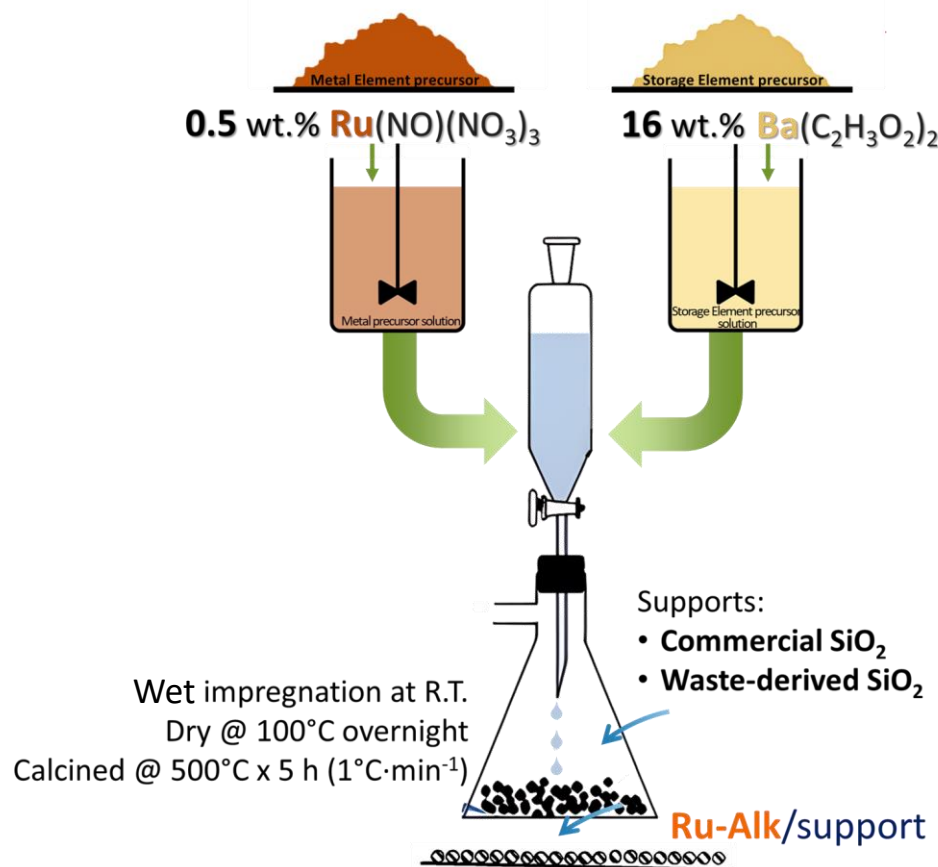
3742 cm^{-1} : isolated silanols.

< 3742 cm^{-1} : heterogeneous population of OH groups.

Presence of Weak Brønsted Acidic sites was observed through PY adsorption tests



Synthesis of DFMs supported on waste-derived Silica



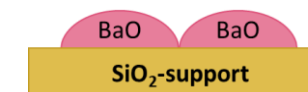
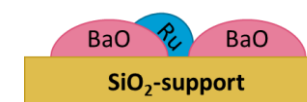
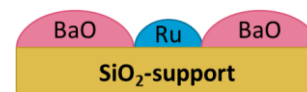
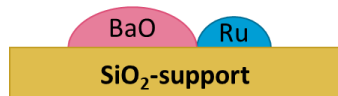
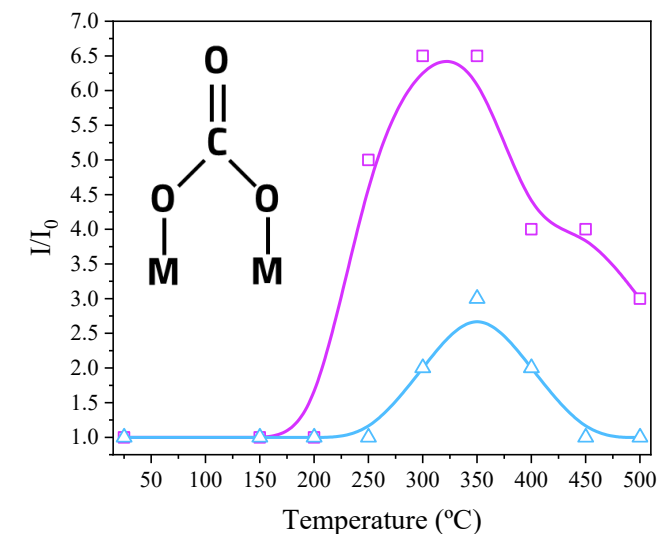
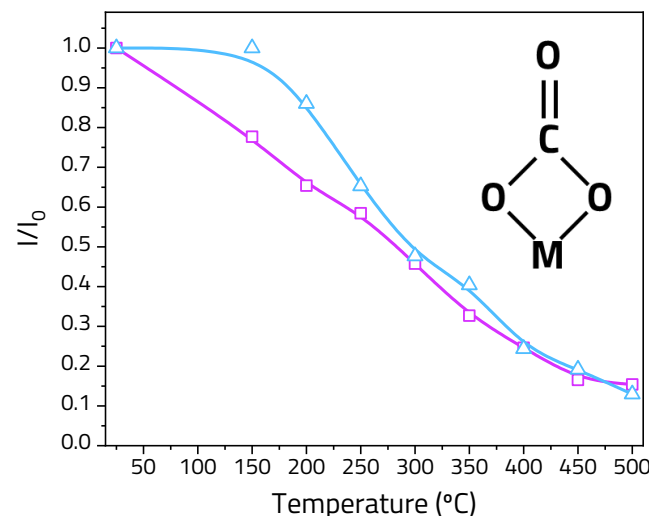
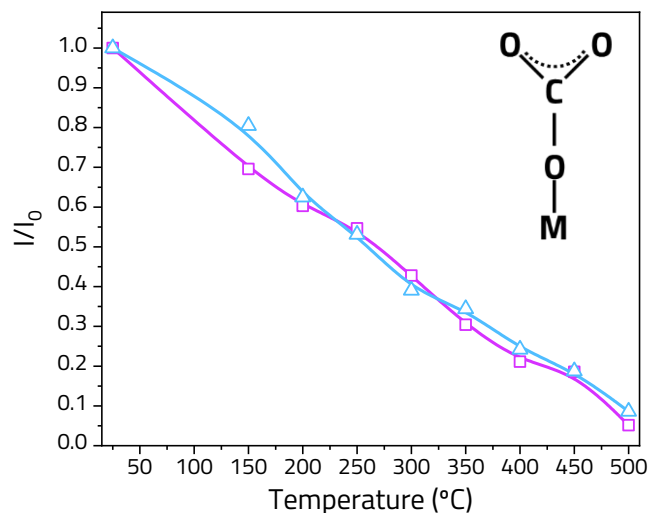
Catalyst	Ru %wt.	Alk %wt.
SiO₂ from FSA		
Ru-Ba/SiO ₂ -PEG	0.5	16
Ru-Ba/SiO ₂ -CTAB	0.5	16
Ru-Ba/SiO ₂ -P123	0.5	16
Commercial SiO₂		
16Ba-Ru/SO ₂	0.5	16
Ru-16Ba/SiO ₂	0.5	16
Ru-32Ba/SiO ₂	0.5	32
Ru-4K/SiO ₂	0.5	4
Ru- X Na ₂ CO ₃ /SiO ₂	0.5	[2.5-20]
ref Ru-Ba/Al ₂ O ₃	0.5	16

S_{BET}, V_p and d_p decrease with Alkali incorporation

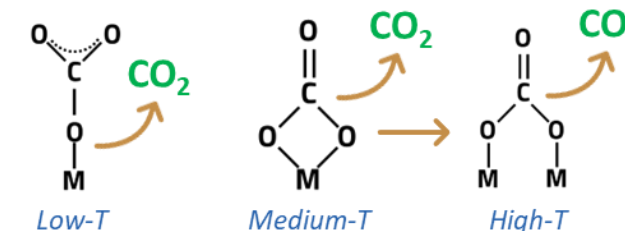
CO₂ Capture of DFMs supported on FSA-derived SiO₂

Thermal evolution of carbonate species by the analysis of CO₂-TPD-FTIR tests

—□— Ru-Ba/SiO₂-PEG
—△— Ru-Ba/SiO₂-CTAB



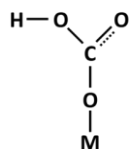
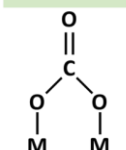
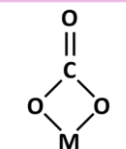
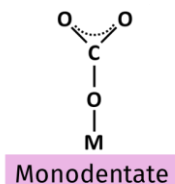
Nature of carbonate species is dependant of support surface area and alkali-promoter distribution and reciprocal proximity



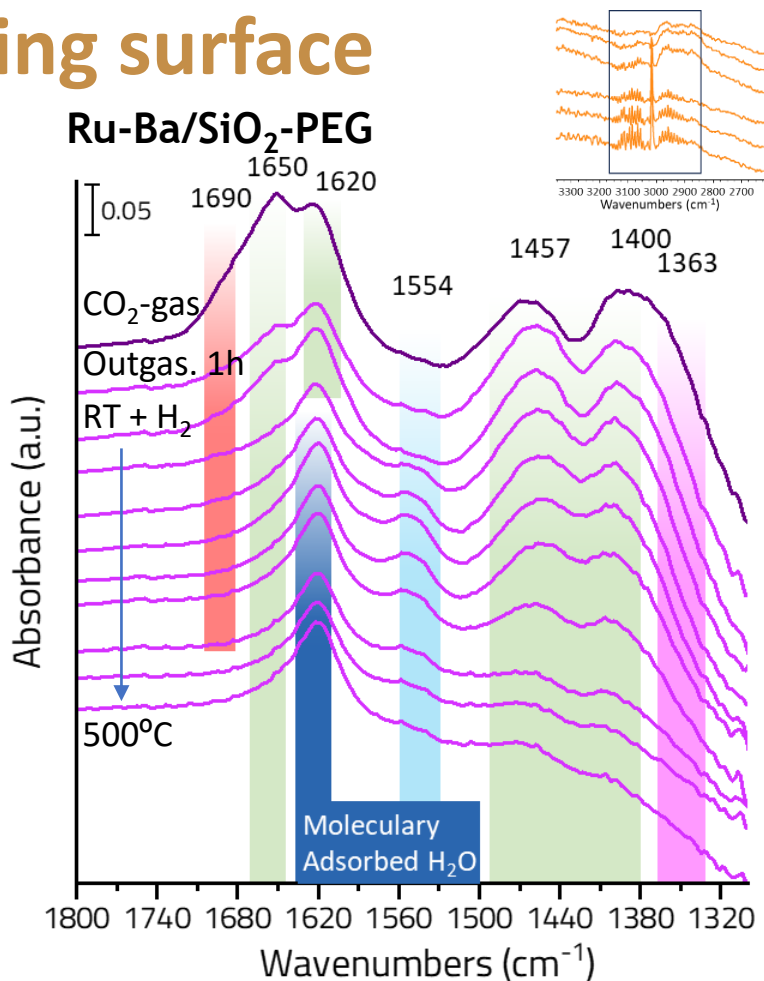


A working surface

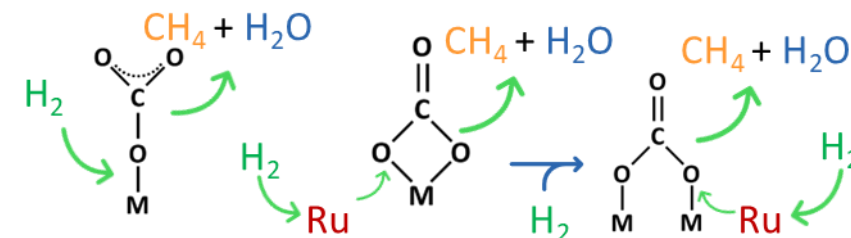
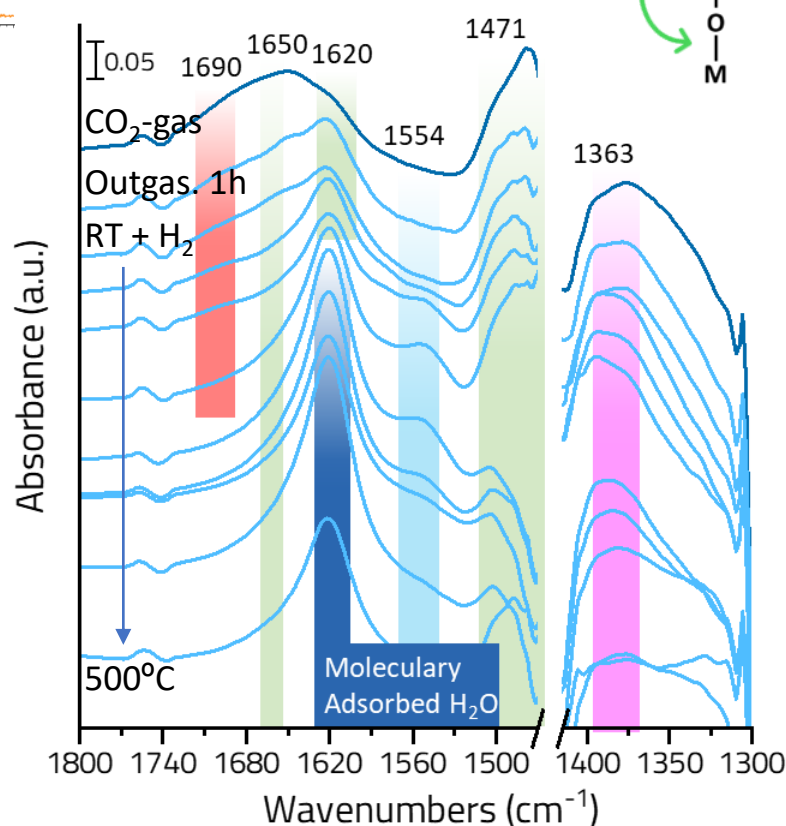
H_2 -TPSR-FTIR



M = metal



Ru-Ba/SiO₂-CTAB



Bidentate carbonate species were consumed by increasing the temperature.

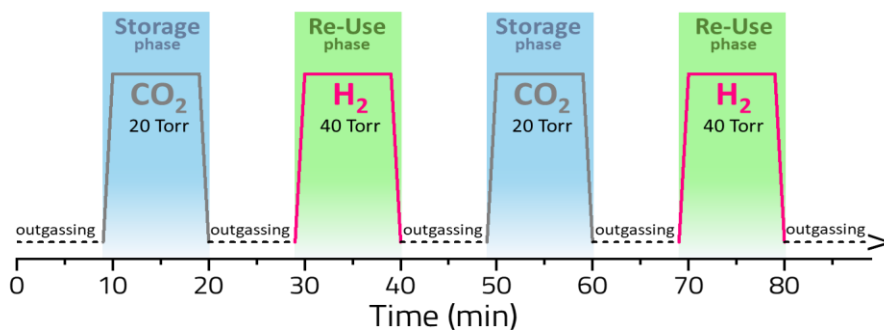
CH₄ is generated from 250 °C

Bridging species at higher temperature ⇒ CH₄

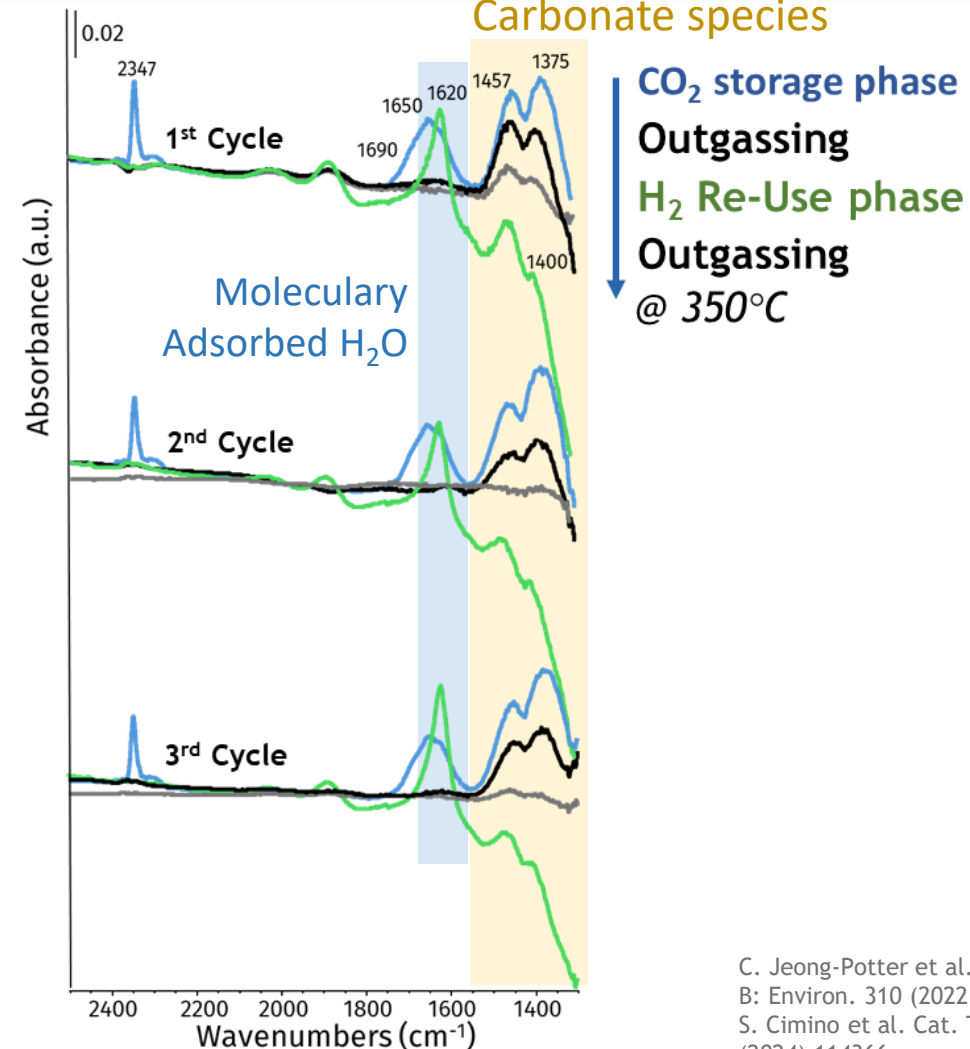
Subtraction spectra of surface species arising from CO₂ adsorption @ R.T and outgassing @ increasing temp in H₂. Pretreatment in H₂/vacuum at 500 °C



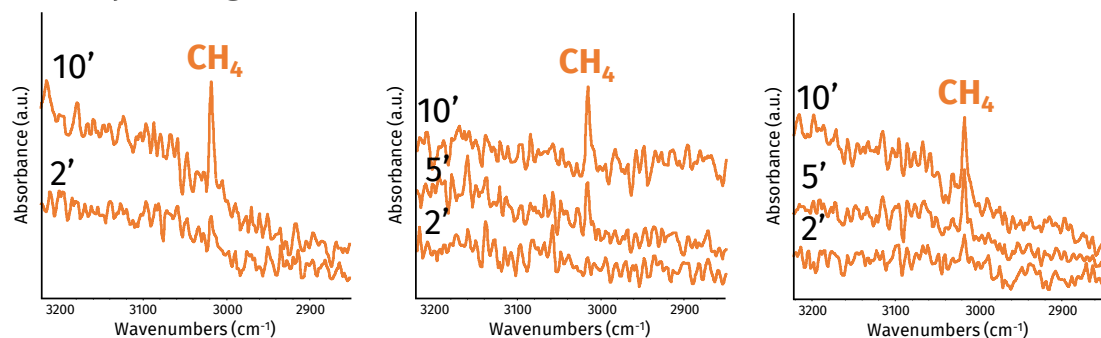
CO₂ Capture & Conversion cycles



Carbonate species



Gas phase @ 350°C



Methane formation in time

Spectroscopic evidence of methanation in repeated cycles

C. Jeong-Potter et al. Applied Cat. B: Environ. 310 (2022) 121294, S. Cimino et al. Cat. Today 424 (2024) 114366



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4. Performance Evaluation of Silica-based DFMs



Giuseppe Nava



GREEN FUEL

CATALYTIC ROUTE

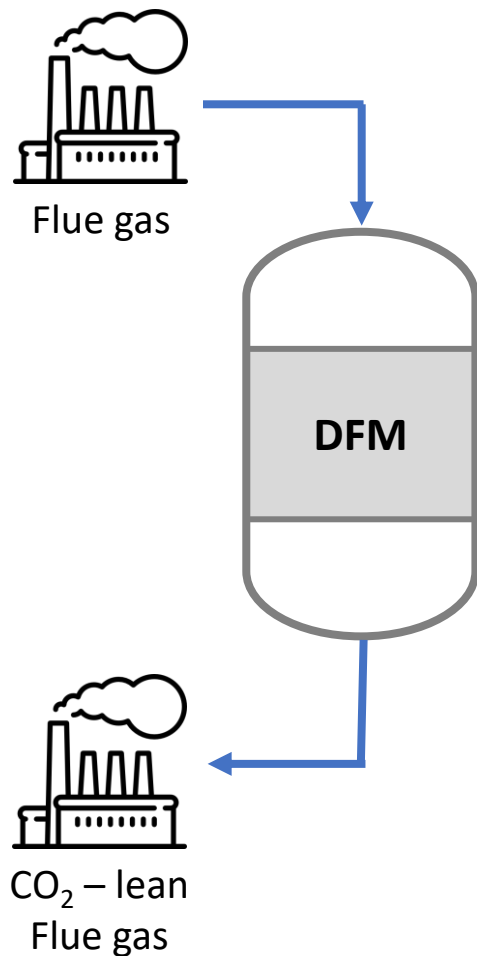
CO₂ Capture and Utilization
by Dual Function Materials



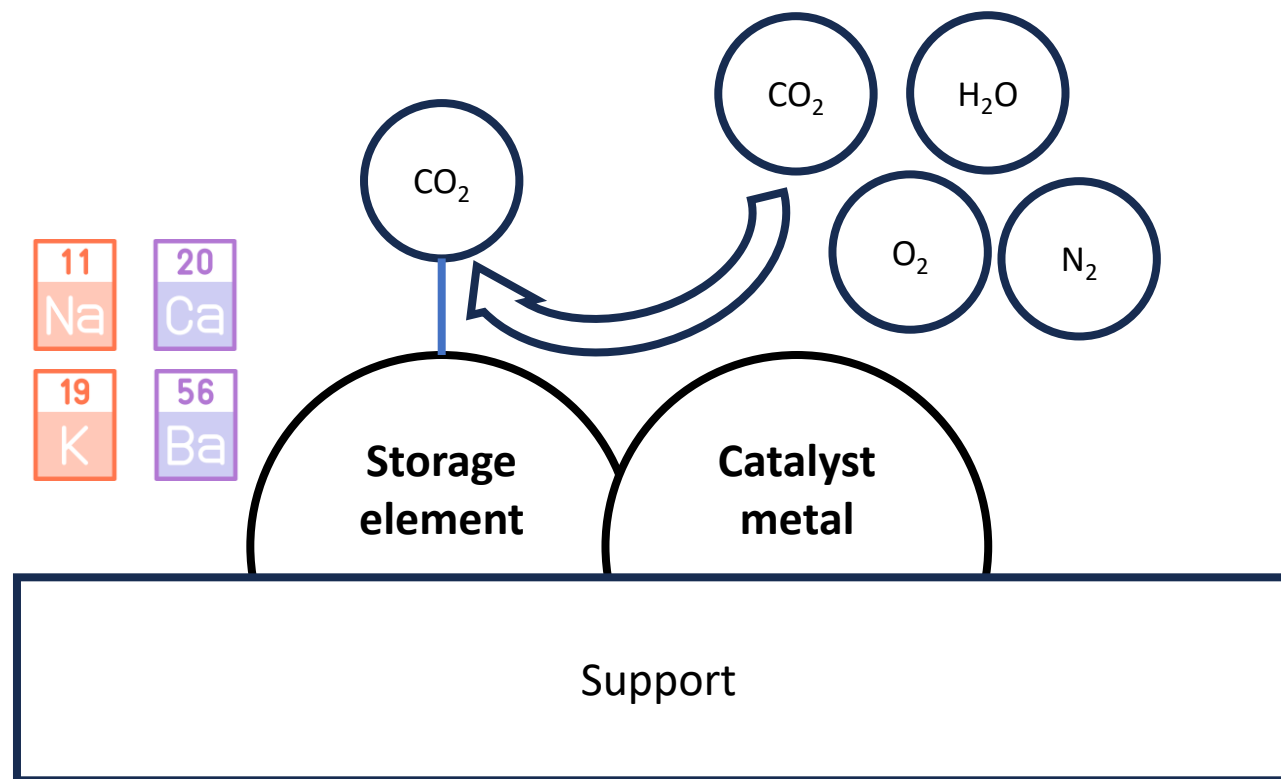
POLITECNICO MILANO 1863
DIPARTIMENTO DI ENERGIA

Laboratory of Catalysis and Catalytic Processes
LCCP

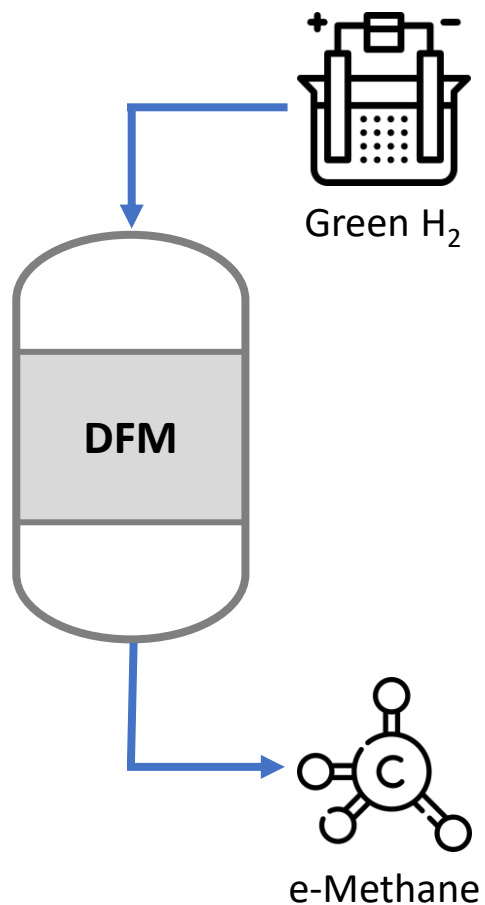
Dual Function Materials (DFMs)



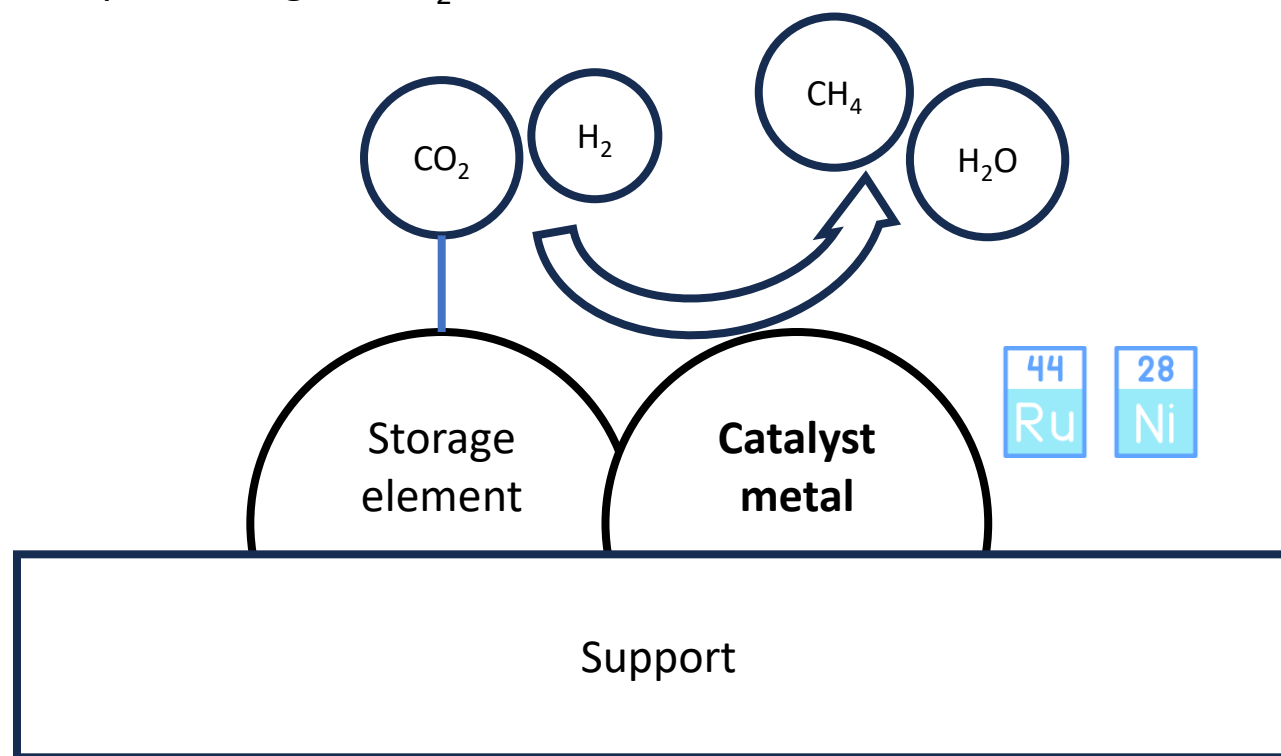
Materials containing an adsorbent (Ba, Ca, Na, K, ...) capable of capturing CO₂ (e.g. from combustion flue gases)



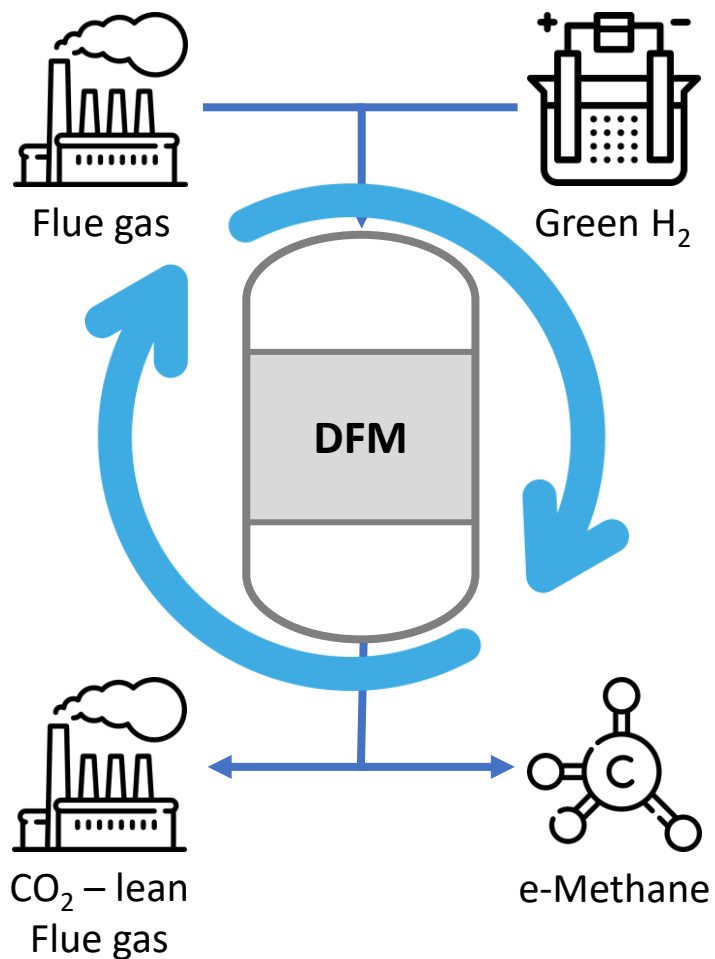
Dual Function Materials (DFMs)



Materials containing an adsorbent (Ba, Ca, Na, K, ...) capable of capturing CO₂ (e.g. from combustion flue gases) **and hydrogenating it** when exposed to green H₂.

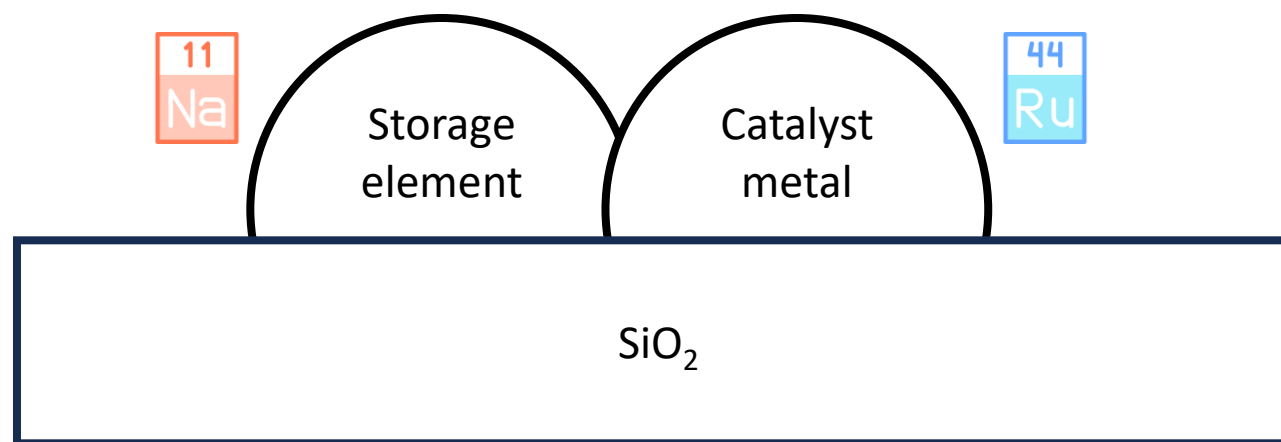


Dual Function Materials (DFMs)

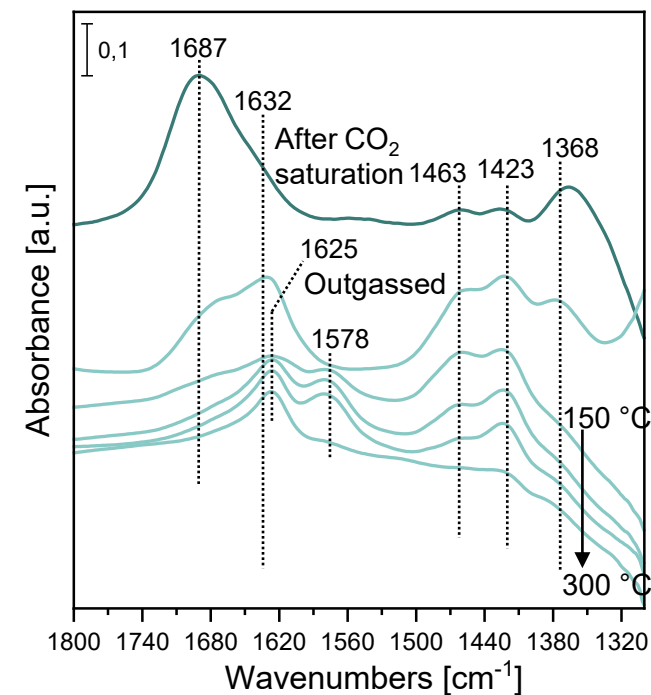
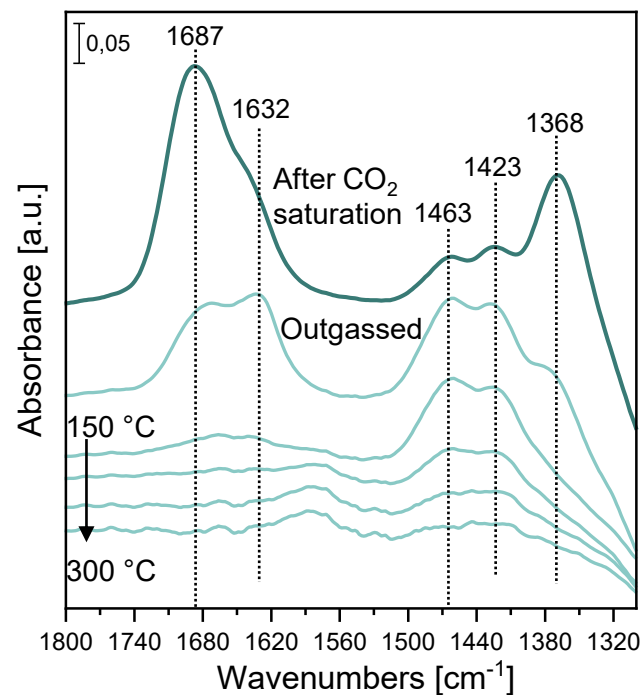
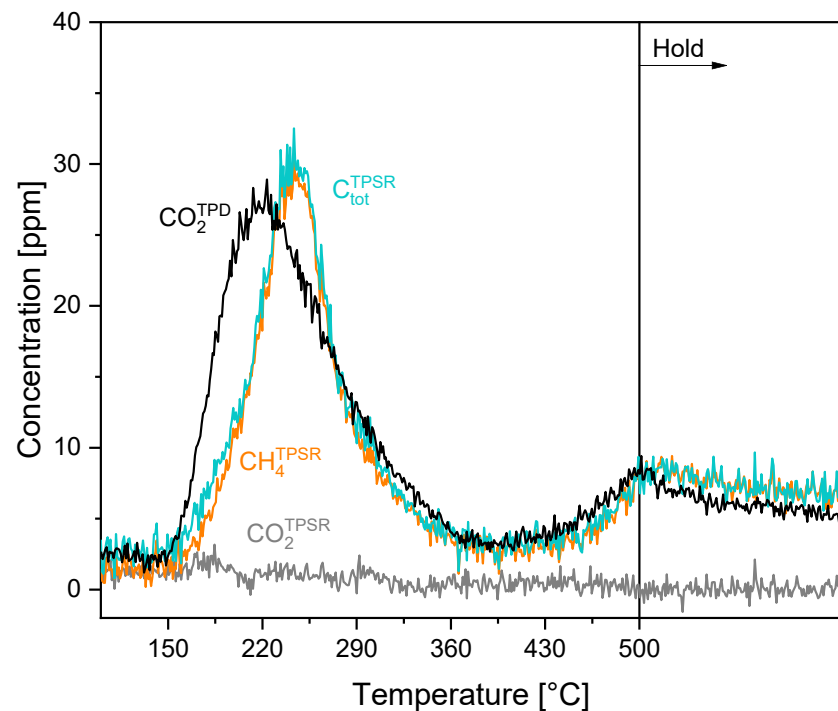


Goals of this study:

- Performance of DFMs with a different support (SiO₂);
- Loading of the storage element (Na₂CO₃);
- Effectiveness of segregated configurations (i.e., physical mixtures)



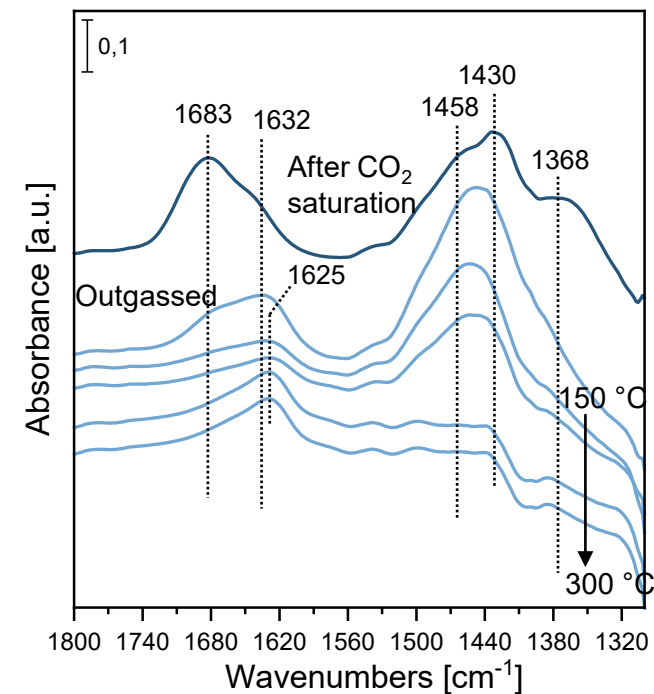
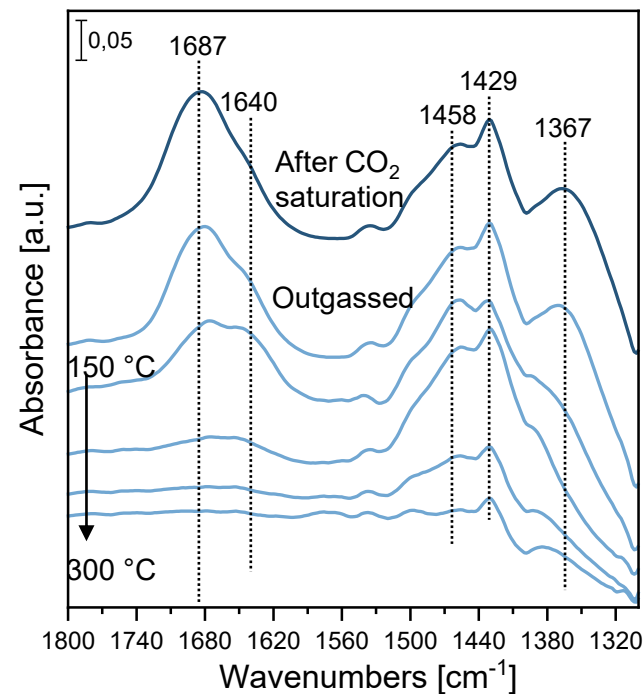
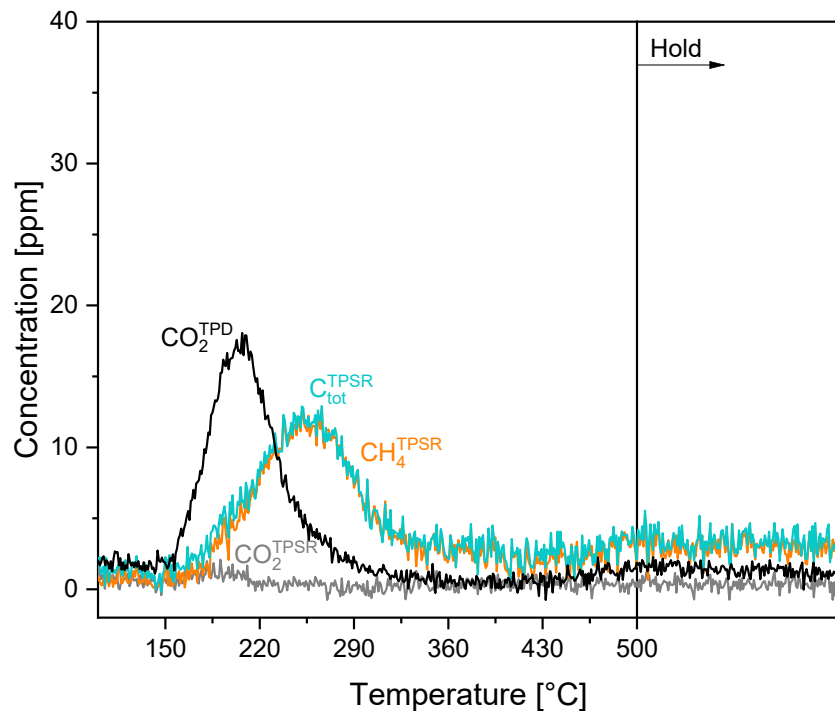
Temperature Programmed experiments: low Na loading (TPSR)



No difference in the stability of carbonates when heating in H_2

DFM: 0.5% Ru/5% $\text{Na}_2\text{CO}_3/\text{SiO}_2$
Process conditions: adsorption 0.5% CO_2/He ; reduction 4% H_2/He
 $T_{\text{ads}} = 150^\circ\text{C}$, GHSV = 100 L(STP)/h/g_{cat}

Temperature Programmed experiments: high Na loading

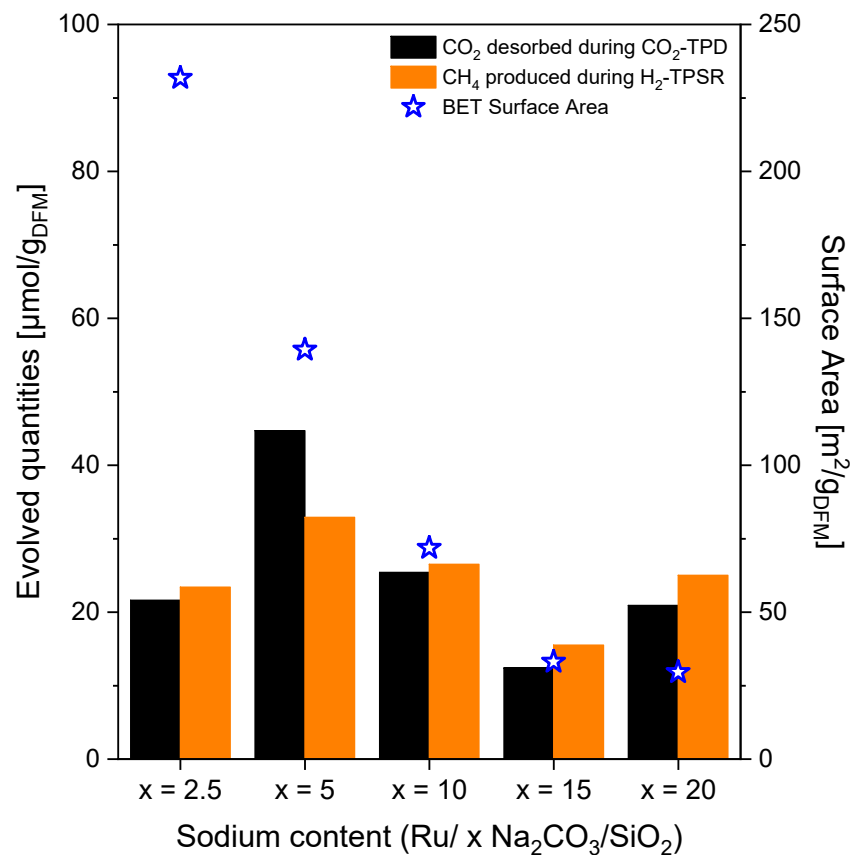


Increasing the Na₂CO₃ loading did not result in enhanced CO₂ capture/desorption properties

DFM: 0.5% Ru/15% Na₂CO₃/SiO₂
Process conditions: adsorption 0.5% CO₂/He; reduction 4% H₂/He
T_{ads} = 150 °C, GHSV = 100 L(STP)/h/g_{cat}



Temperature Programmed experiments: effect of the Na loading



Increasing the Na₂CO₃ loading did not result in enhanced CO₂ capture/desorption properties.

At higher Na₂CO₃ loadings:

- Pore blocking and lower surface area;
- Formation of bulk carbonate species;
- Inhibition of CO₂ methanation activity.

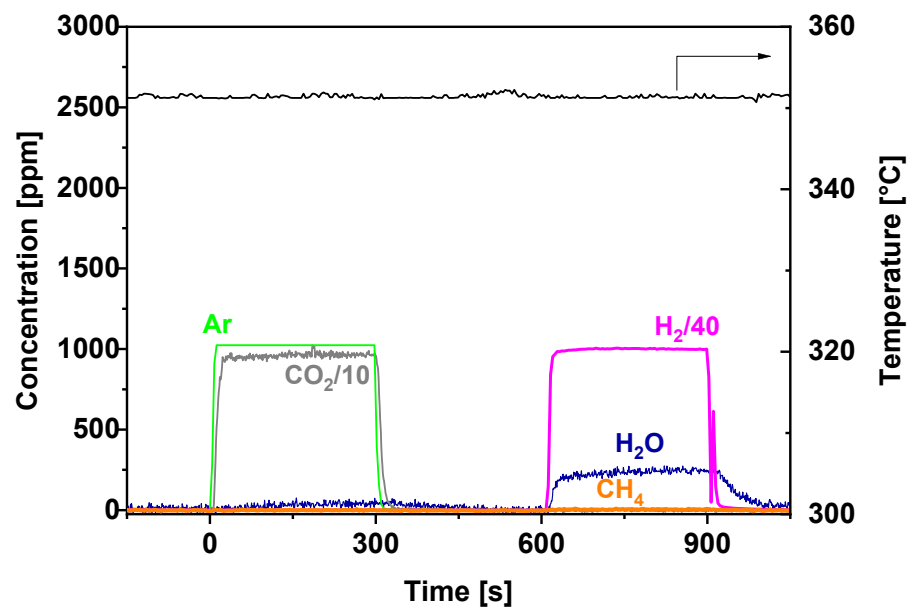
DFMs: 0.5% Ru/x% Na₂CO₃/SiO₂

Process conditions: adsorption 0.5% CO₂/He; reduction 4% H₂/He

T_{ads} = 150 °C, GHSV = 100 L(STP)/h/g_{cat}



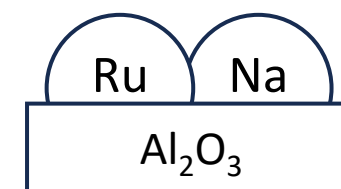
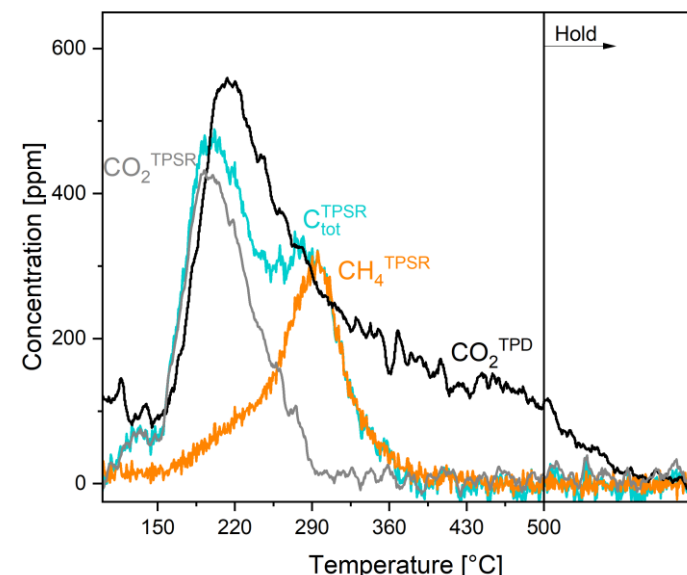
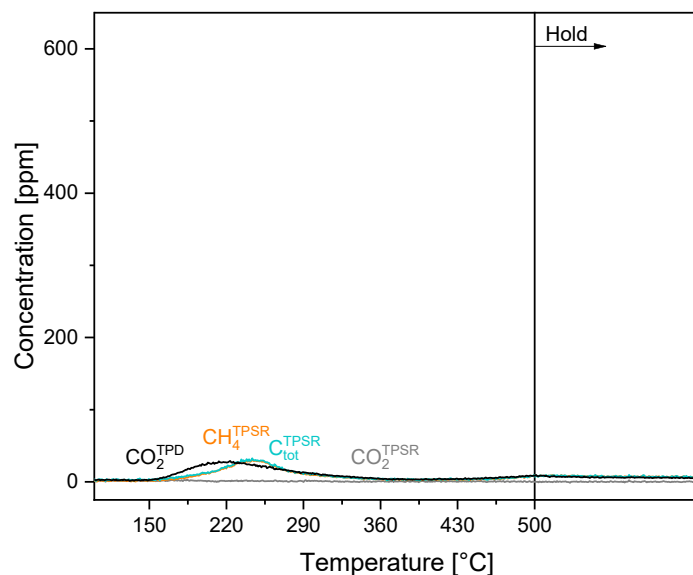
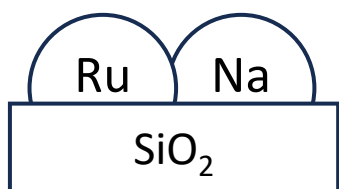
Isothermal cycles



Cycles of CO₂ capture and methanation at 350 °C are limited by the poor CO₂ capture capacity of the materials

DFM: 0.5% Ru/10% Na₂CO₃/SiO₂
Process conditions: capture 1% CO₂/3% O₂/2% H₂O/ He, reduction 4% H₂/He
T = 350 °C, GHSV = 100 L(STP)/h/gcat.

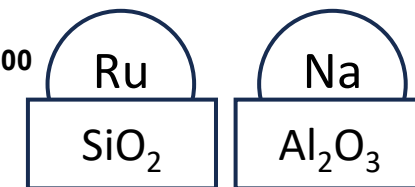
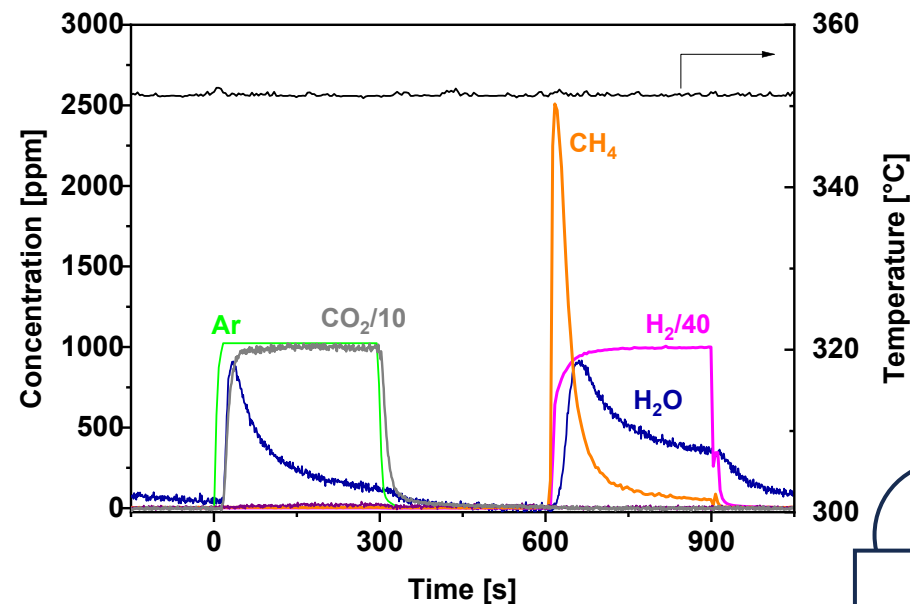
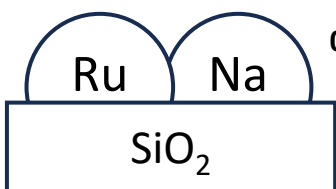
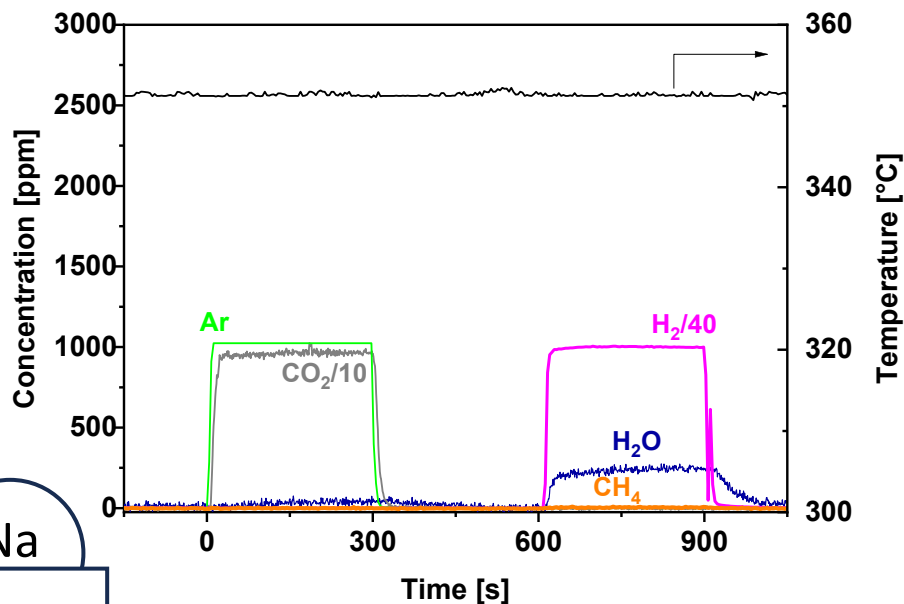
Temperature Programmed experiments: Al₂O₃ comparison



CO₂ uptake with respect to Al₂O₃-supported DFMs is significantly lower: impregnating an alkali metal over SiO₂ is not convenient

DFMs: 0.5% Ru/10% Na₂CO₃/SiO₂ (left), 0.5% Ru/10% Na₂CO₃/Al₂O₃ (right)
Process conditions: capture 0.5% CO₂/He, reduction 4% H₂/He
T_{ads} = 150 °C, GHSV = 100 L(STP)/h/gcat.

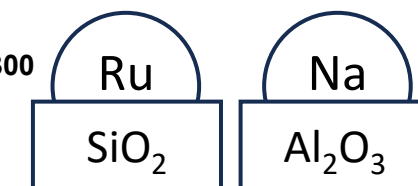
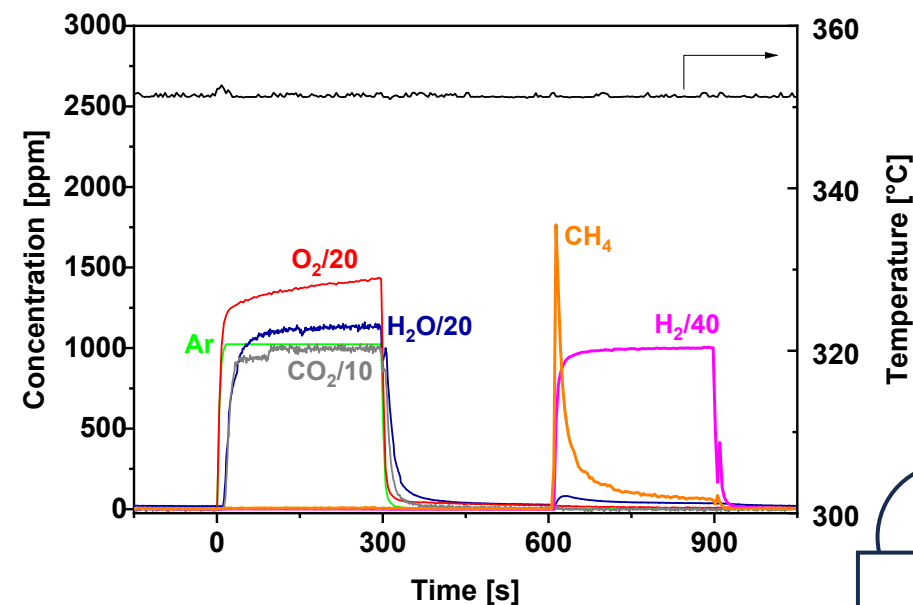
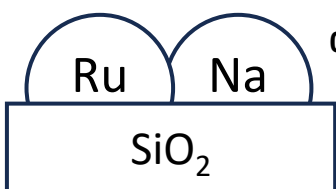
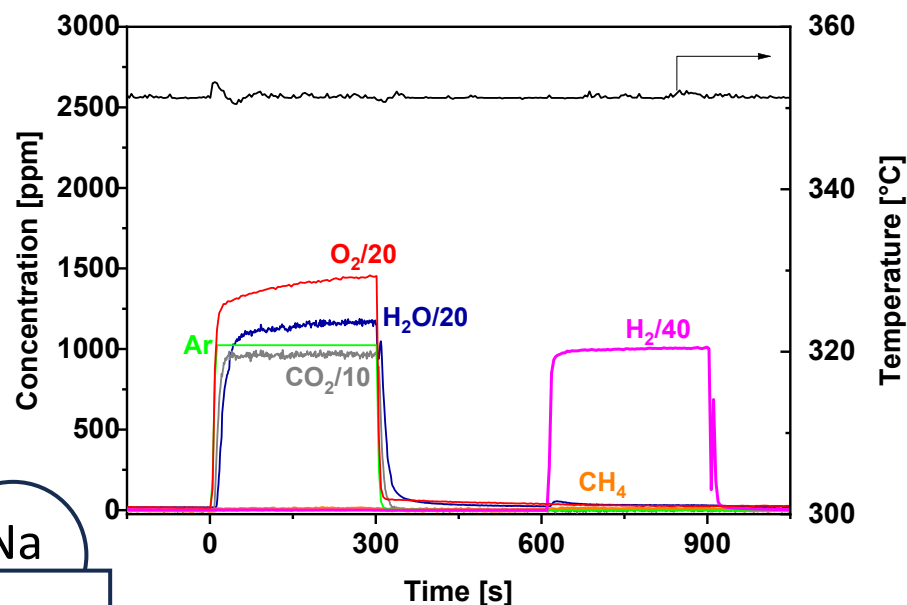
Isothermal cycles



Through the utilization of physical mixtures, coupling Ru/SiO₂ with a CO₂ sorbent (i.e., Na₂CO₃/Al₂O₃) resulted in effective CO₂ capture and methanation

DFM: 0.5% Ru/10% Na₂CO₃/SiO₂ (left);
PM: 0.5% Ru/SiO₂ + 10% Na₂CO₃/Al₂O₃ (right)
Process conditions: capture 1% CO₂/He, reduction 4% H₂/He
T = 350°C, GHSV = 100 L(STP)/h/gcat.

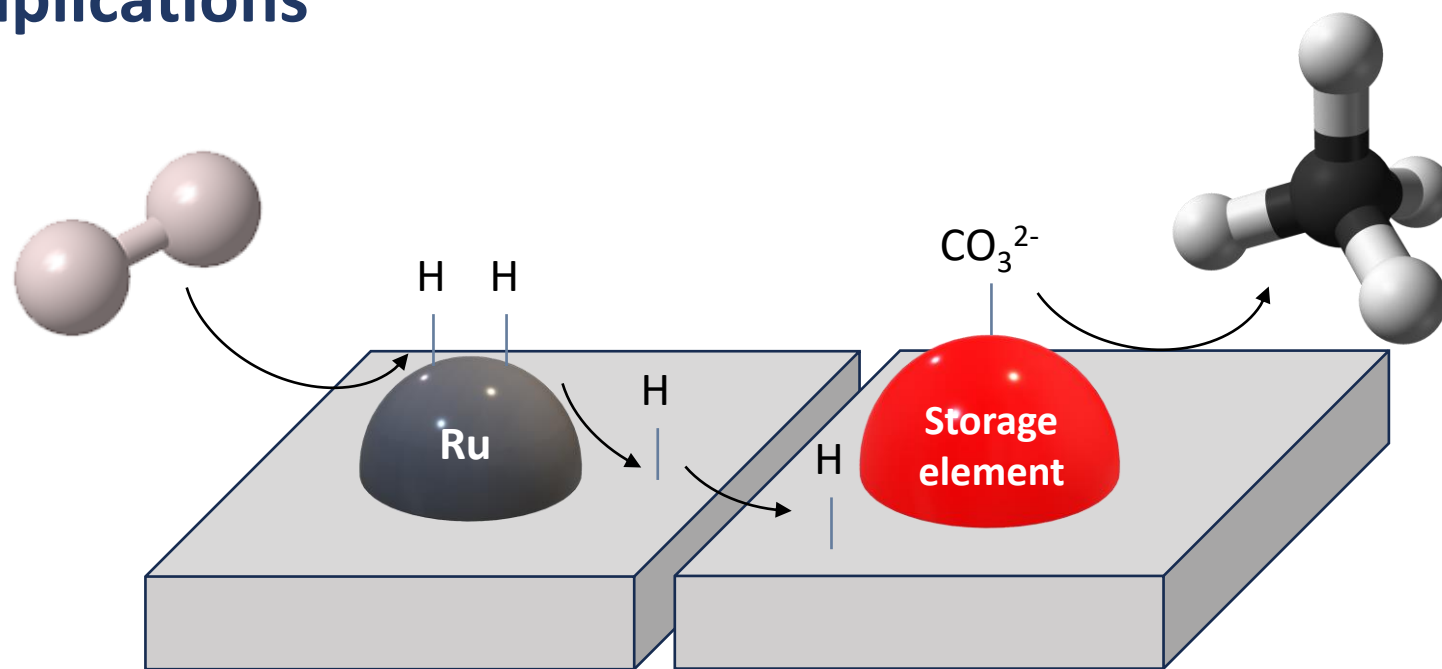
Isothermal cycles



Through the utilization of physical mixtures, coupling Ru/SiO₂ with a CO₂ sorbent (i.e., Na₂CO₃/Al₂O₃) resulted in effective CO₂ capture and methanation even under simulated flue gas conditions

DFM: 0.5% Ru/10% Na₂CO₃/SiO₂ (left);
PM: 0.5% Ru/SiO₂ + 10% Na₂CO₃/Al₂O₃ (right)
Process conditions: capture 1% CO₂/3% O₂/2% H₂O/ He, reduction 4% H₂/He
T = 350°C, GHSV = 100 L(STP)/h/gcat.

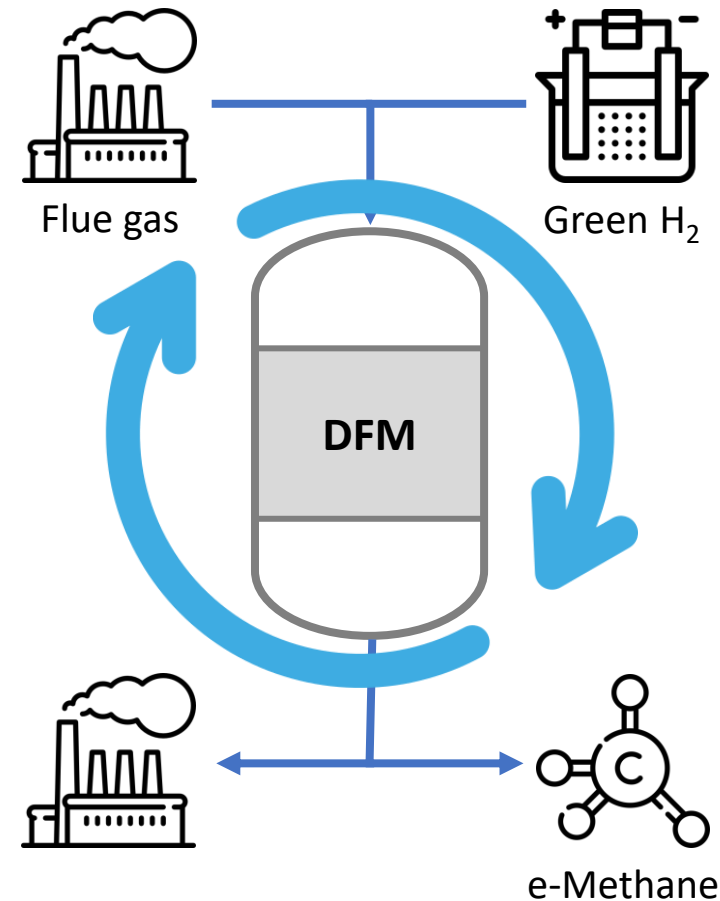
Mechanistic implications



When the storage element (i.e. alkali) is inhibited by the support, an efficient methanation can be performed using physical mixtures thanks to the presence of an **inter-particle H spillover**¹.

Sum up

- SiO_2 -supported DFMs present lower CO_2 capture activity but are active towards CO_2 methanation;
- Increasing the loading of Na does not increase the CO_2 uptake; morphological properties (i.e. surface area, porosity) are modified due to the inertness of SiO_2 ;
- Decoupling of the CO_2 storage and methanation functions using physical mixture allows the optimization of the individual storage and methanation reactivities, thanks to the presence of interparticle hydrogen spillover.





Significance

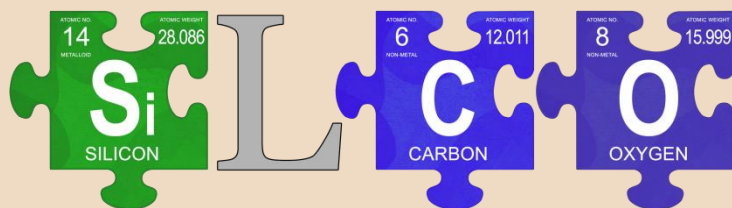
Si-based materials were developed using waste hexafluorosilicic acid and organic templates and functionalized to obtain sorbent materials and DFMs able to adsorb, and convert CO₂

CO₂ capture capability depends on the nature and thermal resistance of the surface carbonate species, which play a key-role in the CO₂ catalytic conversion

Pore blockage at moderate-to-high alkali loadings, strongly bound carbonates formation, inhibition of Ru methanation activity in presence of alkali metals, and non-satisfactory cyclic capture-conversion performance are still open points

For further exploitation of SILCO project results, segregated mechanical mixtures can effectively overcome the above limitations

Missione 4 Istruzione e Ricerca



Turning Waste into Solutions: Silica-Based Sorbents for CO₂ Control

Thank you for your attention