CHANIA 2023

Study of ceria-composite materials for high-temperature CO_2 capture and their ruthenium functionalization for the application in methane production

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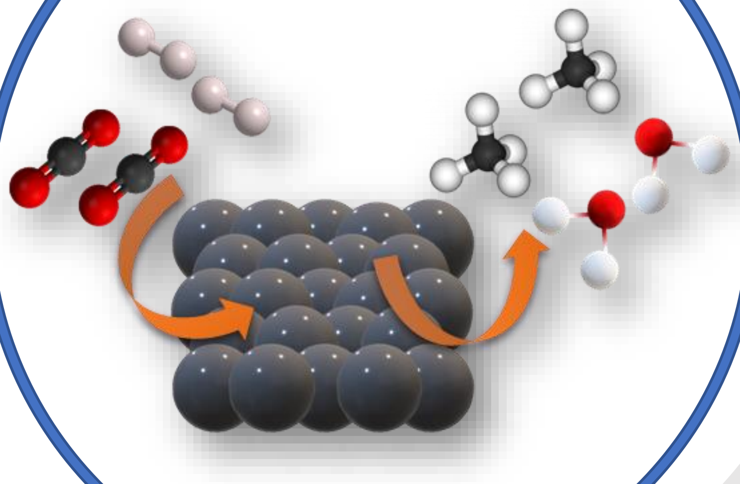
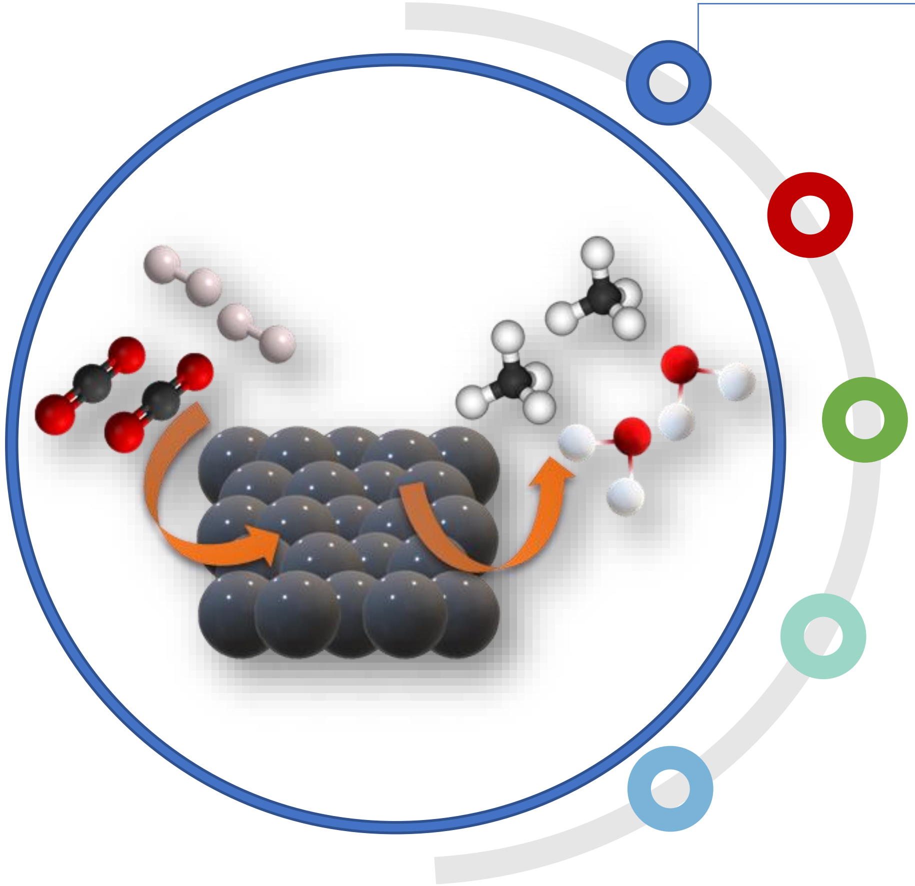
10th International Conference on Sustainable Solid Waste Management

Summary



1. INTRODUCTION
2. MATERIALS & METHODS
3. CHARACTERIZATIONS
4. ADSORPTION & CATALYTIC TESTS
5. CONCLUSIONS & FUTURE PERSPECTIVES

Summary



1 INTRODUCTION

The CO_2 “reduction” challenge

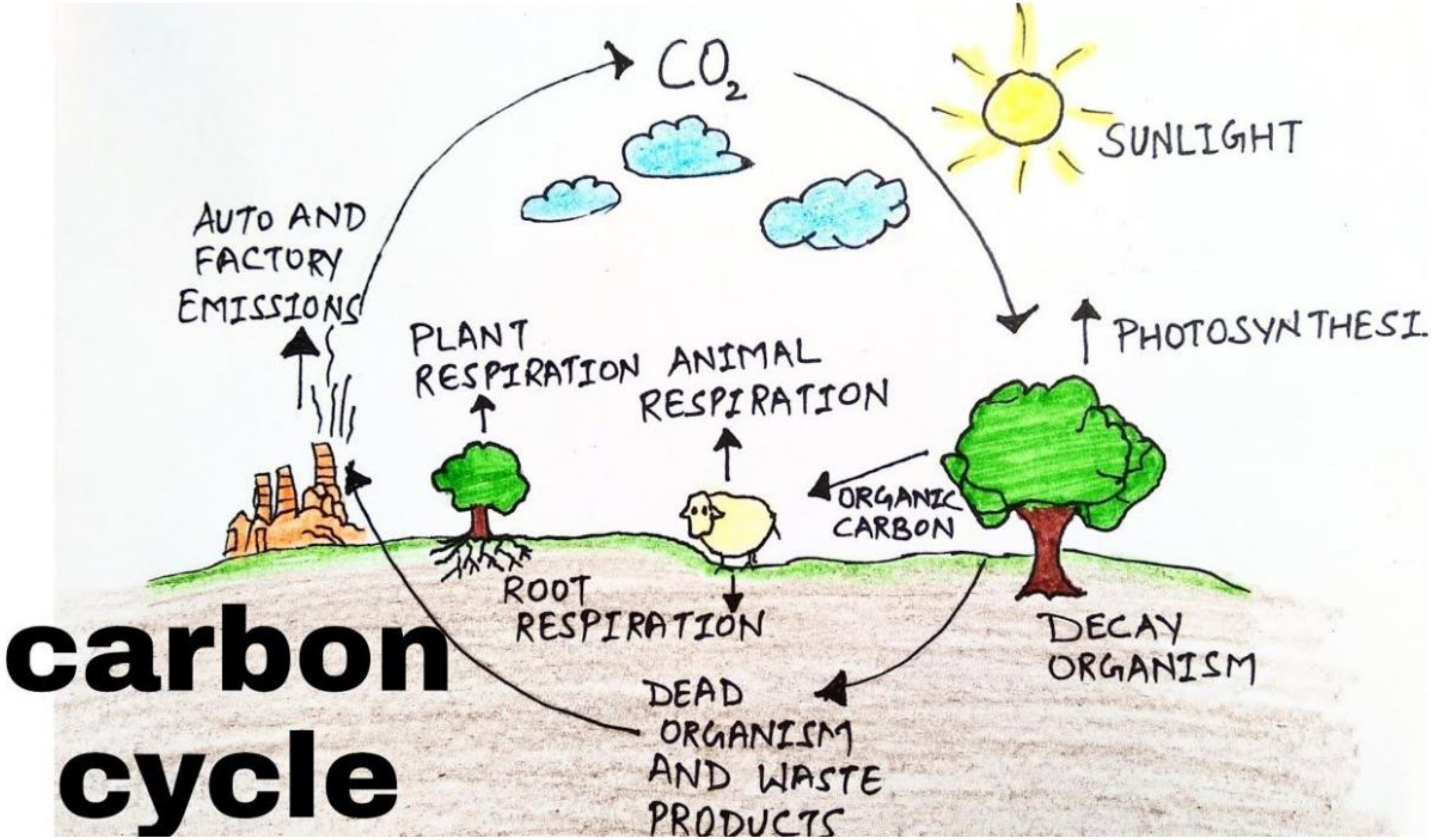
What can we do?!

Dual function materials (DFMs)

Cyclic methanation experiments

My phases

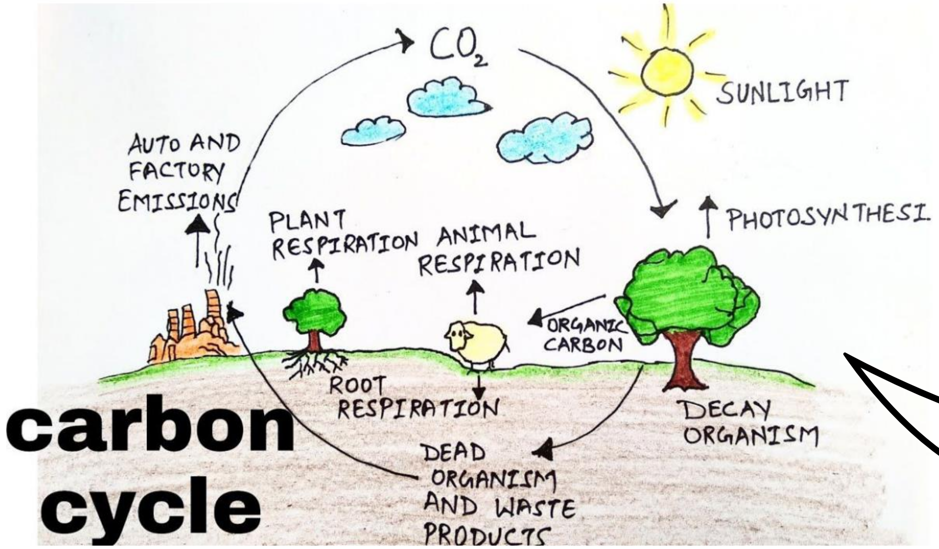
The CO_2 “reduction” challenge



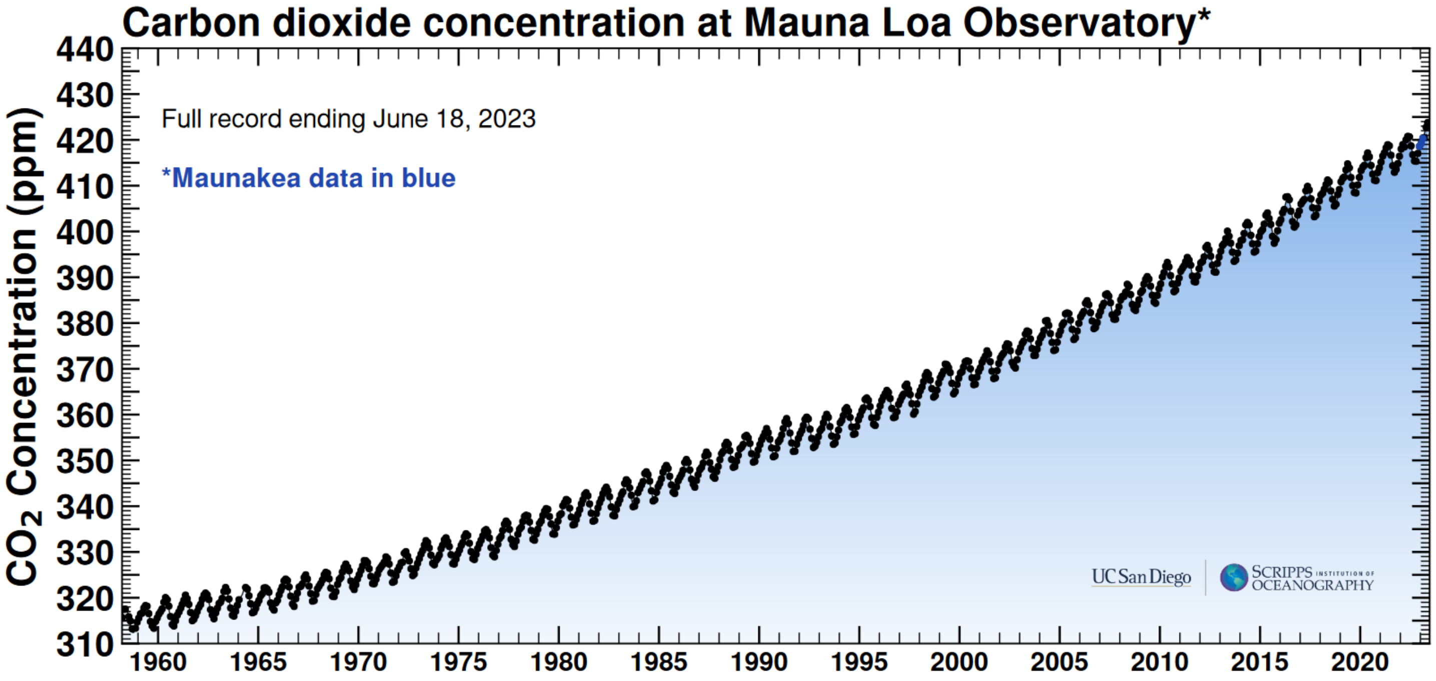
Carbon cycle strongly unbalanced by anthropogenic activity

Low efficiency of photosynthesis (0.5%) unable to fully compensate the emissions.

The CO_2 "reduction" challenge



Latest reading: 422.52 ppm

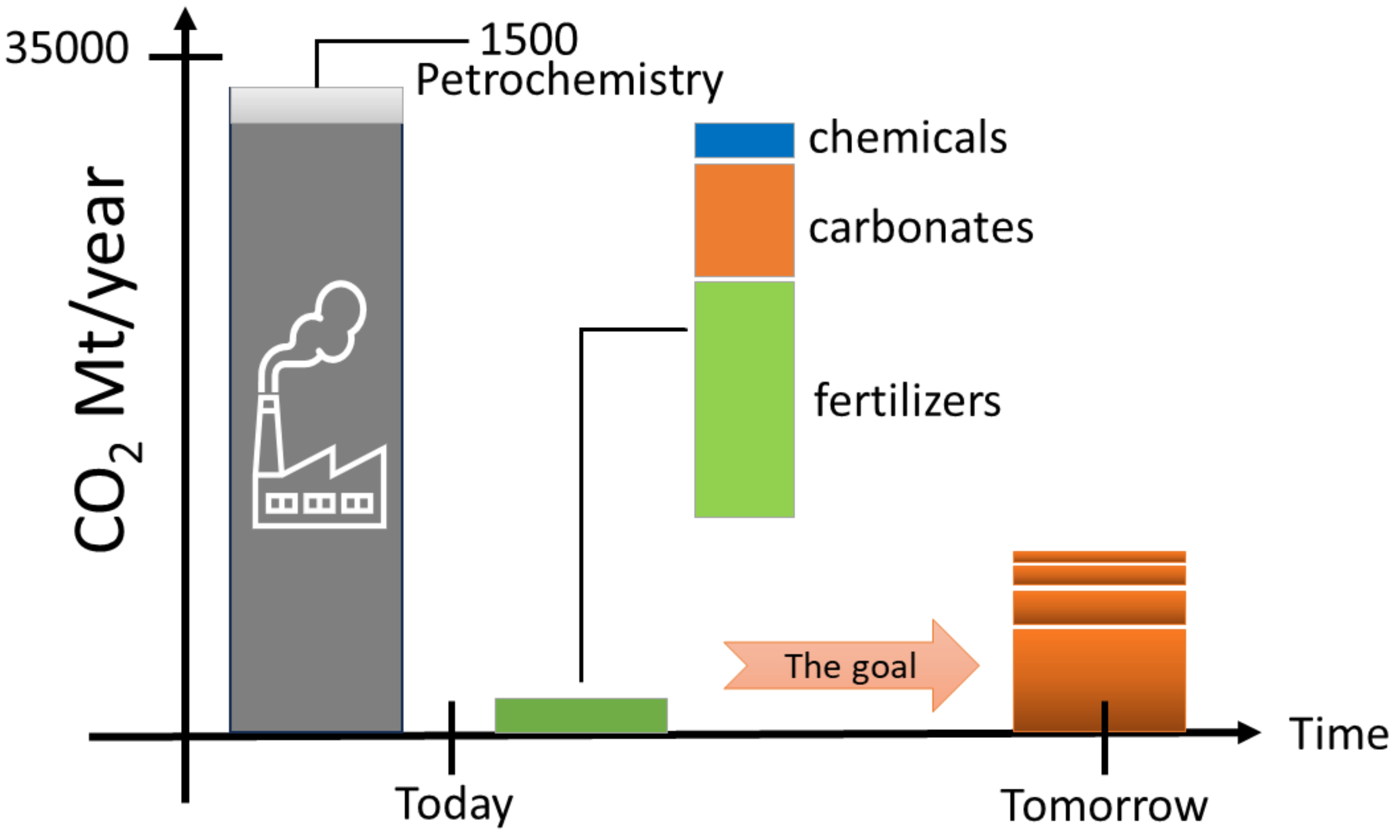


https://keelingcurve.ucsd.edu/

What can we do?!

What can we do?!

Carbon Dioxide (CO_2) as Chemical Feedstock



Aresta, M *et al.*, *Encycl. Inorg. Bioinorg. Chem*, **2014**, 1-18

Garcia-Garcia, G. *et al.*, *ChemSusChem*, **2021**, 14(4), 995-1015

Artz, J. *et al.*, *Chem.* Rev, **2018**, 118, 434–504

What can we do?!

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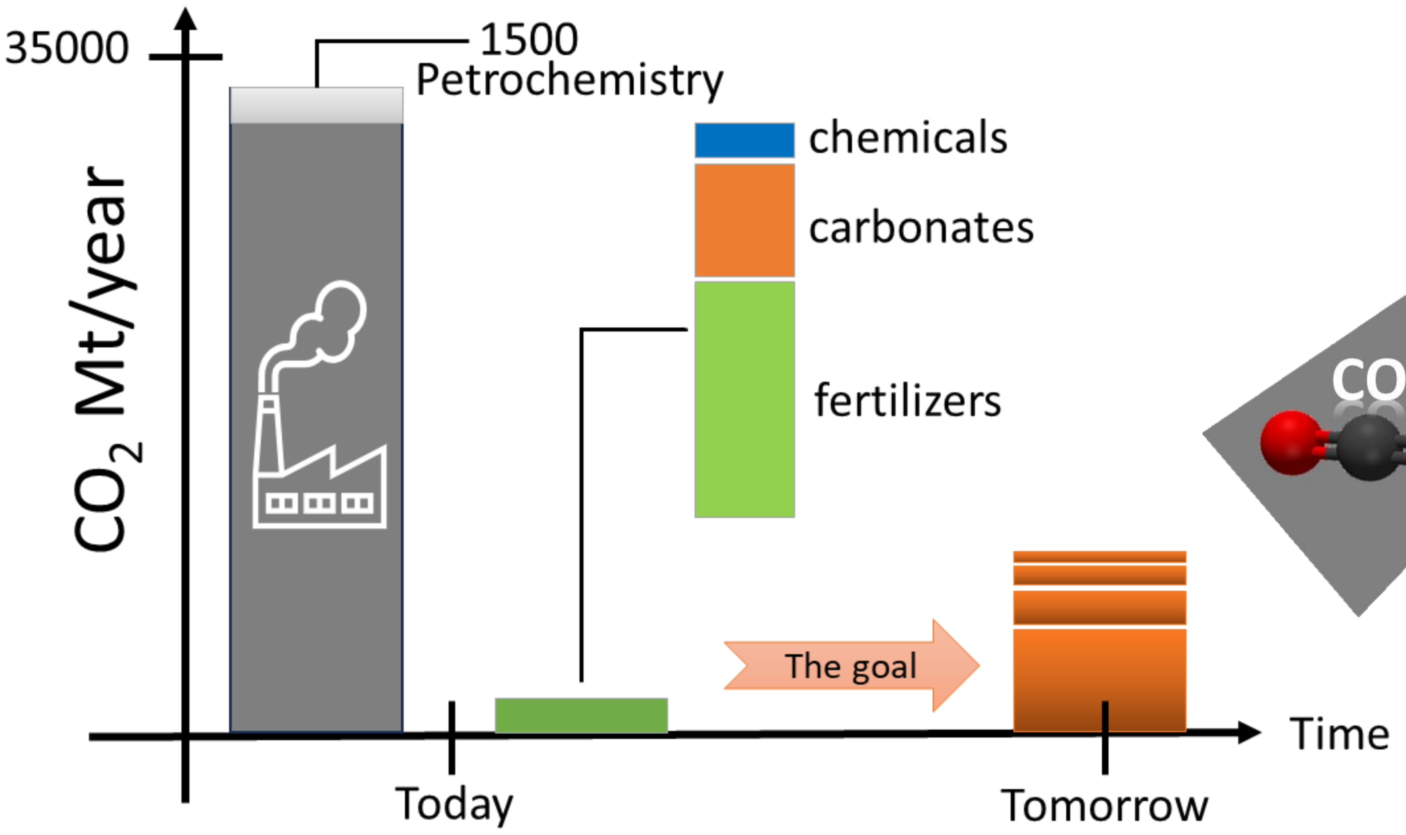

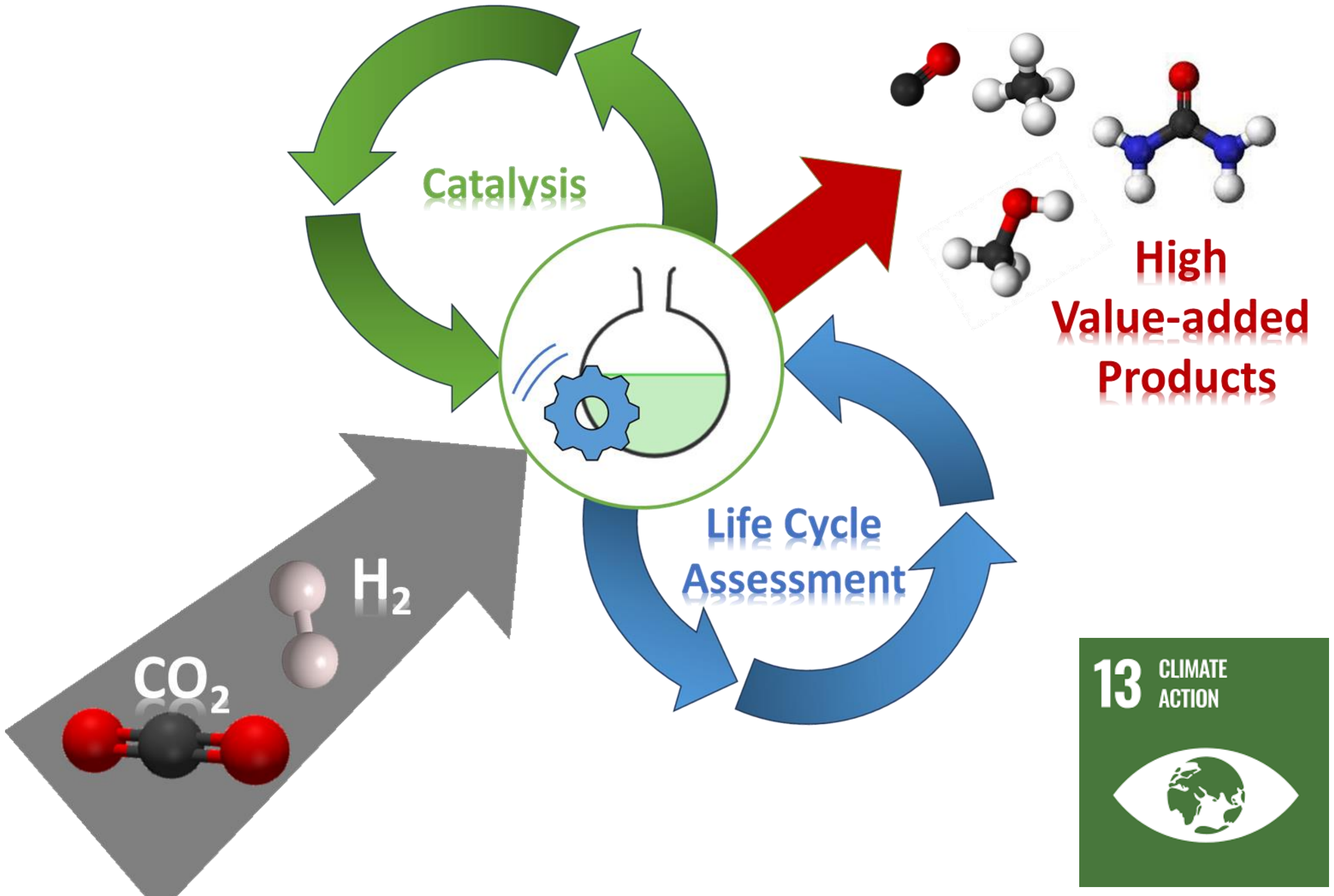

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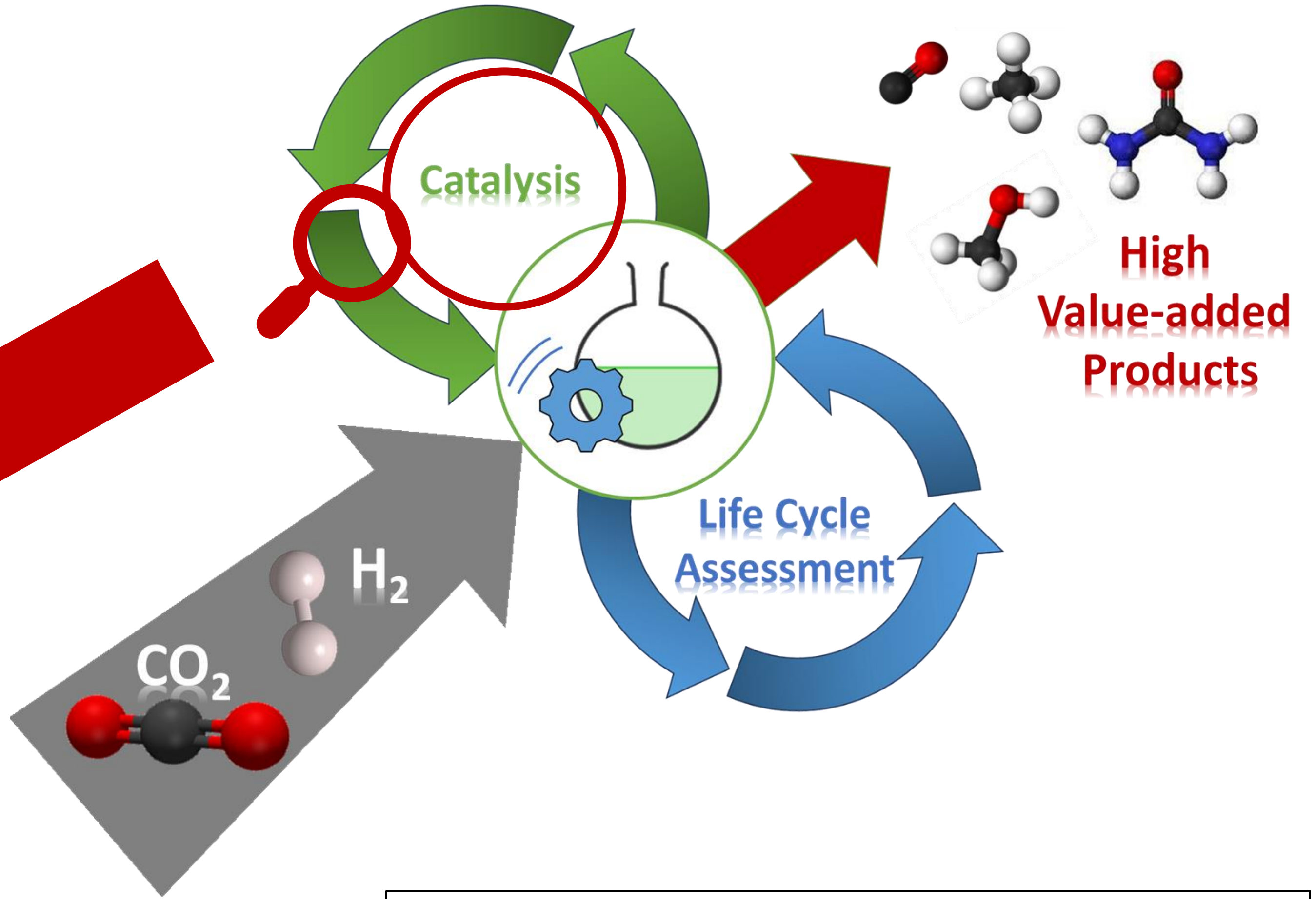
What can we do?!

CCUs
(CO_2 Capture and Utilization systems)



Aresta, M *et al.*, *Encycl. Inorg. Bioinorg. Chem*, **2014**, 1-18

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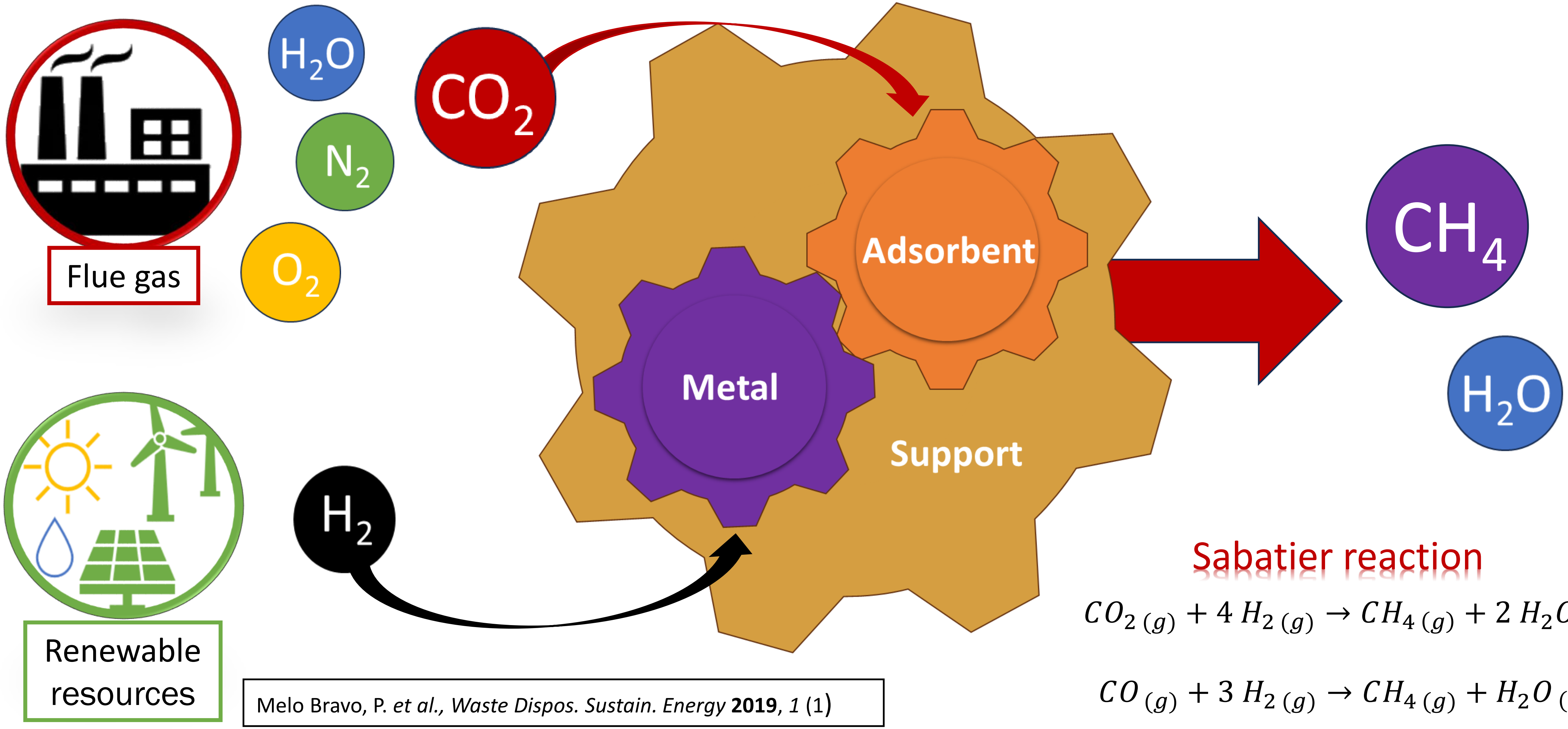
Artz, J. *et al.*, *Chem.* Rev, **2018**, 118, 434–504

Dual function materials (DFMs)



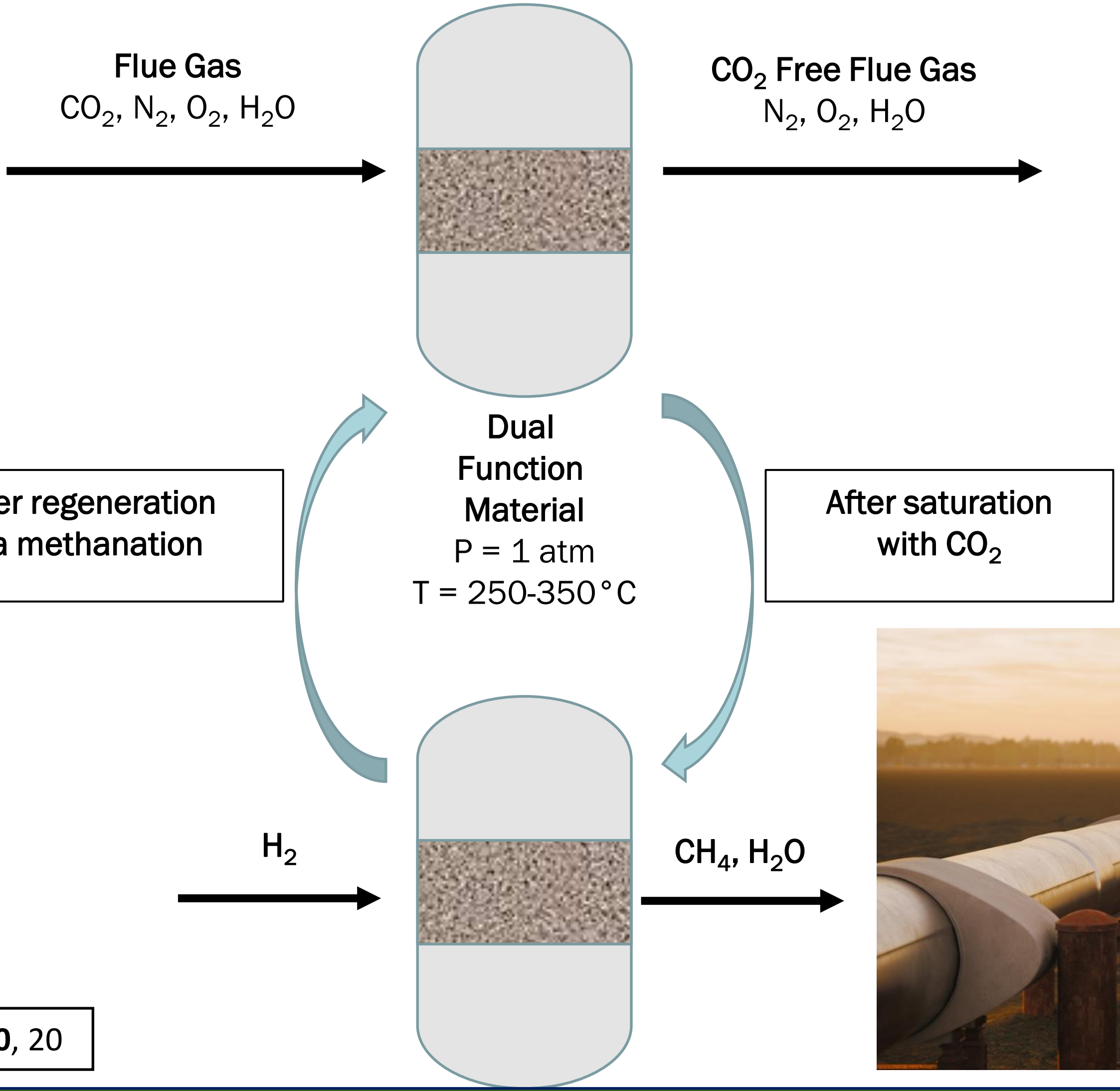
Melo Bravo, P. *et al.*, *Waste Dispos. Sustain. Energy* **2019**, *1* (1)

Sabatier reaction

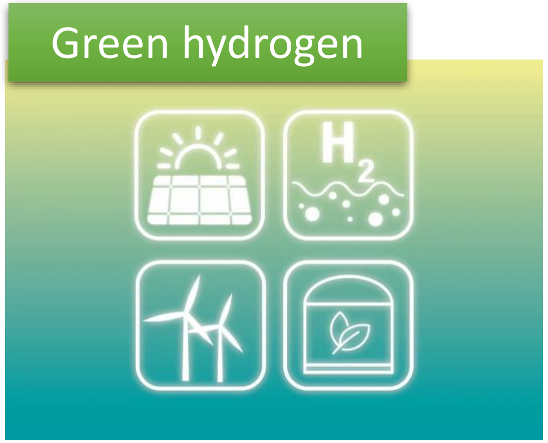
$$CO_{2\,(g)} + 4\,H_{2\,(g)} \rightarrow CH_{4\,(g)} + 2\,H_2O_{\,(g)}$$

$$CO_{\,(g)} + 3\,H_{2\,(g)} \rightarrow CH_{4\,(g)} + H_2O_{\,(g)}$$

Cyclic methanation experiments

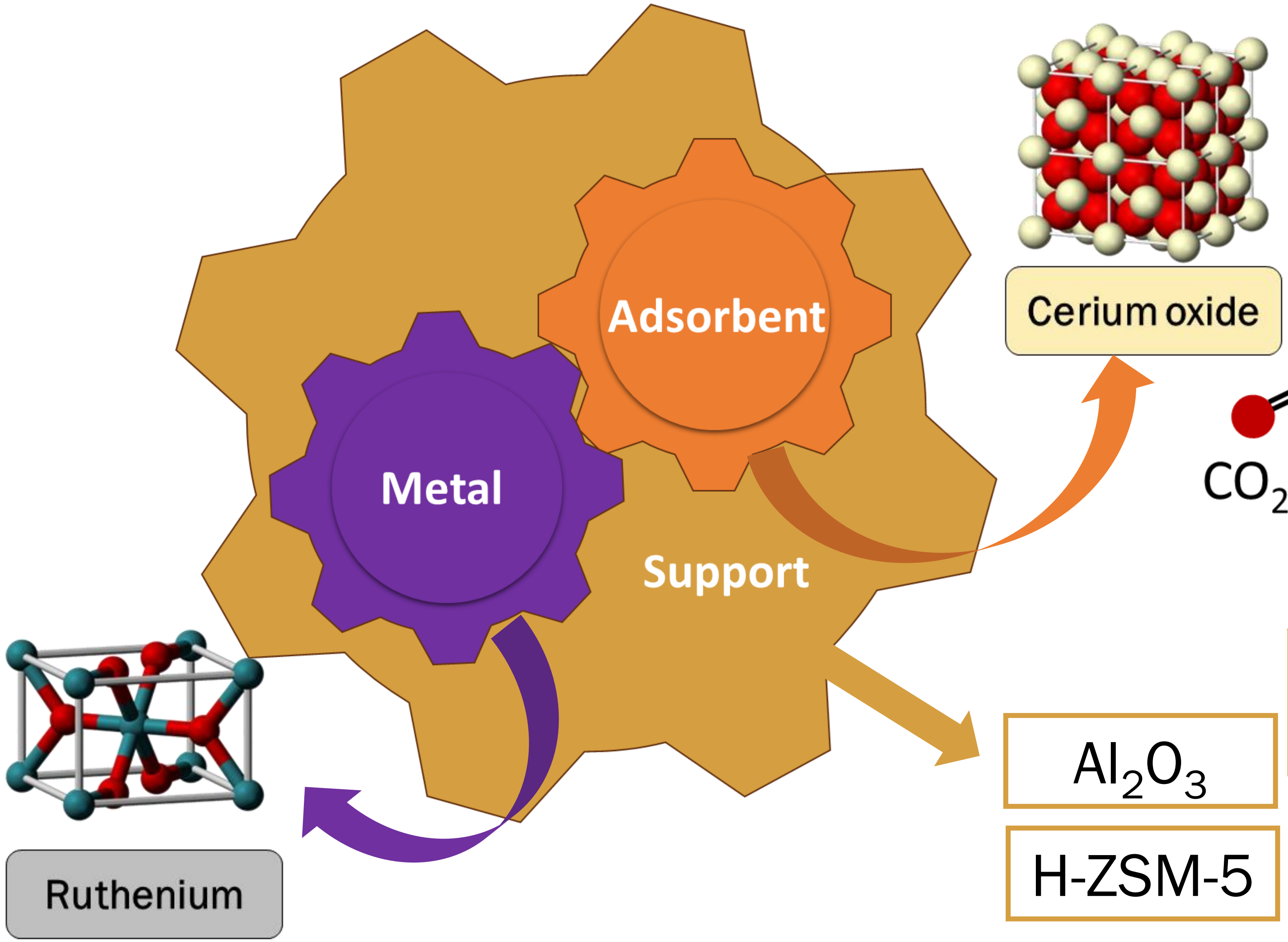


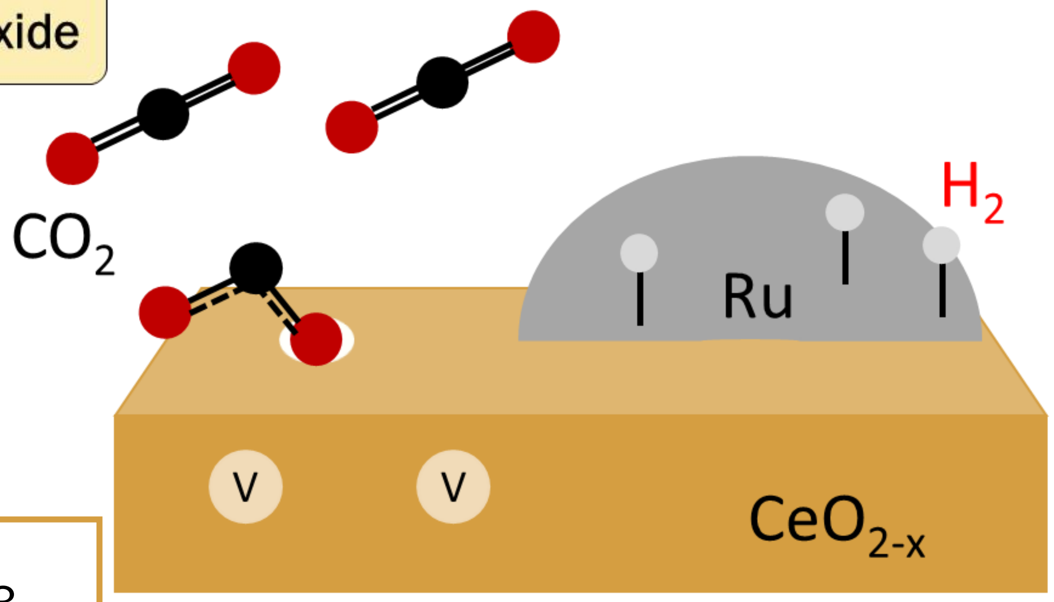
https://www.unep.org



Omodolor, I. S. et al., *Ind. Eng. Chem. Res.* **2020**, 20

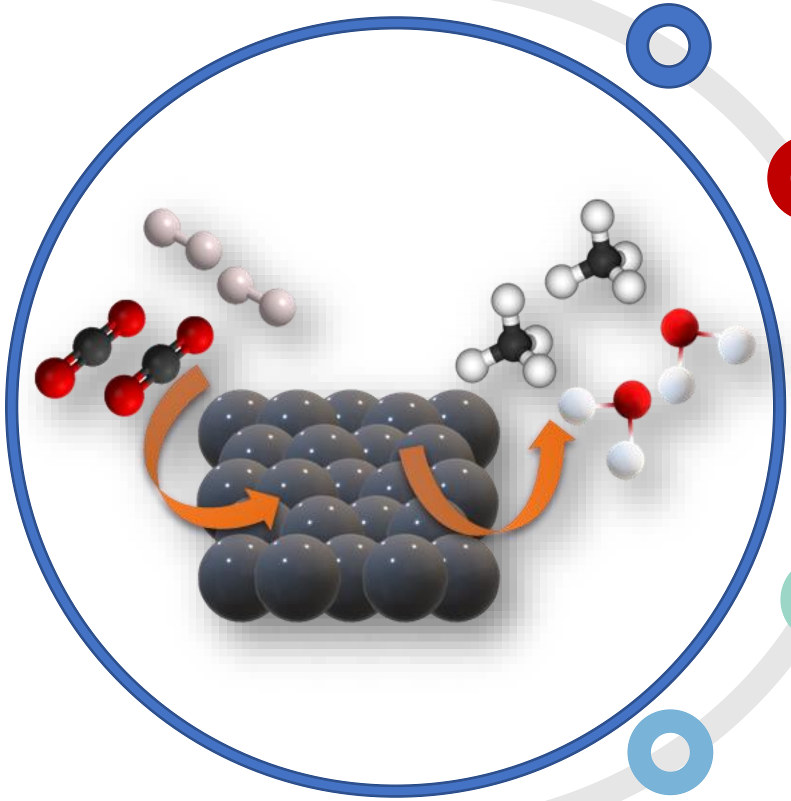
My phases





López-Rodríguez, S. *et al.*, *J. Am. Chem. Soc.* **2016**, *138* (19), 6298–6305

Summary

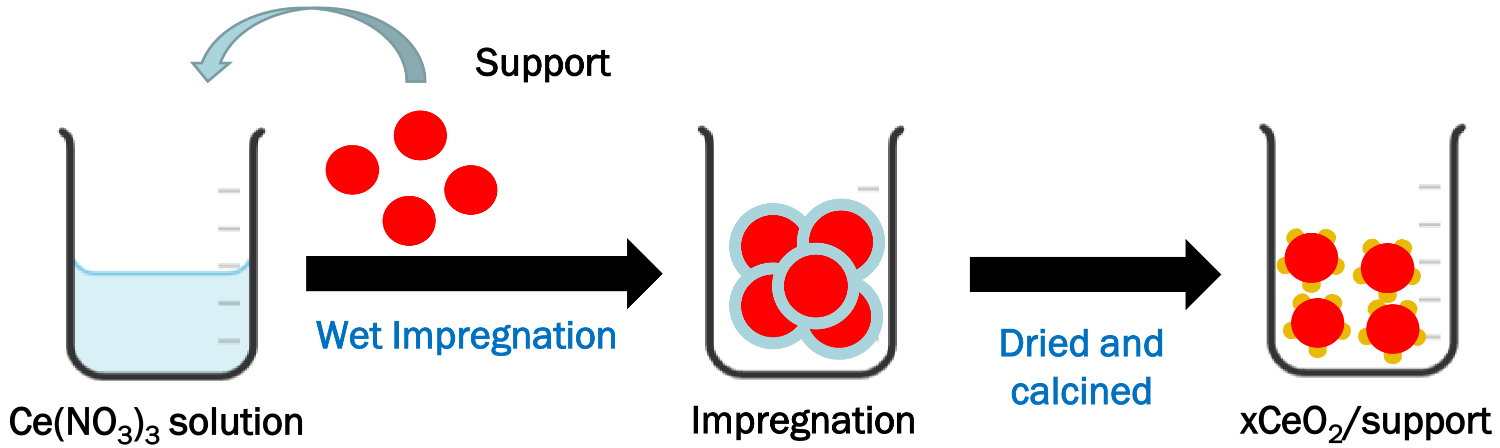


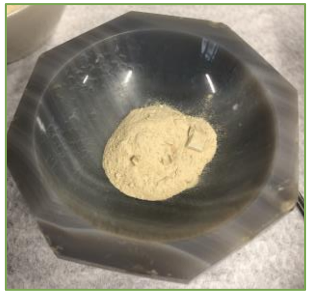
2 MATERIALS & METHODS

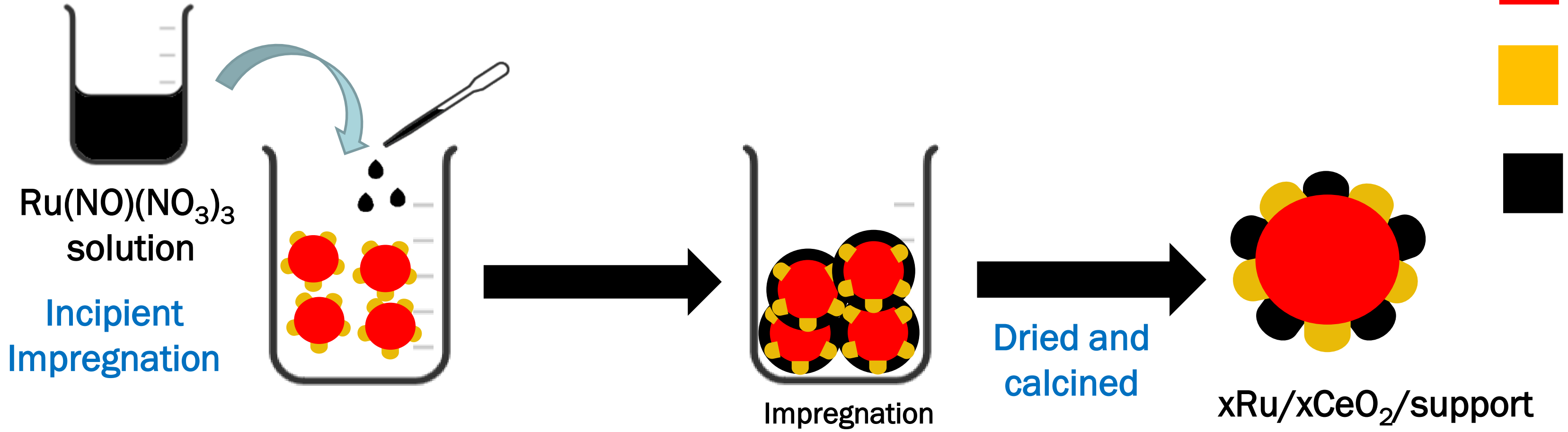
Synthesis procedure

Catalysts prepared

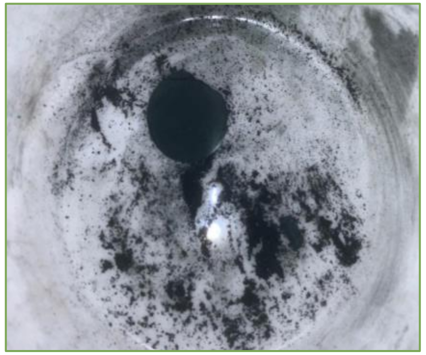
Synthesis procedure…







- Al_2O_3 and/or H-ZSM-5
- Cerium oxide (CeO_2)
- Ruthenium oxide (RuO_2)



Tada *et al.*, *Int. J. Hydrog. Energy*, **2014**, 39, 10090-10100

…and samples

$xCeO_2$/support

10 % CeO_2	
20 % CeO_2	@ **Al_2O_3**
30 % CeO_2	

10 % CeO_2	
20 % CeO_2	@ **H-ZSM-5**
30 % CeO_2	

Adsorption tests

150°C – 200°C – 250°C

…and samples

$xCeO_2$/support

10 % CeO_2
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10 % CeO_2
20 % CeO_2 @ **H-ZSM-5**
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SPOILER ALERT

…and samples

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Adsorption tests

150°C – 200°C – 250°C

$xRu/xCeO_2$/support

2% Ru/30 % CeO_2 @ **Al_2O_3**

2% Ru/30 % CeO_2 @ **ZSM-5**

Methanation tests

X-ray diffraction

N_2 physisorption at 77 K

XPS

CO_2 TPD analysis

H_2 TPR analysis

ICP-MS

HRTEM-EDX

***In situ* FT-IR**

Sample	Nomenclature
1	10CZ
2	20CZ
3	30CZ
4	2R30CZ
5	10CA
6	20CA
7	30CA
8	2R30CA

…and samples

xCeO_2/support

- 10 % CeO_2
- 20 % CeO_2 @ **Al_2O_3**
- 30 % CeO_2

- 10 % CeO_2
- 20 % CeO_2 @ **H-ZSM-5**
- 30 % CeO_2

Adsorption tests

150°C – 200°C – 250°C

xRu/xCeO_2/support

- 2% Ru/30 % CeO_2 @ **Al_2O_3**
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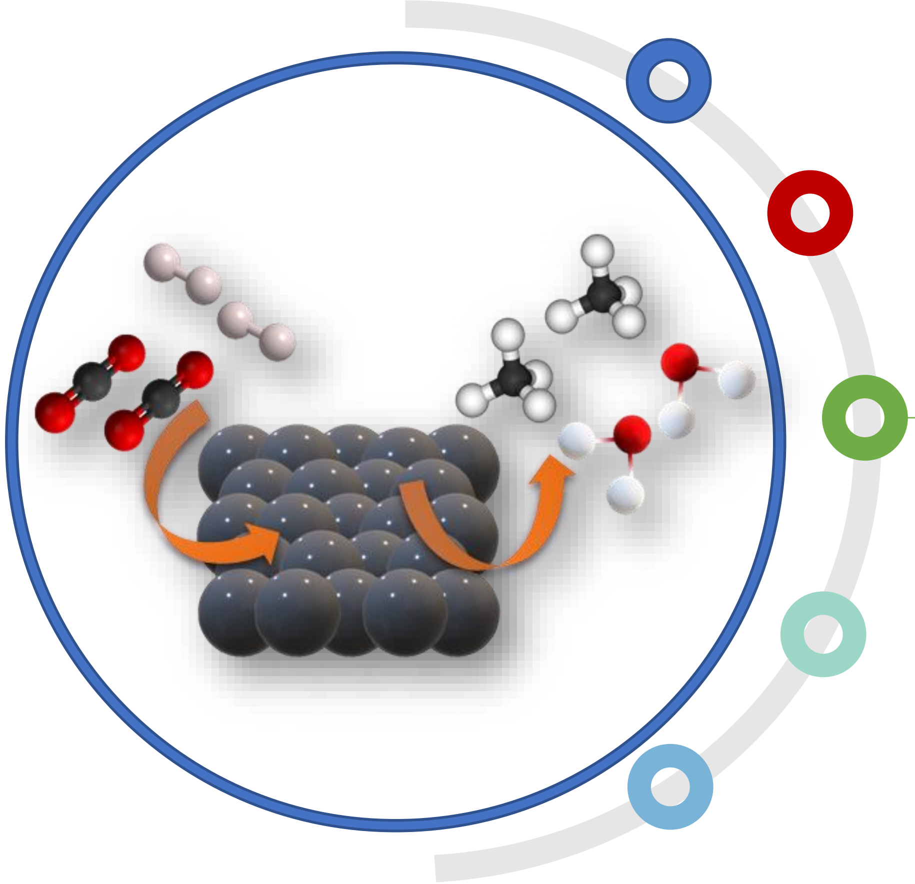
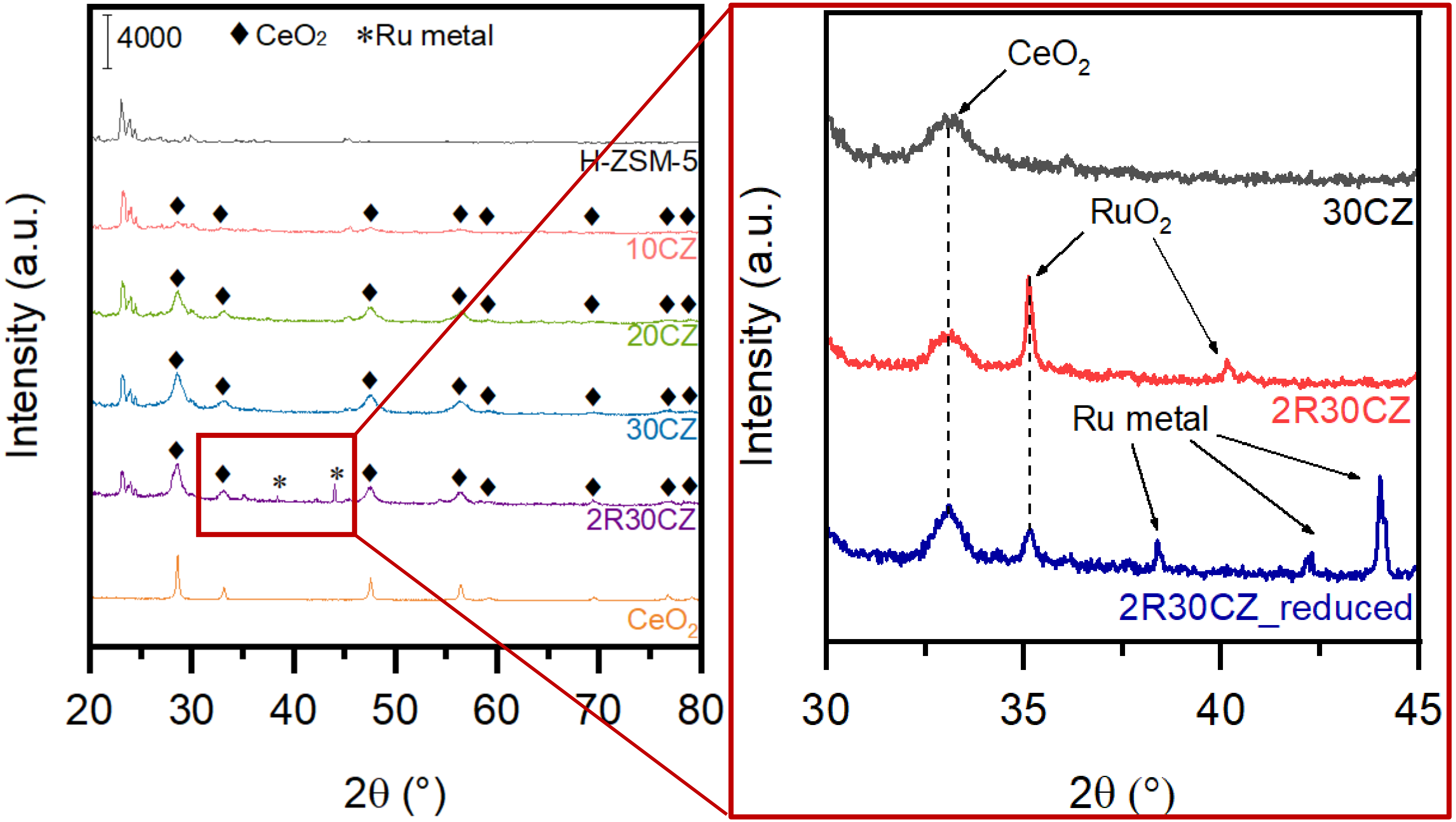


3 CHARACTERIZATIONS

X-Ray Diffraction

CO_2-Temp. Program. Desorption

X-Ray Diffraction

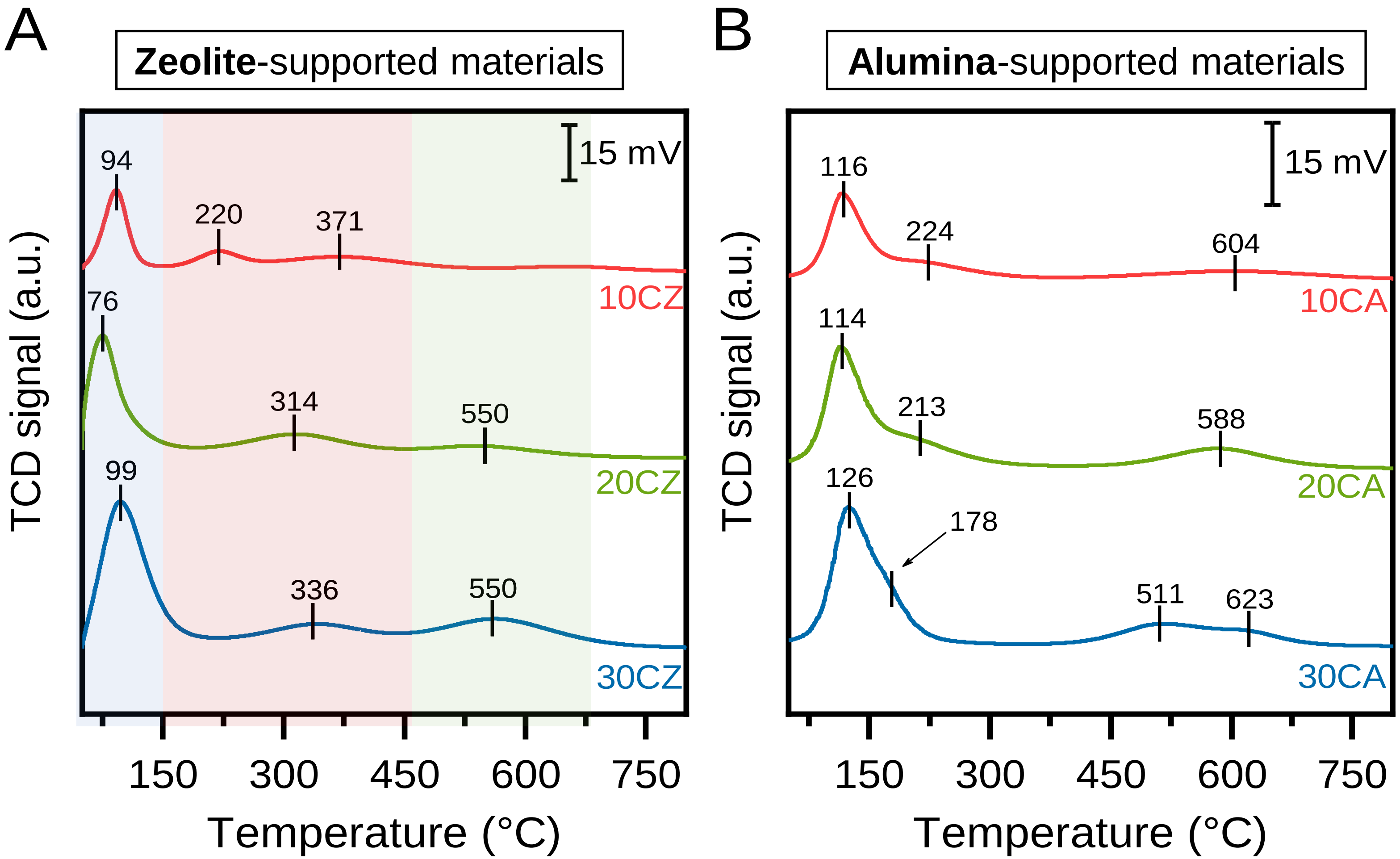


Growth of reflex intensity of fluorite crystal structure characterized the pattern of pure cerium oxide

Ruthenium precursor impregnation allows the formation of RuO_2 phase 35° (101) and 40° (200)

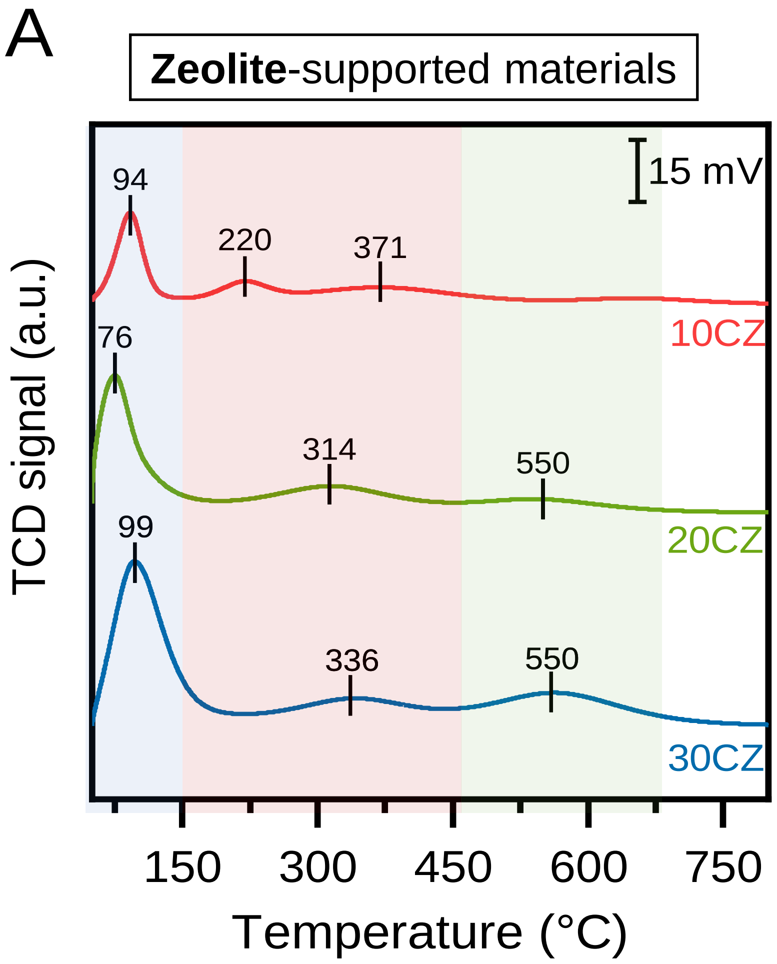
Ru metal appears after a reductive treatment with 5% H_2/N_2 (500°C – 1h)

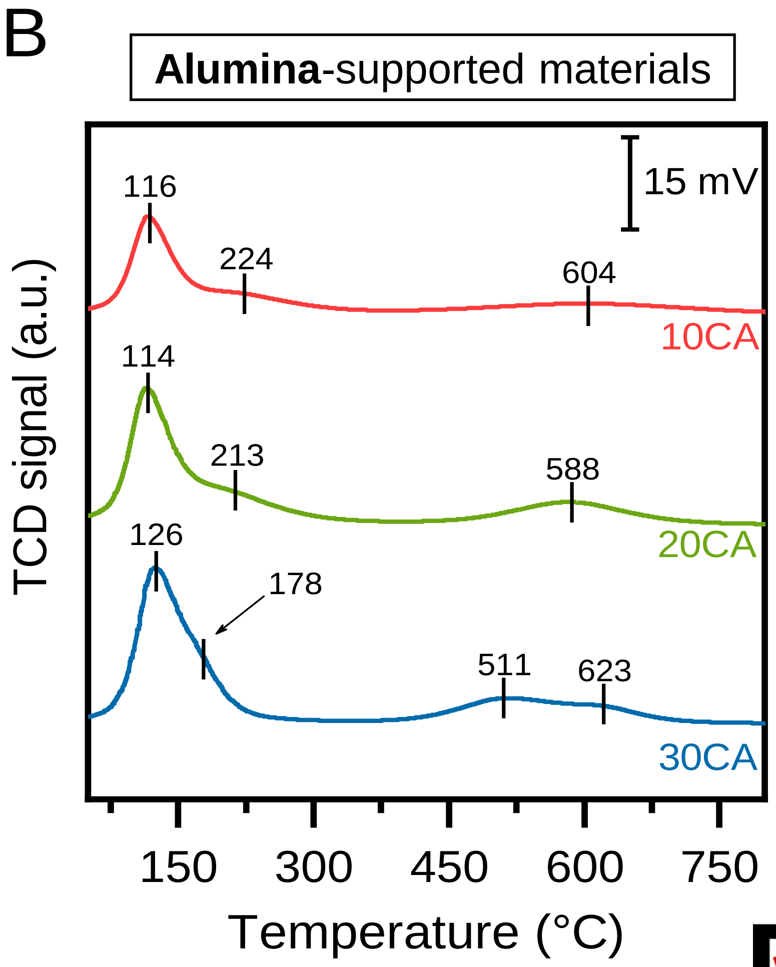
CO_2 – Temperature Programmed Desorption



Cat.	Weak basic sites	Medium basic sites	Strong basic sites
		$\mu mol_{CO2}/g_{cat}$	
10CZ	143.6	131.2	29.8
20CZ	265.8	137.6	43.2
30CZ	286	132.8	163.6
10CA	125.5	93.2	45.5
20CA	242.8	36.5	123.8
30CA	309.6	16.7	161.1

CO_2 – Temperature Programmed Desorption





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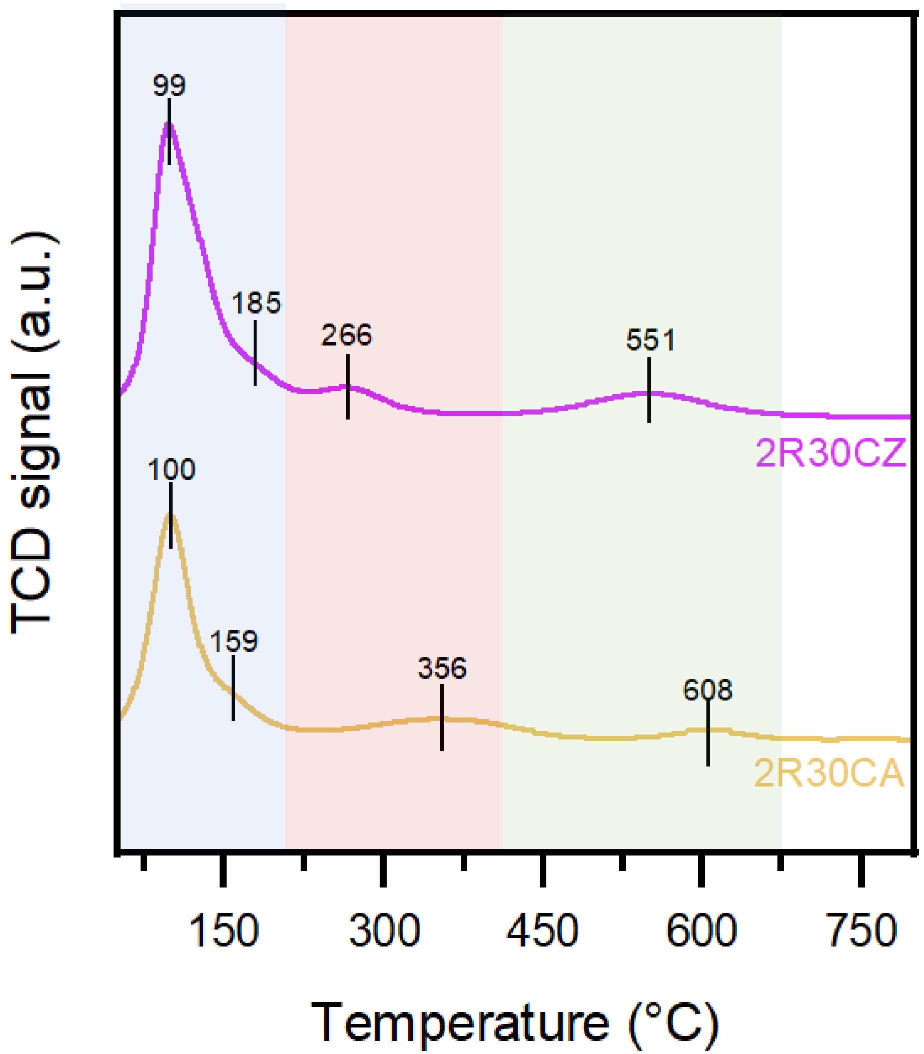
✔ **CeO_2/zeolite: > 50% CO_2 adsorbed available**

✘ **CeO_2/Al_2O_3: < 50% CO_2 adsorbed available**

CO_2 – Temperature Programmed Desorption



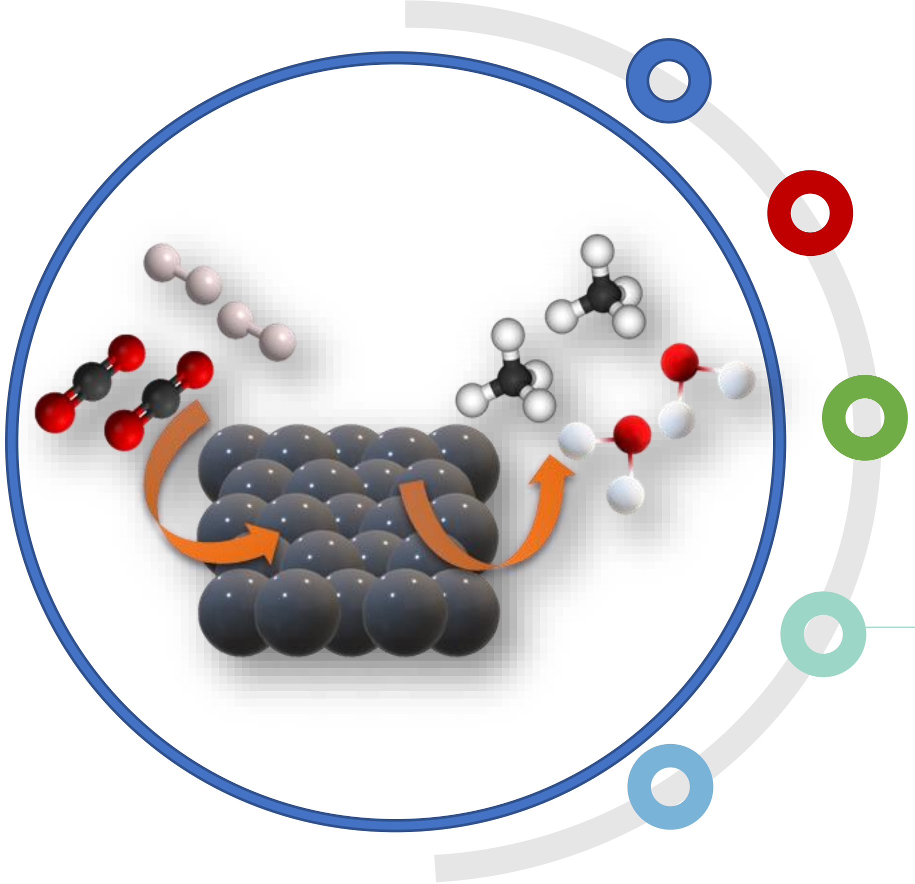
Cat.	Weak basic sites	Medium basic sites	Strong basic sites
		$\mu mol_{CO2}/g_{cat}$	
2R30CZ	309	84	199
2R30CA	299.4	75	26.6

CeO_2/zeolite: ~ 50% CO_2 adsorbed available

CeO_2/Al_2O_3: ~ 25% CO_2 adsorbed available

Possible effect of the functionalisation

Summary

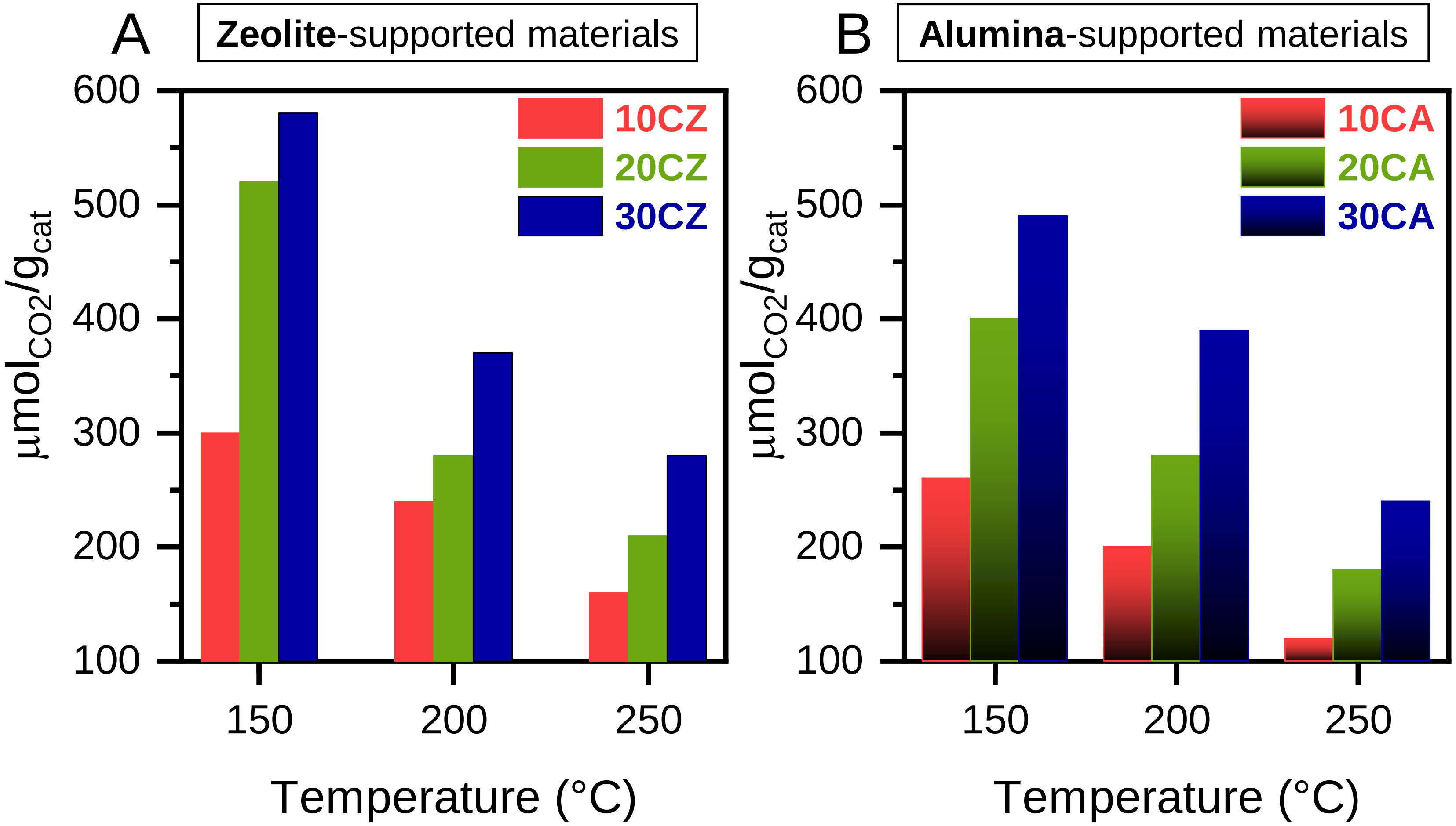


CO_2 adsorption tests & results

Methanation tests & results

4 ADSORPTION & CATALYTIC TESTS

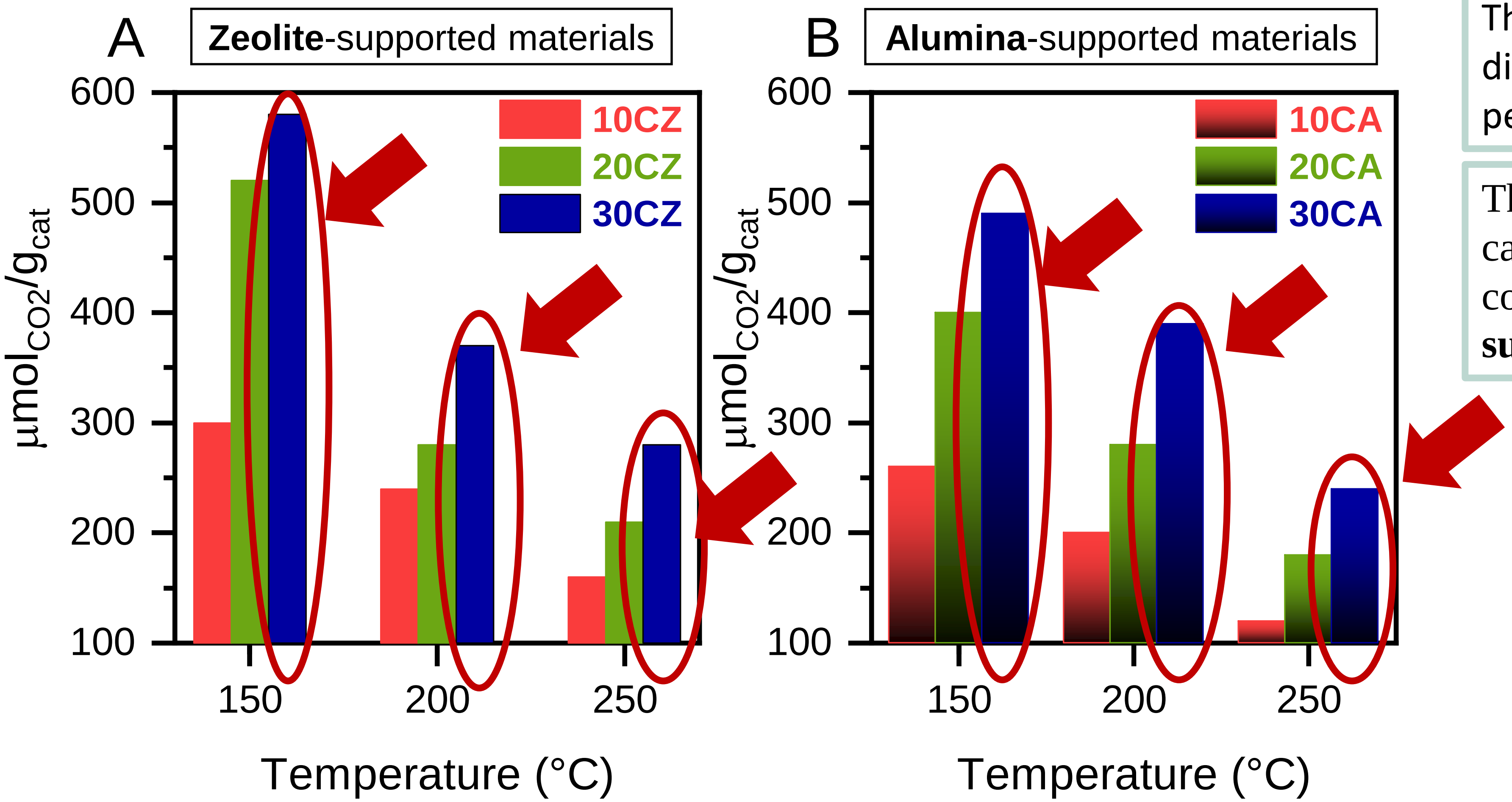
CO_2 adsorption tests: results



Adsorption tests at 3 different temperatures (150, 200, 250 °C) at atmospheric pressure.

Test condition for the methanation experiments

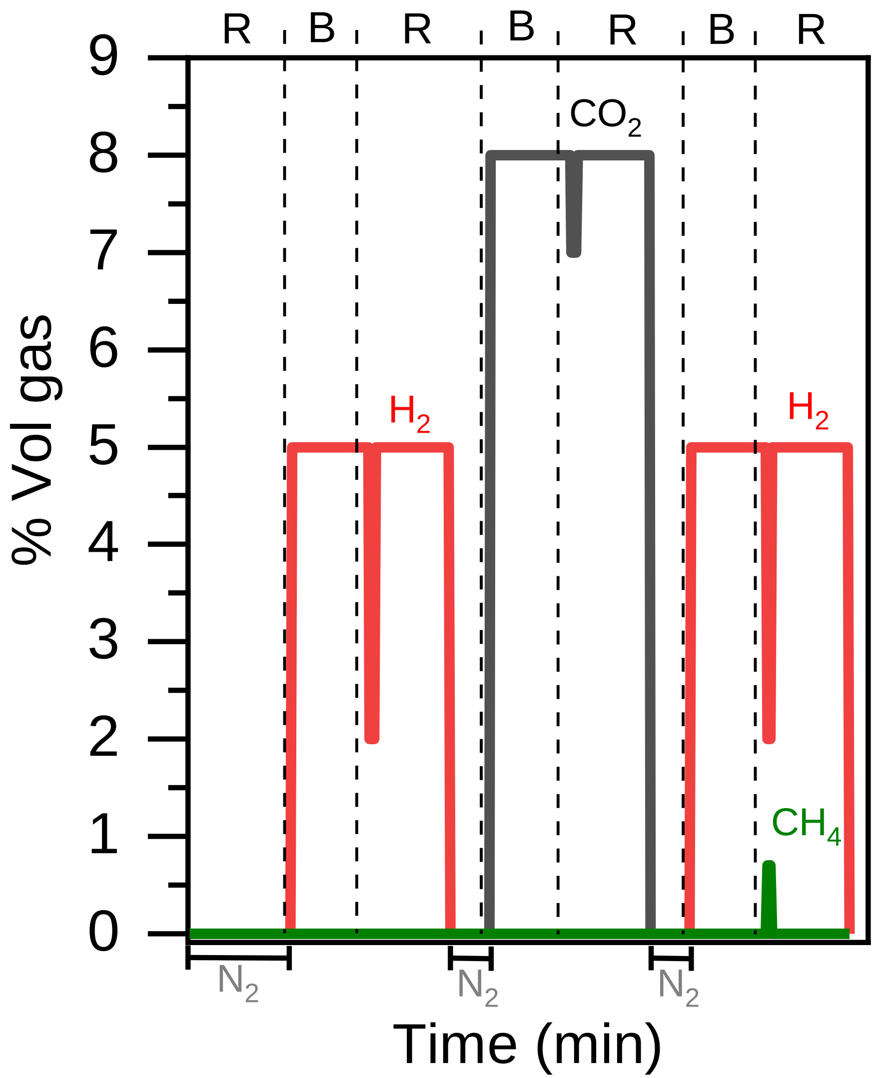
CO_2 adsorption tests: results



The materials with 30% of cerium dioxide obtained the best performances.

The gap between the adsorption capacities of 30CA and 30CZ could be ascribable to the **role of support**.

Methanation tests: experiment procedure



R = Reactor
B = by-pass

Pre-treatment →

150 mL/min **100% N_2**

- Heating ramp: 5°C/min
- Set-point: 500°C
- Dwell time: 1 h

Surface reduction →

150 mL/min **5% H_2/N_2**

- Set-point: 500°C
- Dwell time: 1 h

Purge & cooling ↓

150 mL/min **100% N_2**

- Colling up to: **250°C**

CO_2 adsorption ←

150 mL/min **8% CO_2/N_2**

- Set-point: **250°C**
- Dwell time: until complete saturation

Purge ←

150 mL/min **100% N_2**

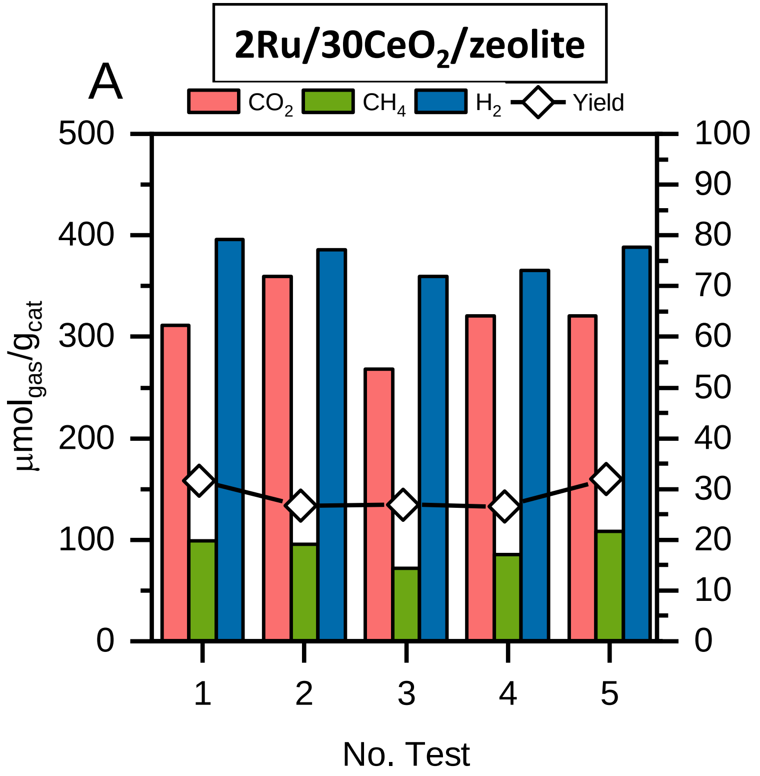
- Set-point: **250°C**

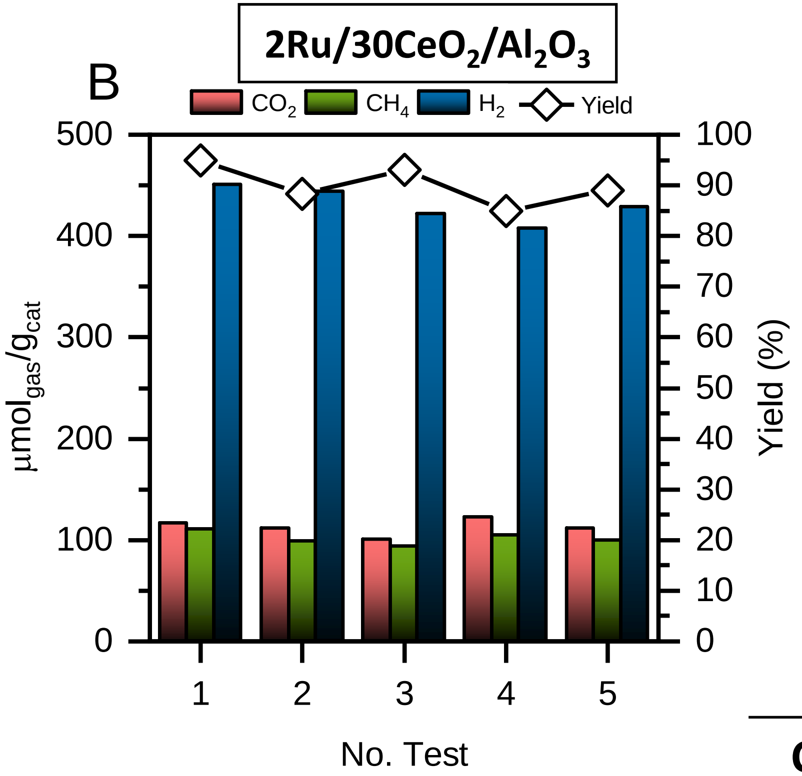
Methanation

150 mL/min **5% H_2/N_2**

- Set-point: **250°C**

Methanation tests: results

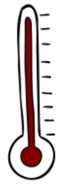




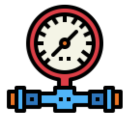
Almost the **same amount of methane** produced by the two catalysts

Different conversion yield mainly due to an unequal amount of activated CO_2

Stable catalytic performances



Temperature kept constant (250°C)



Pressure kept constant (1 atm)

Cyclic experiments

CO_2 adsorption

150 mL/min **8% CO_2/N_2**

- Set-point: **250°C**

→

Purge

150 mL/min **100% N_2**

- Set-point: **250°C**

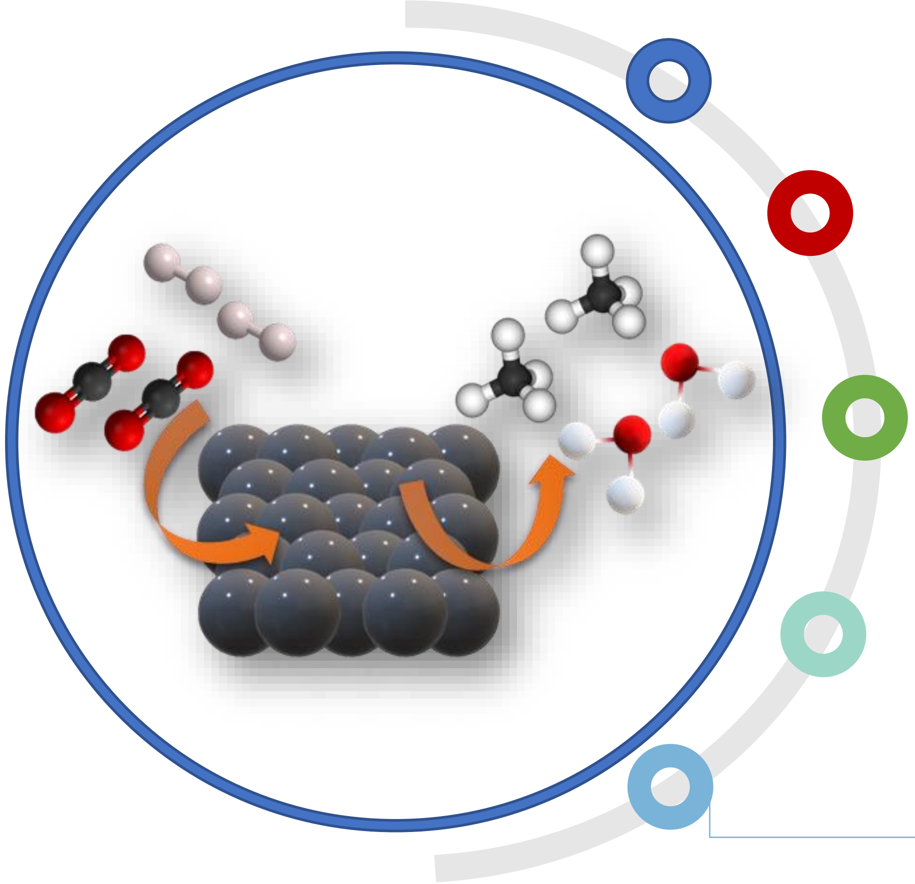
→

Methanation

150 mL/min **5% H_2/N_2**

- Set-point: **250°C**

Summary



5 CONCLUSIONS & FUTURE PERSPECTIVES

Conclusions…

Adsorption test →

Ceria-base materials are effective for:

- ✓ CO_2 adsorption at high temperature
- ✓ Zeolite support further increased the adsorption capacity

Methanation test →

DFMs synthesised proved:

- ✓ CH_4 selectivity
- ✓ Large & easy regeneration @ lower temperature
- ✓ Stability/ durability
- ✓ Cost (metal loading)

Conclusions…& Future Perspectives

Adsorption test

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Methanation test

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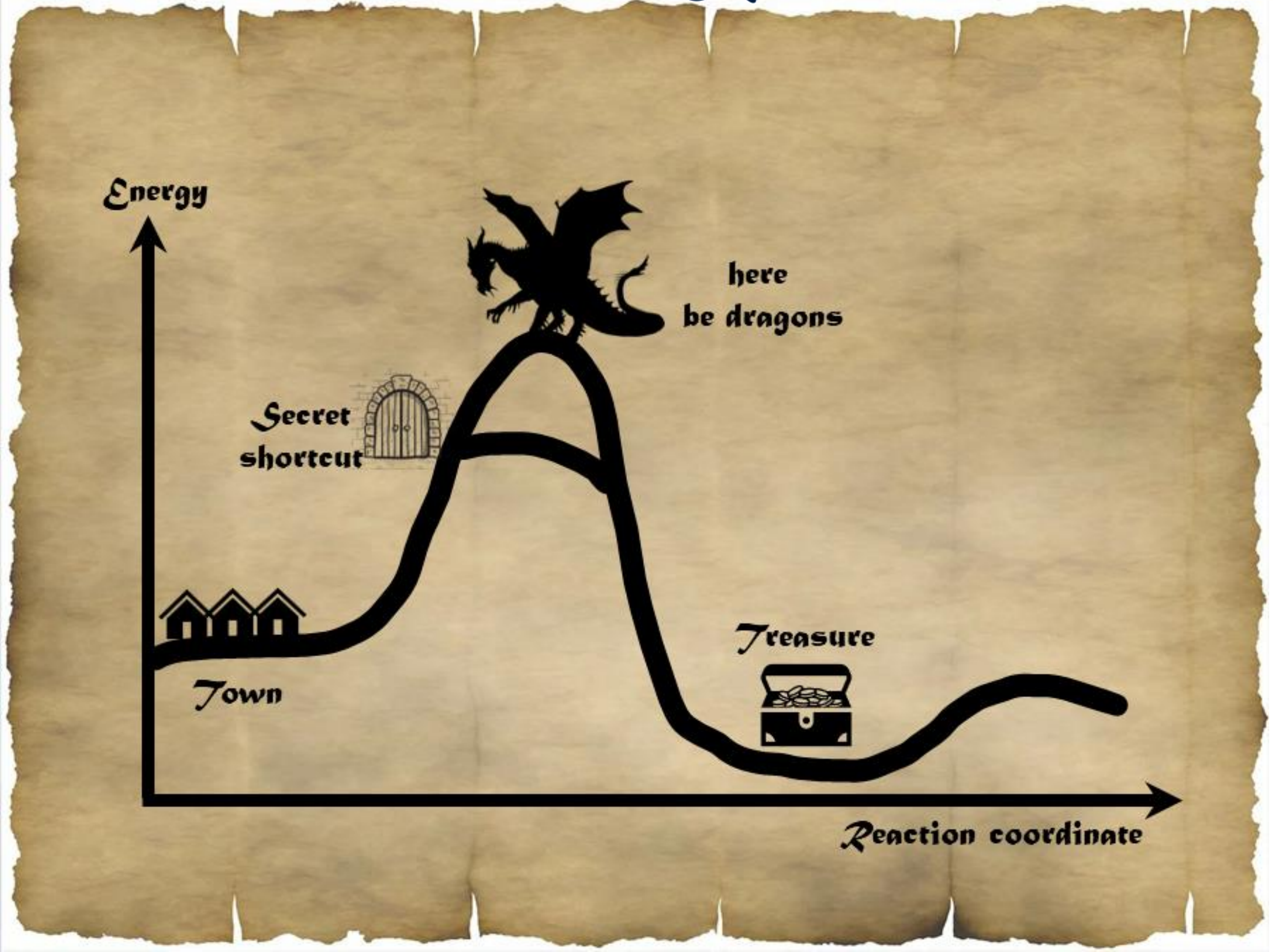
Catalyst optimization

1. Diversify the synthesis of the catalysts
2. Further investigation of the reaction mechanism

Test optimization

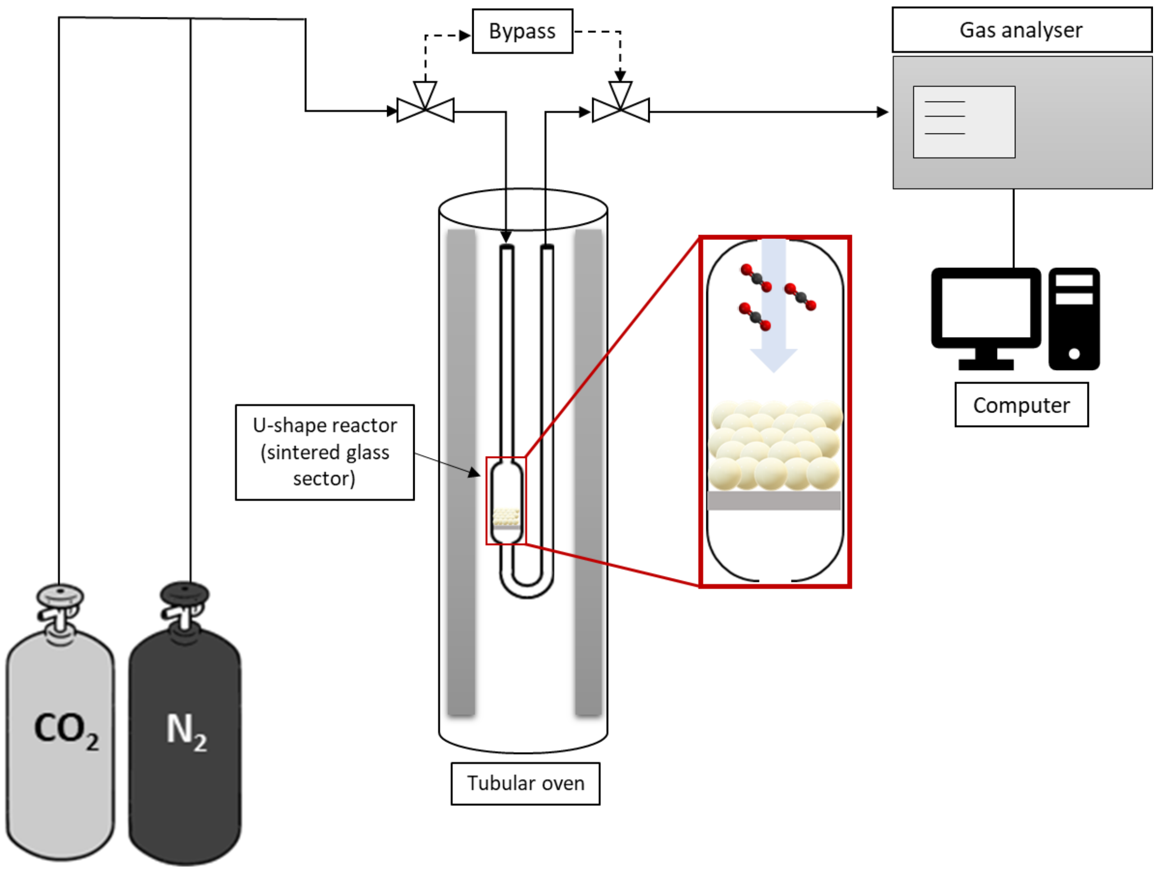
1. Use of real gas atmosphere (humidity)
2. Different test temperature
3. Pressure

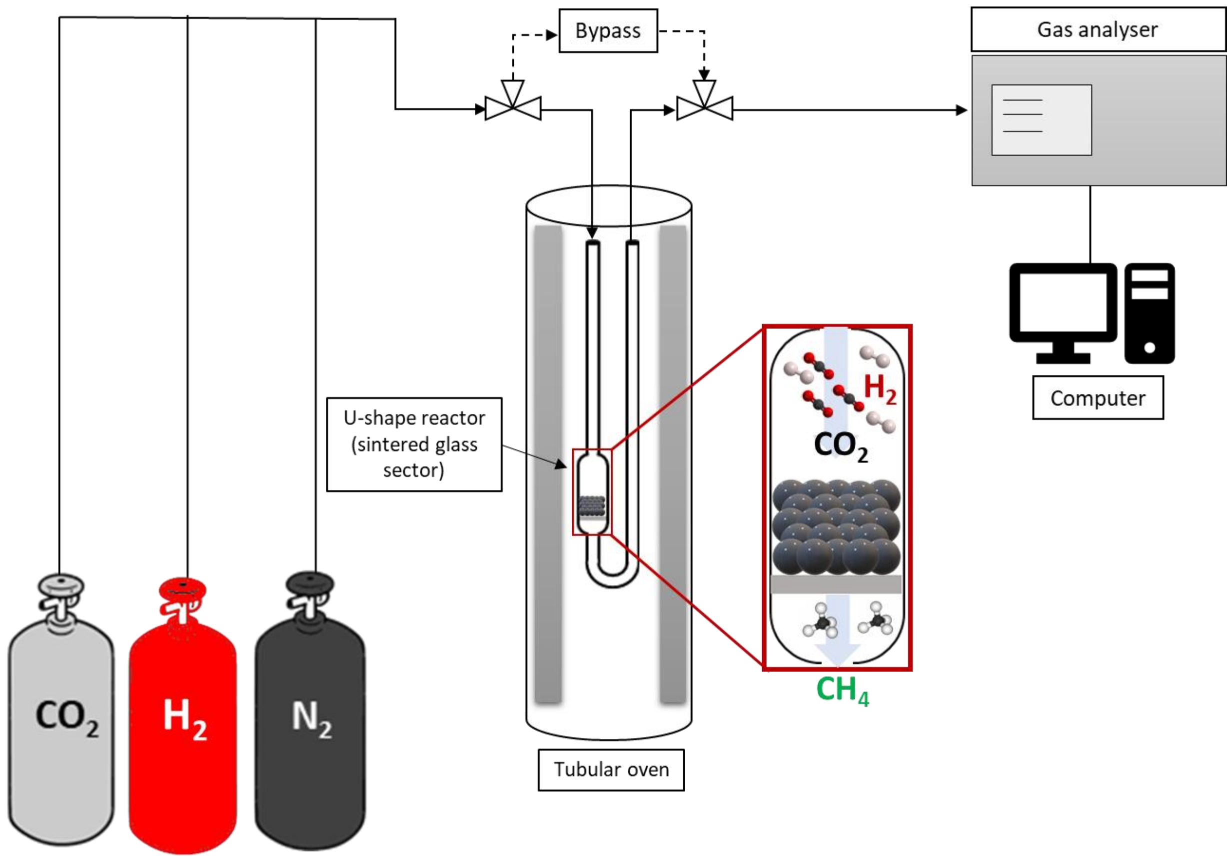


THANK YOU FOR YOUR KIND ATTENTION!!

SUPPORTING INFORMATION

Adsorption & methanation set-up

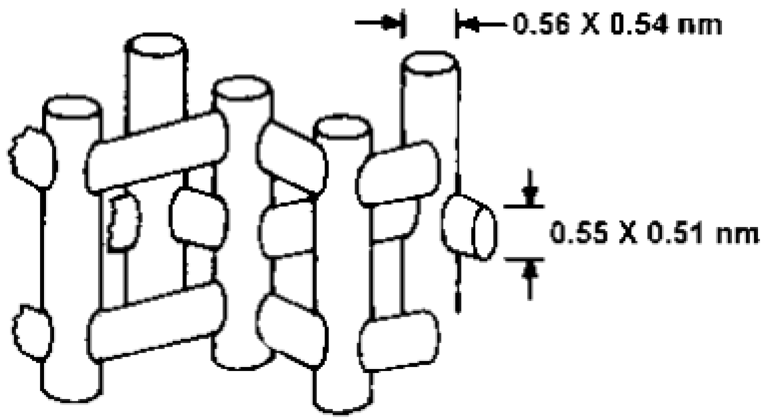




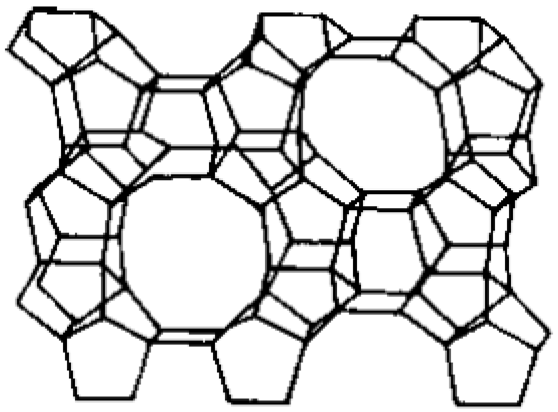
MFI zeolite type

10-membered ring apertures are the entrances to the sinusoidal channels.

There are two channel systems in ZSM-5: a straight channel running parallel to (010) with 10-ring openings of 5.4 x 5.6 Å, and a sinusoidal channel parallel to the (100) axis with 10-ring openings of dimension 5.1 x 5.5 Å.



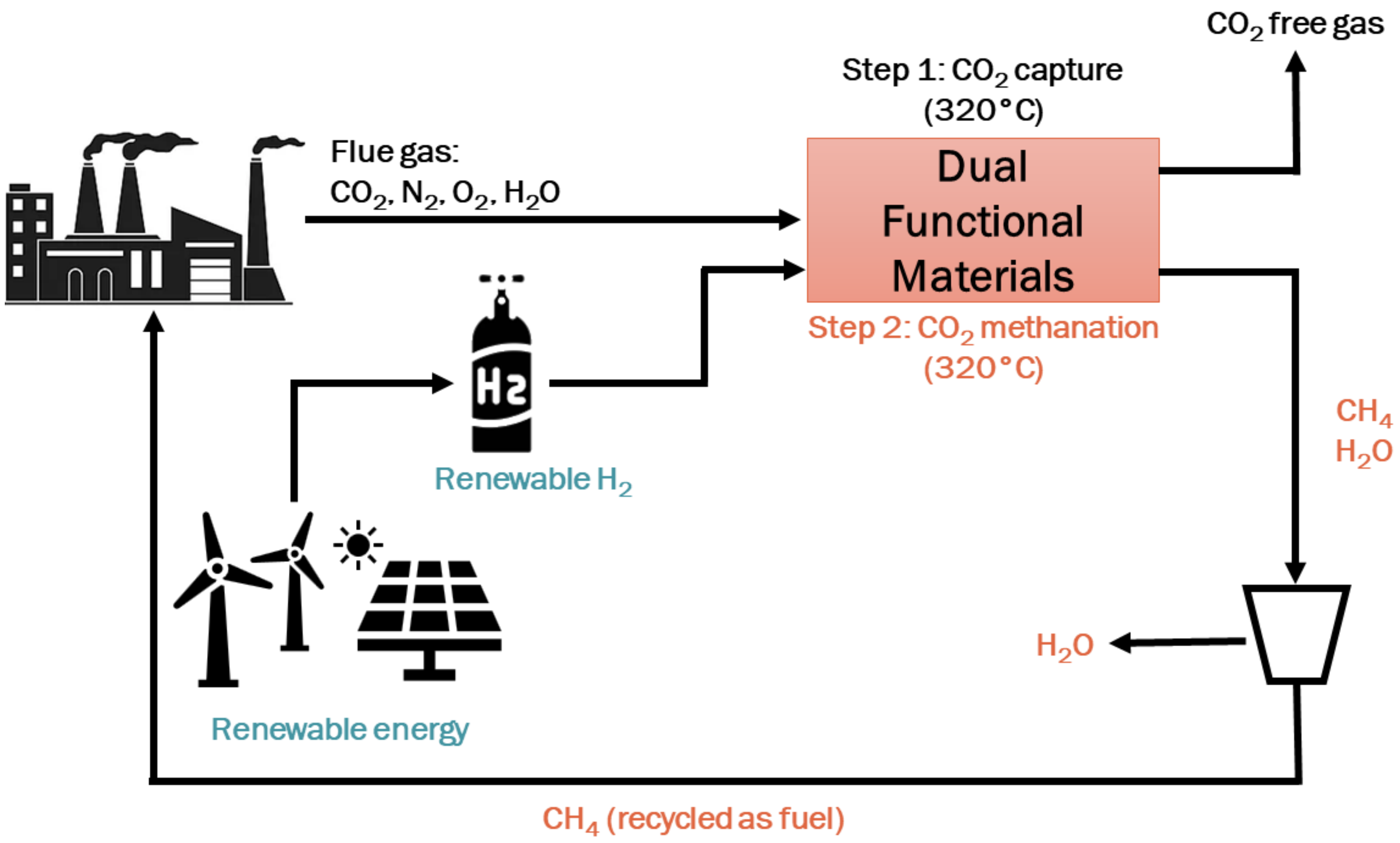
Channel structure



(100) sheet of ZSM-5

Payra, P.; Dutta, P. K., ***J. Am. Chem. Soc***, 2003, 126, 21-22.

Dual Function Materials (DFMs)



- **Dual Function Materials** 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

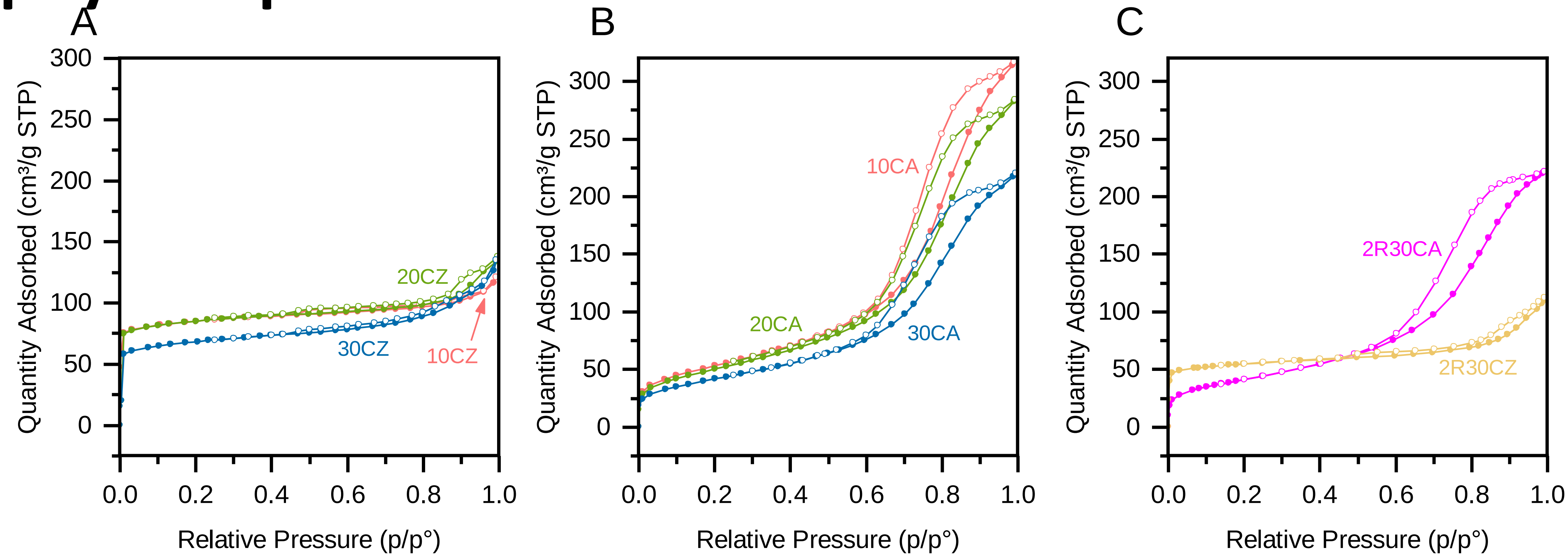
Catalytic methanation activity (work @ lower temperature)

- ✓ 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

A. I. Tsiotsias *et al.*, ***Catalysts,*** 2020, 10, 812

Kosaka *et al.* ***ACS Sustain. Chem. Eng***. 2021, 9, 3452–3463

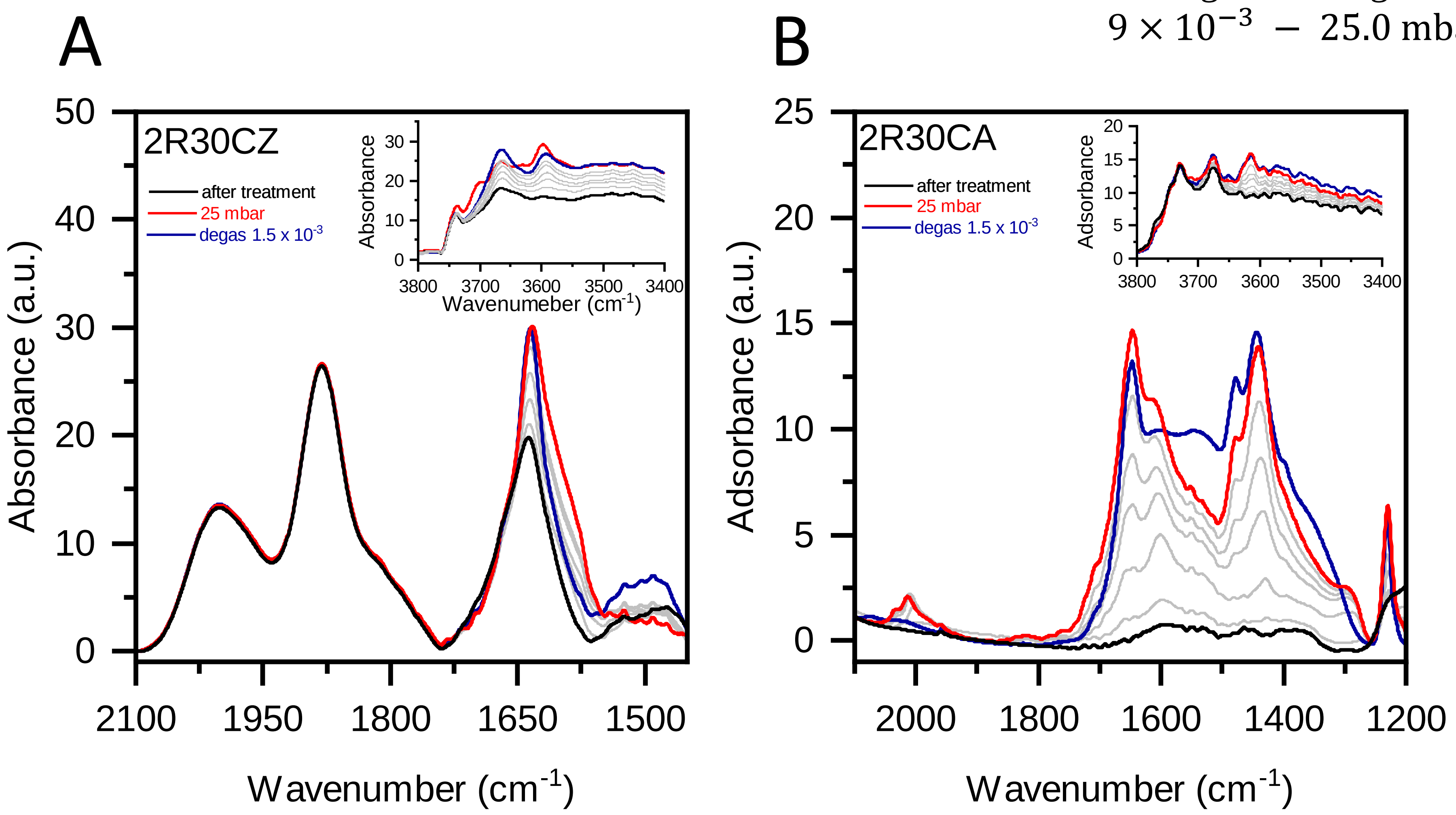
N_2 physisorption at 77 K



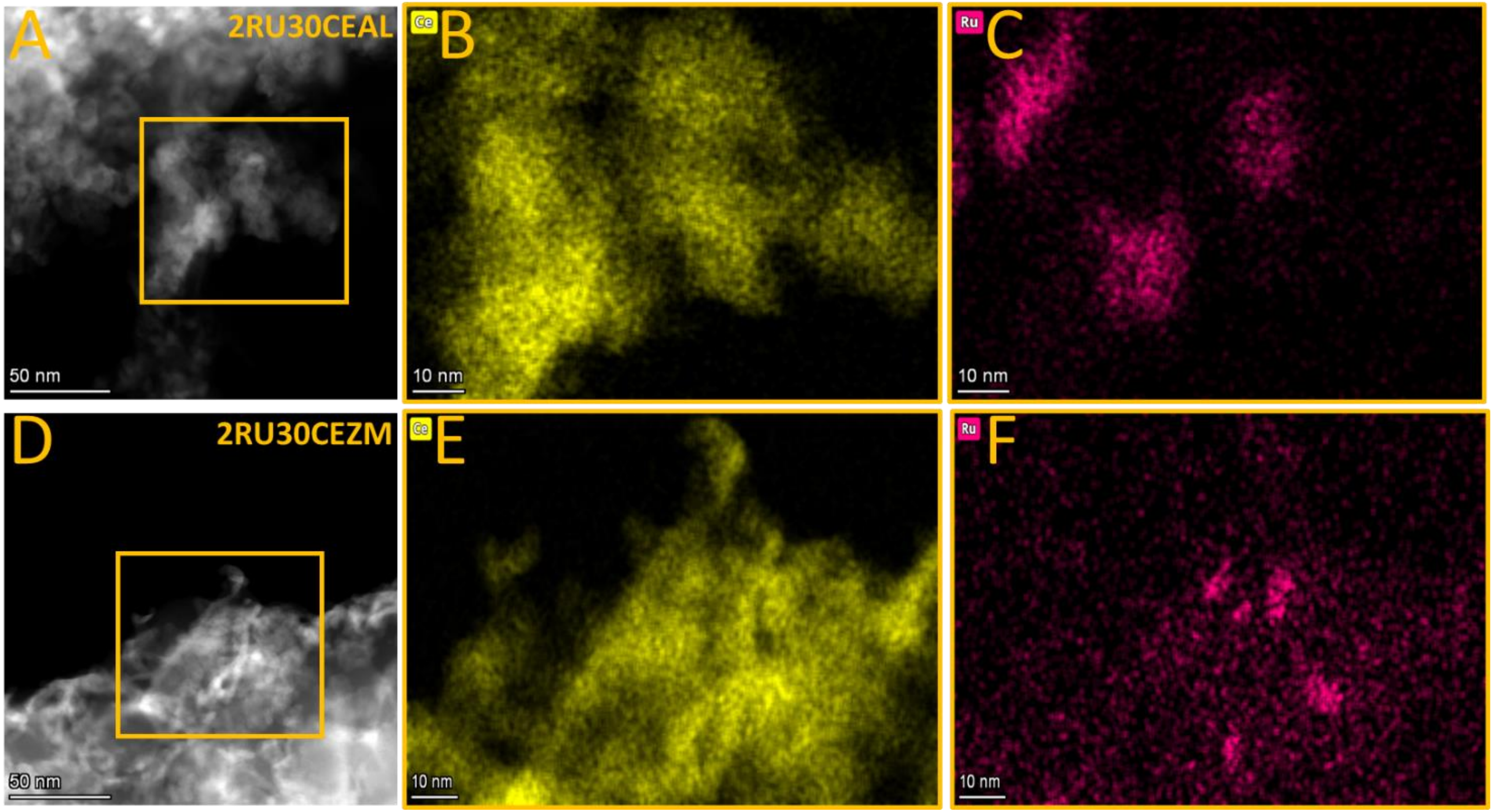
Sample	Pore Volume (cm³/g)	SSA (m²/g)
10CZ	0.18	270
20CZ	0.21	267
30CZ	0.21	229
2R30CZ	0.17	187
10CA	0.48	192
20CA	0.44	183
30CA	0.34	150
2R30CA	0.29	130

In situ FT-IR

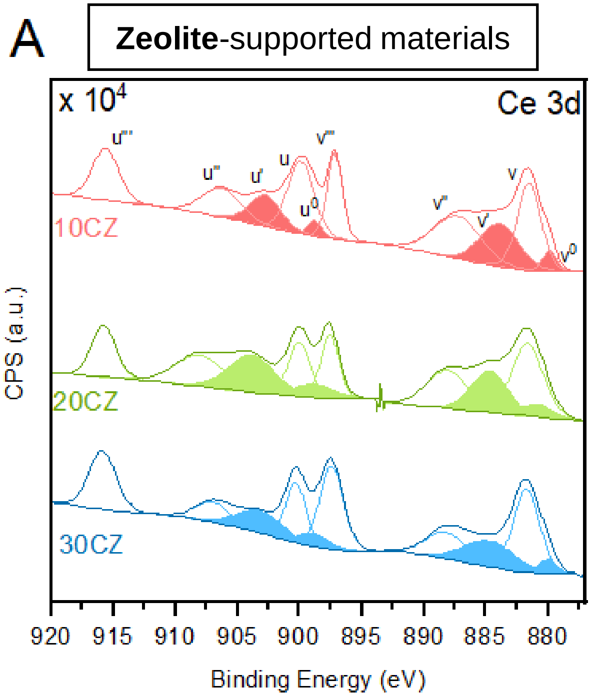
Dosing increasing amount of CO2 from
$9 \times 10^{-3} - 25.0$ mbar equilibrium pressure range

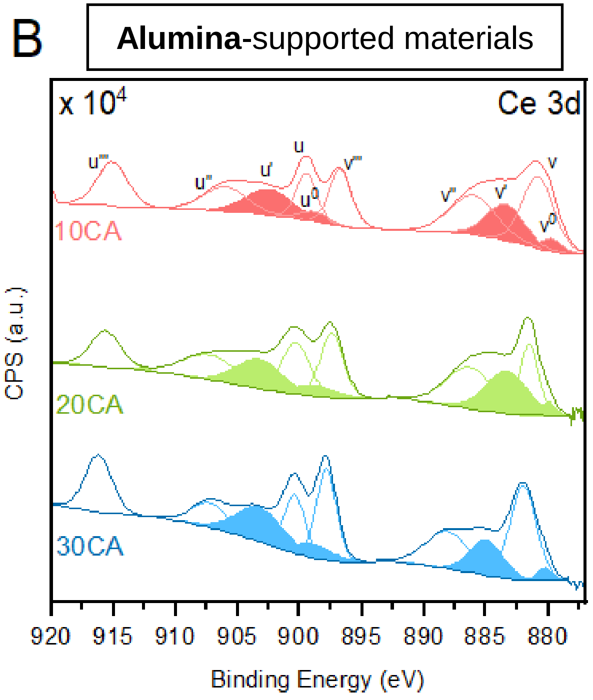


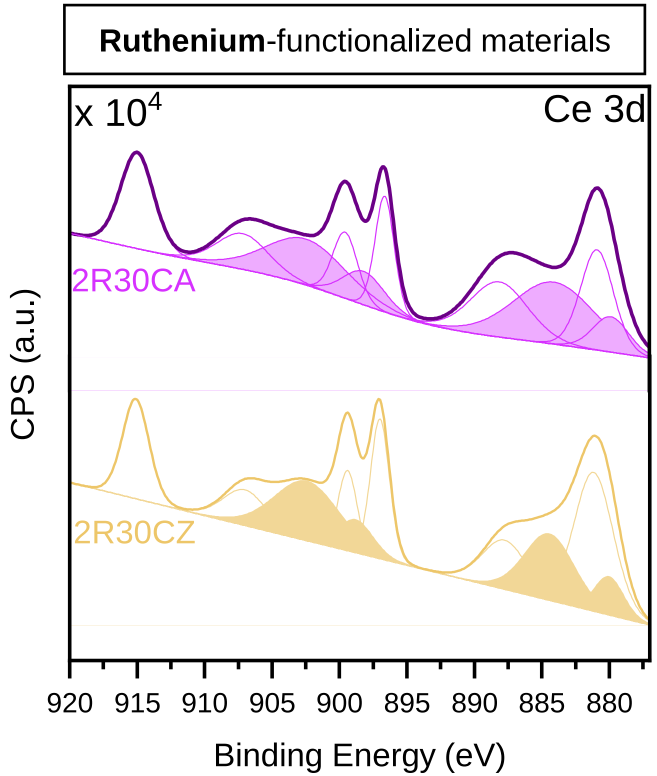
HRTEM-EDX


A
2RU30CEAL
50 nm
Ce
B
10 nm
Ru
C
10 nm
D
2RU30CEZM
50 nm
Ce
E
10 nm
Ru
F
10 nm

X-RAY PHOTOELECTRON SPECTROSCOPY

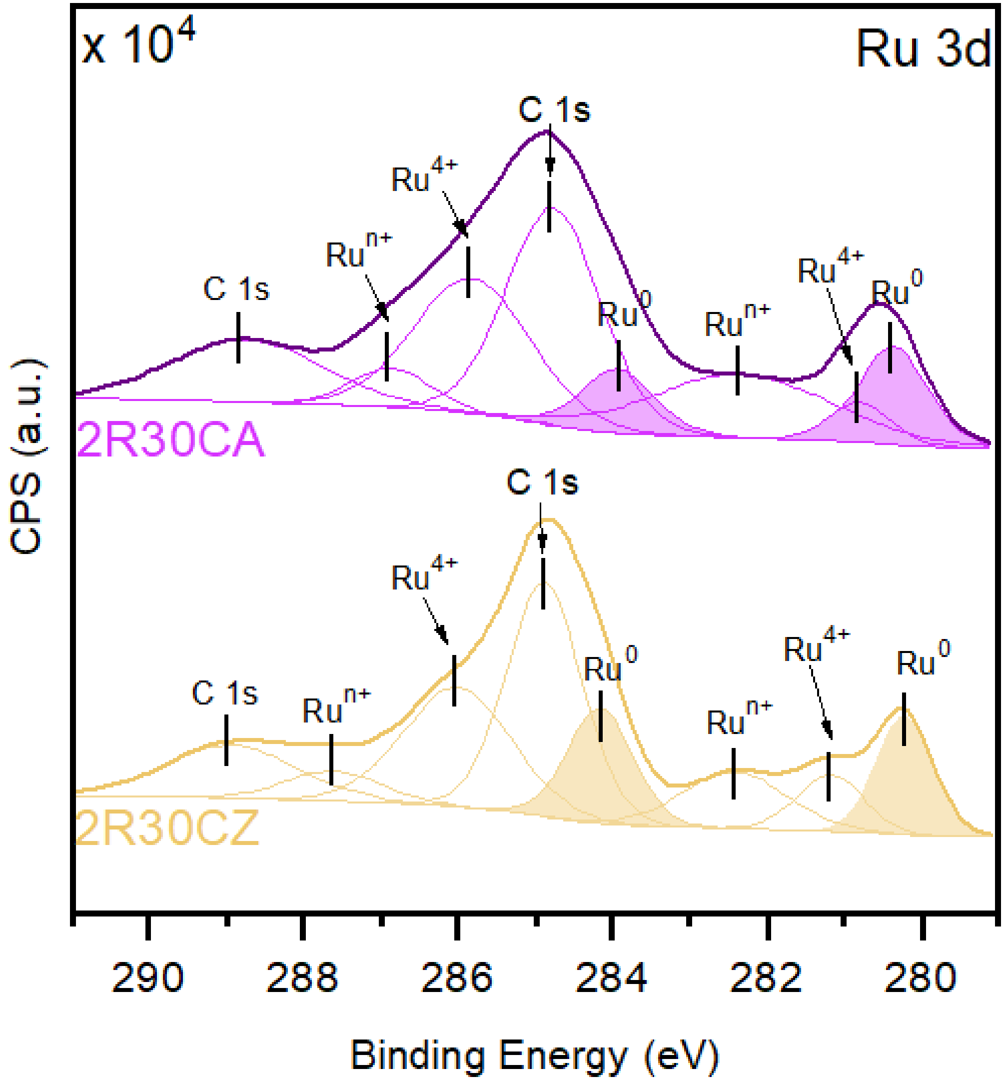






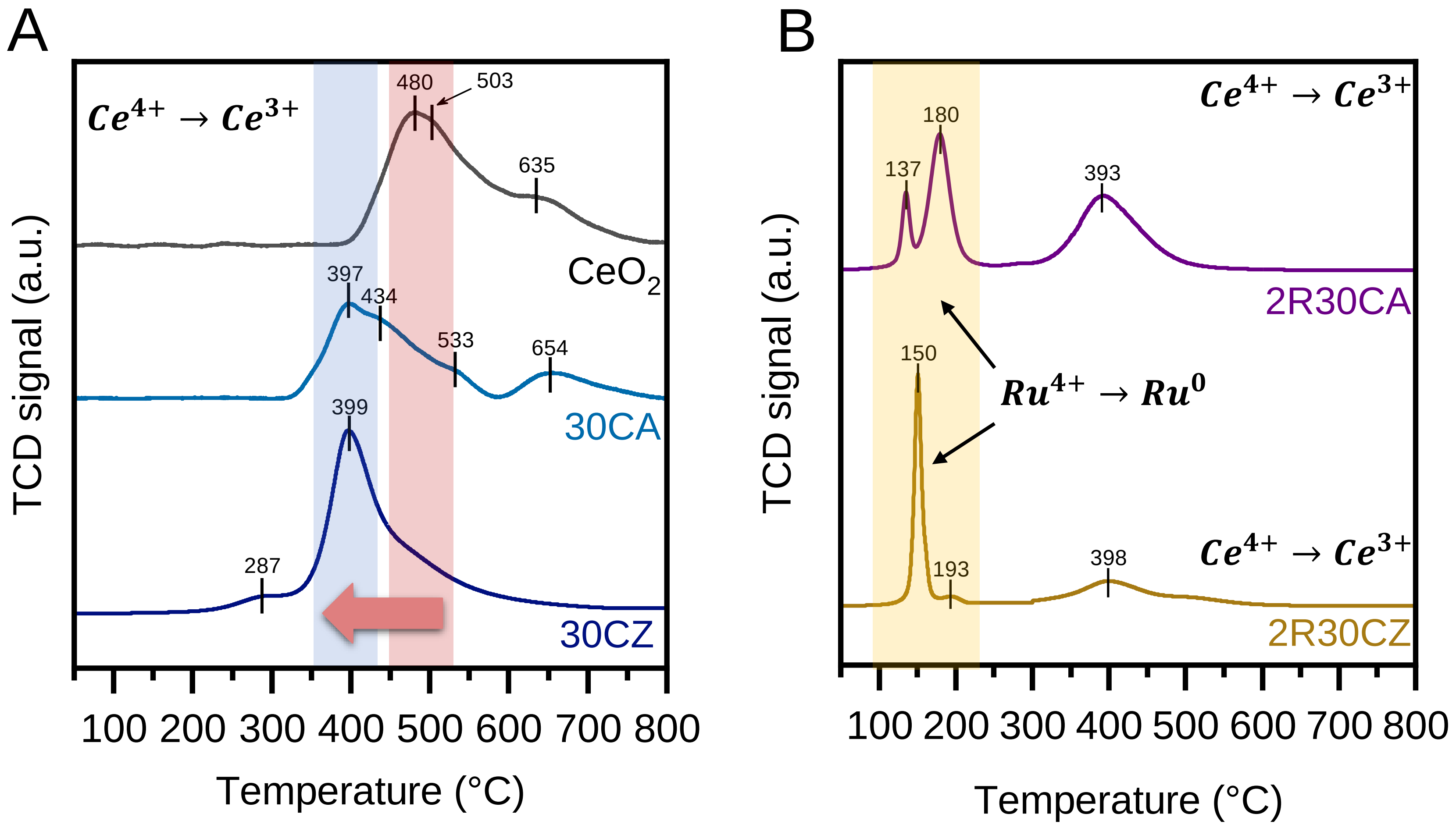
Sample	Ce^{3+}/Ce^{4+}
10CZ	0.78
20CZ	0.79
30CZ	0.76
2R30CZ	0.67
10CA	0.68
20CA	0.67
30CA	0.67
2R30CA	0.69

X-RAY PHOTOELECTRON SPECTROSCOPY (2)



Sample	Ru
2R30CZ	Ru^0 (20.51%), Ru^{4+} (23.77%), Ru^{n+} (12.48%)
2R30CA	Ru^0 (7.03%), Ru^{4+} (11.38%), Ru^{n+} (9.01%)

H_2 – Temperature Programmed Reduction



Sample	% Ru red	% Ce red
CeO_2 std	---	6.4
30CA	---	15.4
30CZ	---	15.2
2R30CA	132.7	14.4
2R30CZ	142.8	14.5

CeO_2 reduction peak shifted to lower temperatures. The presence of the support makes part of the ceria surface more reducible

Different Ru reduction signals:

1. < T°C well-dispersed RuO_x species, interacting CeO_2 surface (Ru−O−Ce)
2. > T°C well-crystallized RuO_2 species.

Conclusions…& Future Perspectives

The six ceria-base materials were tested at three different temperatures (150. 200 and 250°C) and the adsorption experiments demonstrated that:

1. An increment of the cerium oxide phase led to a greater amount of CO_2 adsorbed at high temperature
2. The synergic action of zeolite support further increased the adsorption capacity.

The results achieved in methanation tests demonstrated that the two catalysts are selective to methane production and effective at ambient pressure.

The **zeolite-supported** catalyst presents **higher CO_2** adsorption not balanced by a corresponding conversion to methane.

Optimization of the catalyst:
1. Diversify the synthesis of the catalysts
2. Further investigation of the reaction mechanism

New tests conditions:
1. Use of real gas atmosphere (humidity)
2. Different test temperature
3. Pressure