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TAILORING THE CATALYTIC FEATURES OF 3D HYBRID SYSTEMS FOR ONE-POT CO_2-TO-DME HYDROGENATION BY DIRECT INK WRITING

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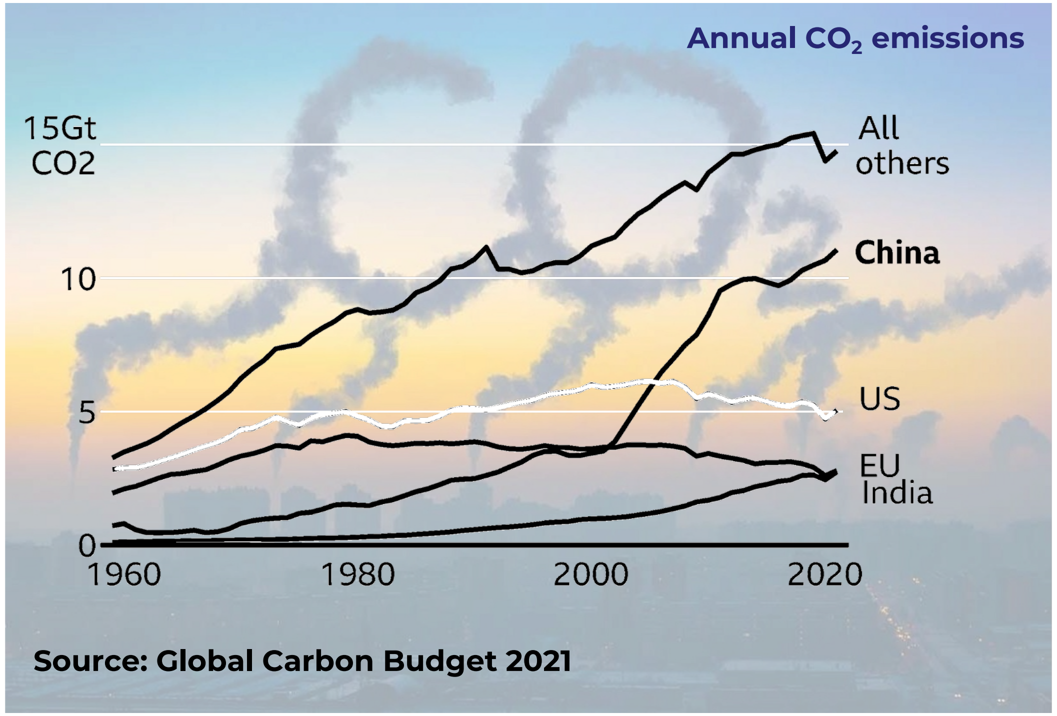
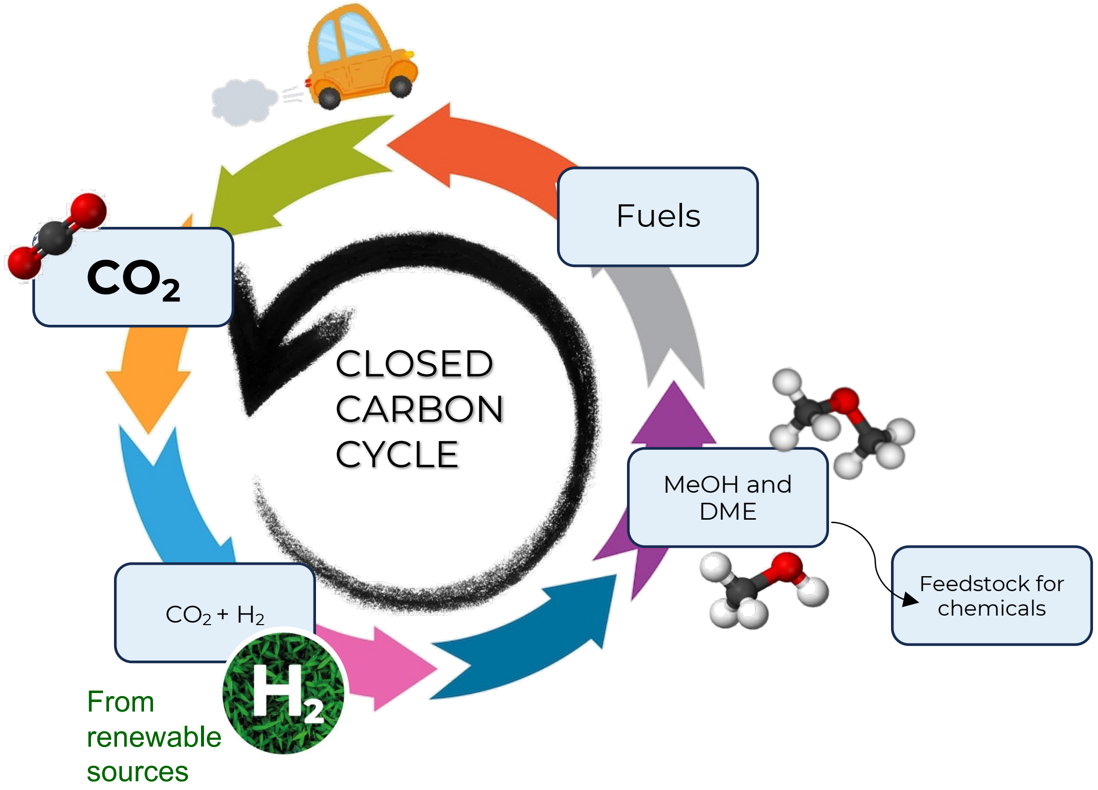
Overview

- Carbon Capture and Utilization technologies (CCU)
- DME: a multipurpose chemical & a fuel
- Conventional two-step processes
- Integrated one-step hydrogenation CO_2-to-DME
- Catalyst design, formulations and structures
- Conclusions and open issues

The World's Greatest Environmental Challenge

CCU strategies for a neutral CO_2 footprint





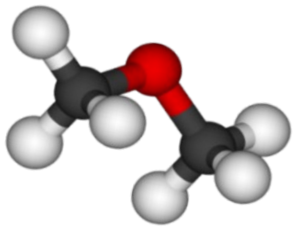
United Nations Climate Change

COP27 SHARM EL-SHEIKH EGYPT 2022

NEED FOR GREEN H_2

DME, a valuable future fuel

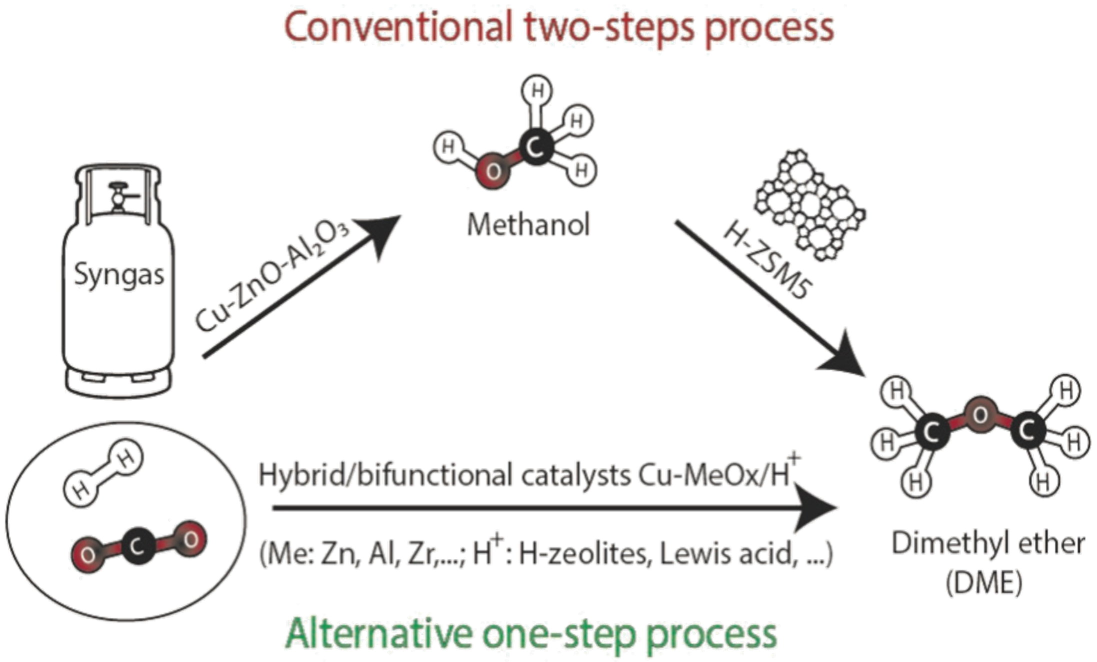
Properties
- High cetane number
- High efficiency of combustion
- Low-emission of NO_x, SO_x and CO



Applications
- LPG alternative
- Transportation fuel
- Power generation

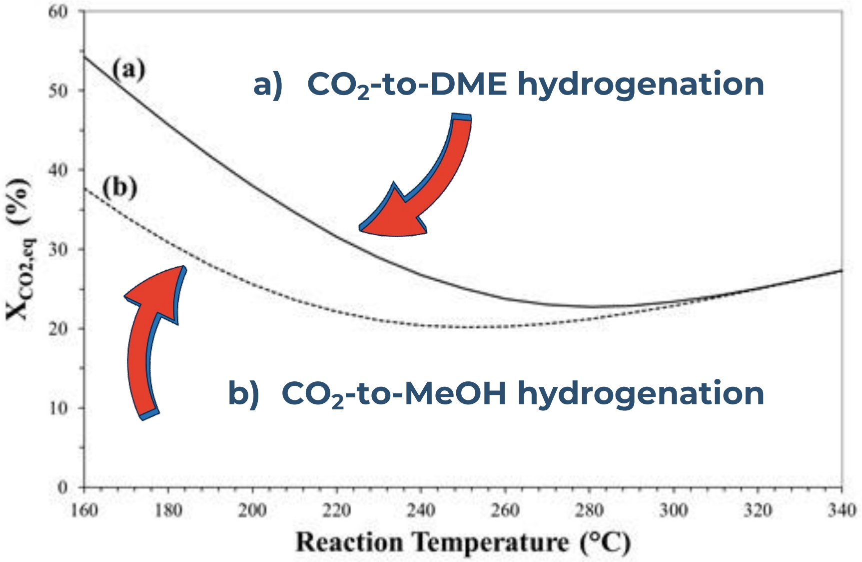
Property	Unit	DME	Diesel
Carbon content	mass%	52.2	86
Hydrogen content	mass%	1–3	14
Oxygen content	mass%	34.8	0
Carbon-to-hydrogen ratio	-	0.337	0.516
Liquid density	kg/m^3	667	831
Cetane number	-	>55	40–50
Autoignition temperature	K	508	523
Stoichiometric air/fuel mass ratio	-	9.6	14.6
Normal boiling point	K	248.1	450–643
Enthalpy of vaporization	kJ/kg	467.1	300
Lower heating value	MJ/kg	27.6	42.5
Ignition limits	vol% in air	3.4/18.6	0.6/6.5
Elastic Modulus	N/m^2	6.37×10^8	14.86×10^8
Liquid kinematic viscosity	cSt	<0.1	3
Surface tension (at 298 K)	N/m	0.012	0.027
Vapour pressure (at 298 K)	kPa	530	<10

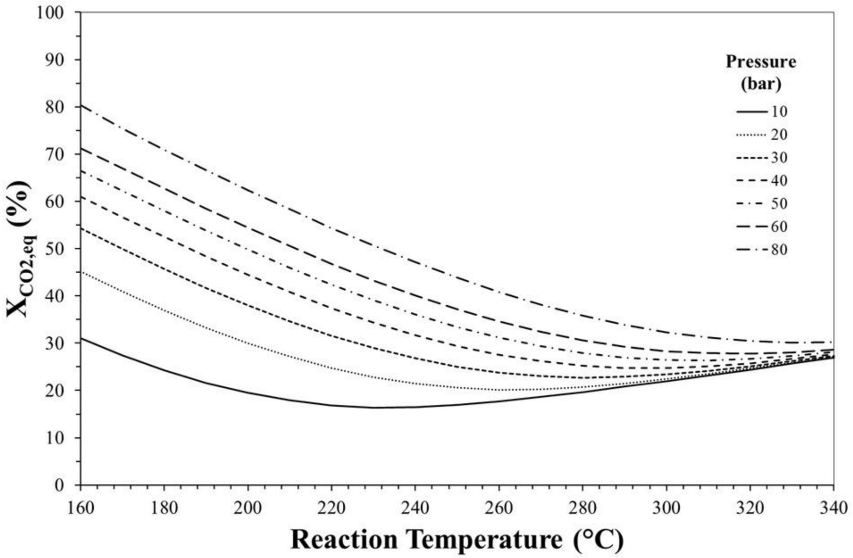
Catizzone et al., Molecules 2018, 23(1), 31



Thermodynamics of CO_2 hydrogenation

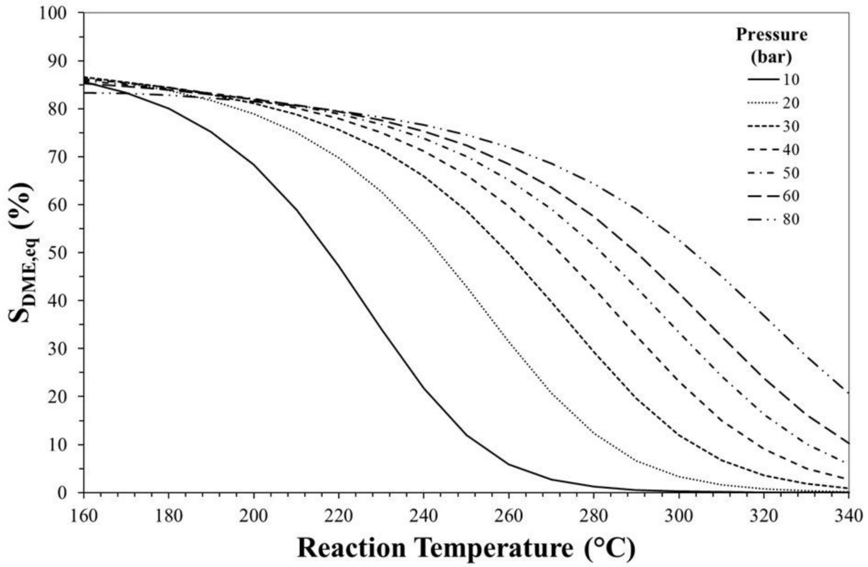
Catizzone et al., Molecules 2018, 23(1), 31



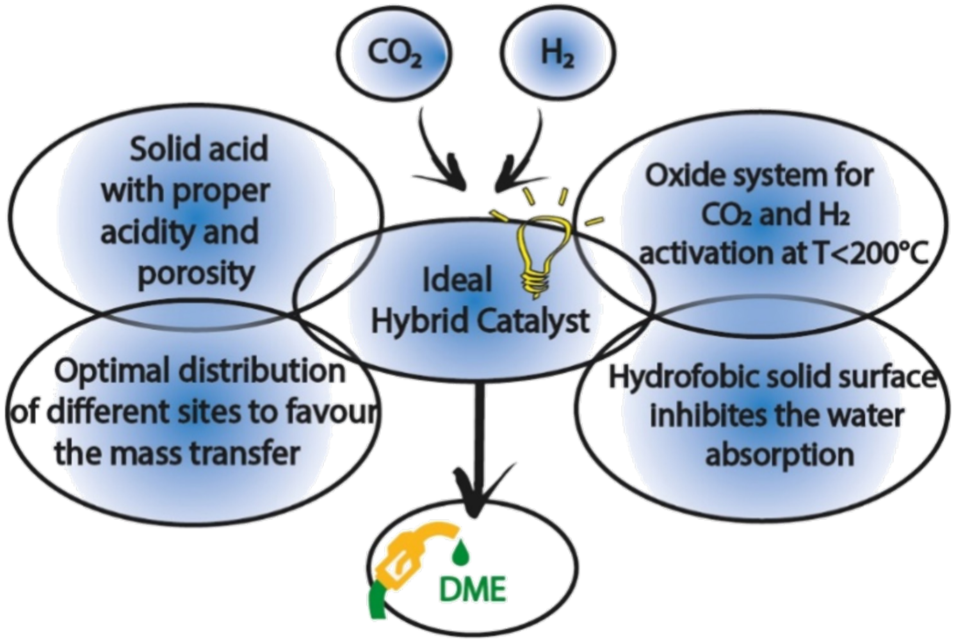


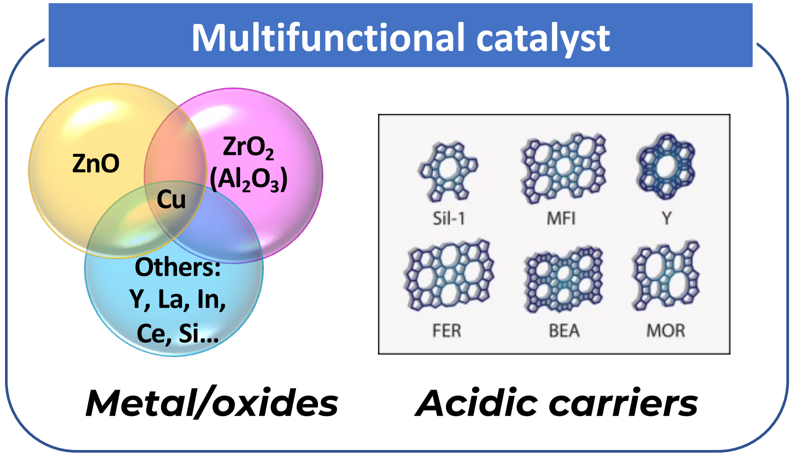
Reactions involved

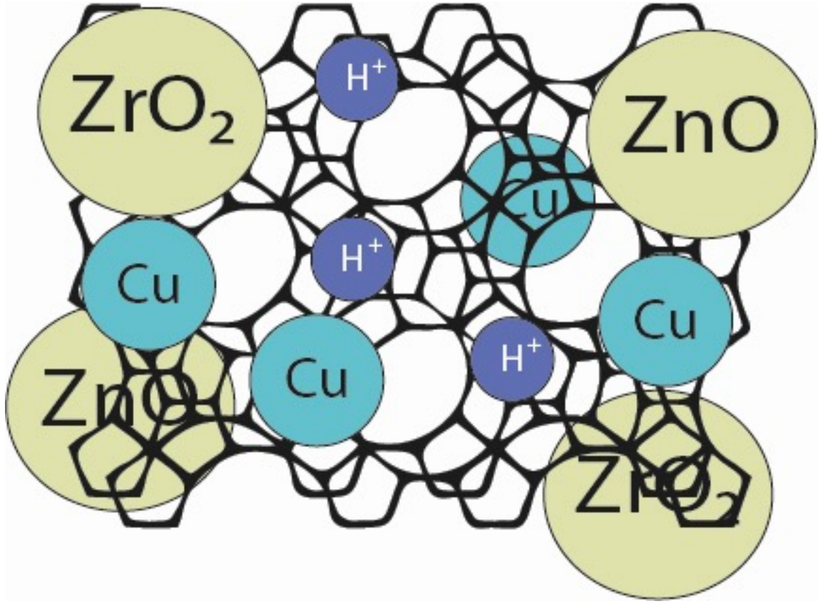
	$CO_2 + 3H_2 \Leftrightarrow CH_3OH + H_2O$	$\Delta\tilde{H}_R^o = -49.4 kJ \cdot (mol_{MetOH})^{-1}$
rWGS	$CO_2 + H_2 \Leftrightarrow CO + H_2O$	$\Delta\tilde{H}_R^o = +41.2 kJ \cdot (mol)^{-1}$
	$2CH_3OH \Leftrightarrow CH_3OCH_3 + H_2O$	$\Delta\tilde{H}_R^o = -24 kJ \cdot (mol_{DME})^{-1}$
	$CO + 2H_2 \Leftrightarrow CH_3OH$	$\Delta\tilde{H}_R^o = -90 kJ \cdot (mol_{MetOH})^{-1}$
	$2CO_2 + 6H_2 \Leftrightarrow CH_3OCH_3 + 3H_2O$	$\Delta\tilde{H}_R^o = -122 kJ \cdot (mol_{DME})^{-1}$



Design and synthesis of hybrid catalyst



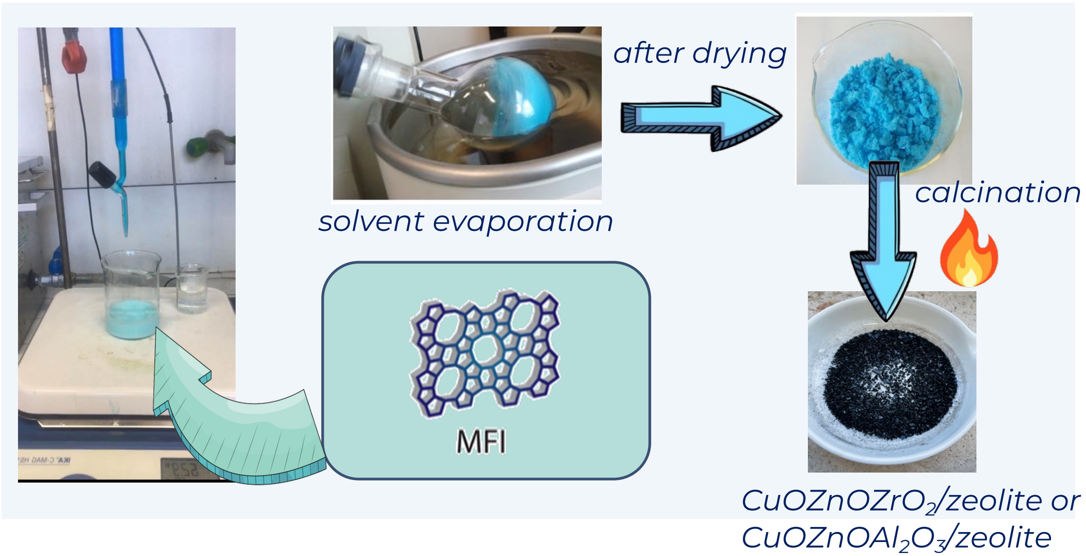




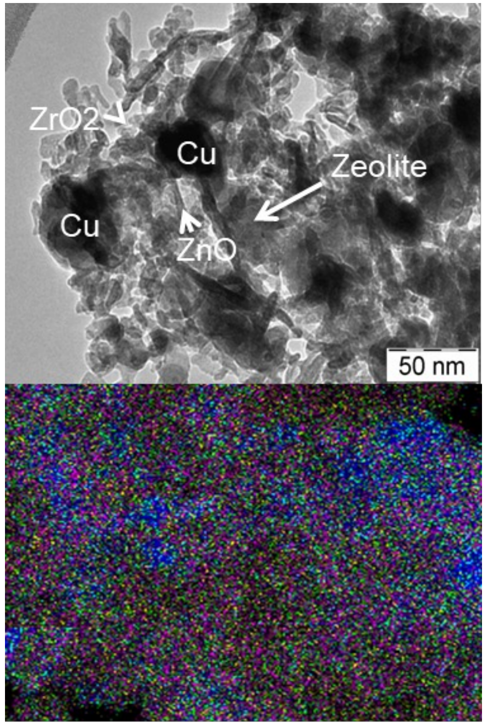
Combination of metal/oxides and acidic functionalities in a single solid system

Design and synthesis of hybrid catalyst

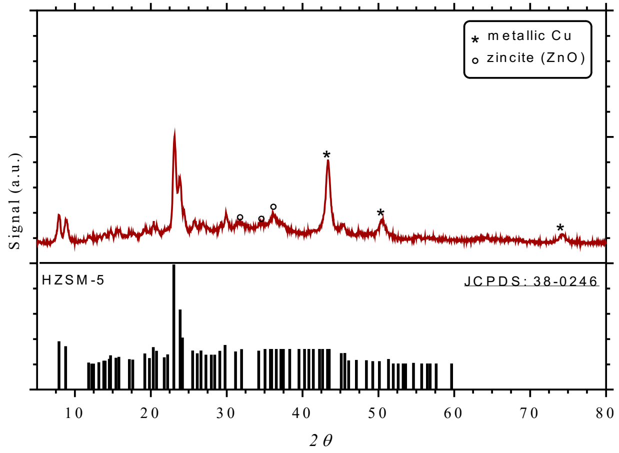
Gel oxalate coprecipitation method



Coprecipitation of metallic precursors (60/30/10 at.%) by oxalic acid in a slurry solution containing the zeolite



EDAX: CuZnZr:SiAl



Good homogeneity of metallic precursors, with long-range distribution of elements per unit of zeolite surface

Bonura *et al.*, Appl. Catal., B 176 (2015) 522-531.

Printing Strategies for Catalysts : Material Extrusion

a) Direct Ink Writing (DIW)

b) Fused Deposition Modeling (FDM)

c) Selective Laser Melting (SLM)

d) Stereolithography (SLA)

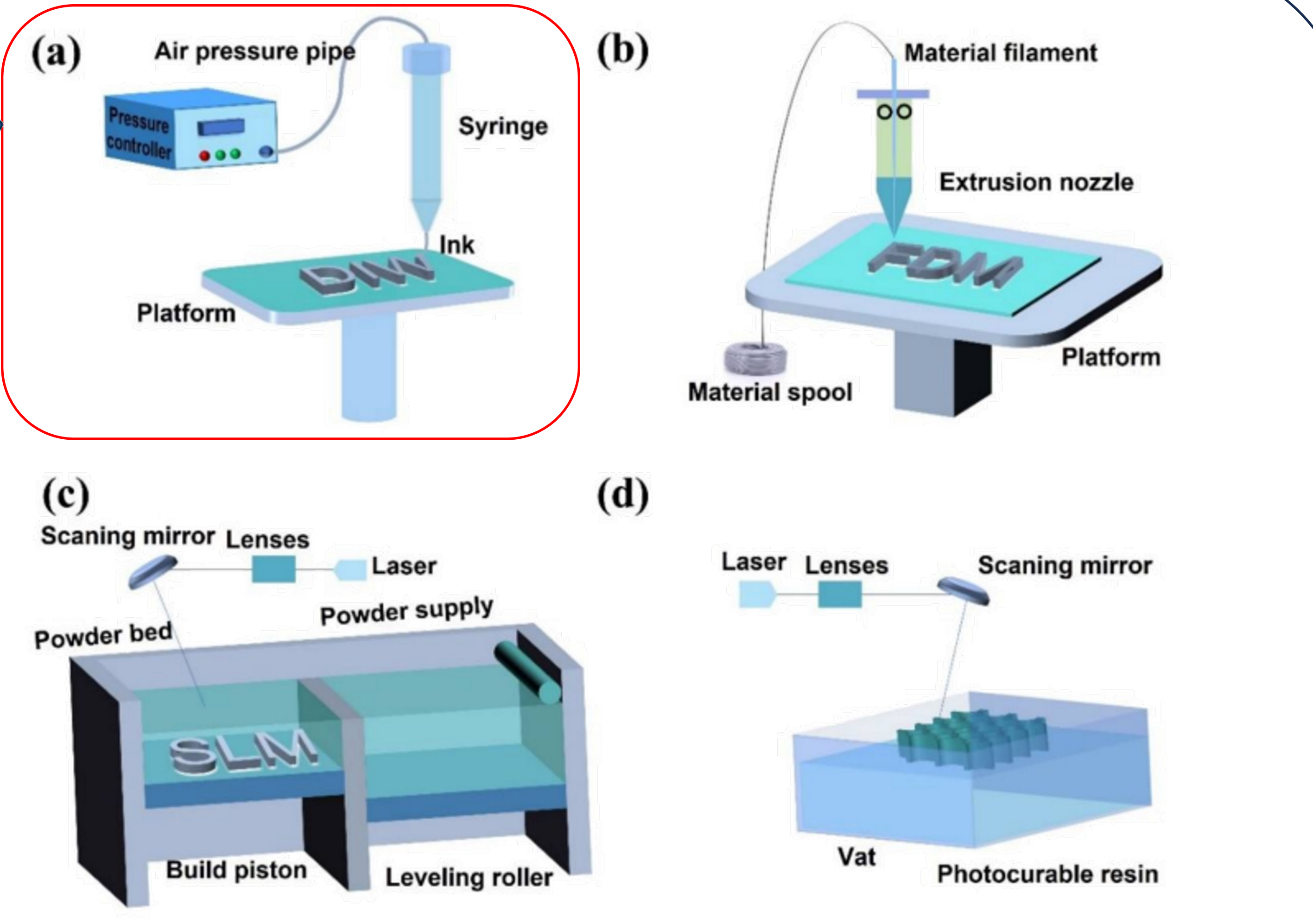


Figure 1. Schematic diagrams for (**a**) DIW, (**b**) FDM, (**c**) SLM and (**d**) SLA 3D printing strategies.

Chen et al., Catalysts 2022, 12, 1081

3D printing technologies for hybrid catalysts

Preparation of catalytic inks

Binders
- *Polyethylenimine (PEI)*
- *hydroxypropylmethyl* cellulose (HPMC)
- *Methyl cellulose (MC)*
- *Bentonite*

powder of CZA/MFI or CZZ/MFI

mixing

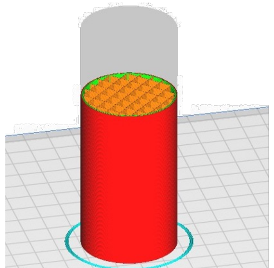
+ water + binder

ball mill

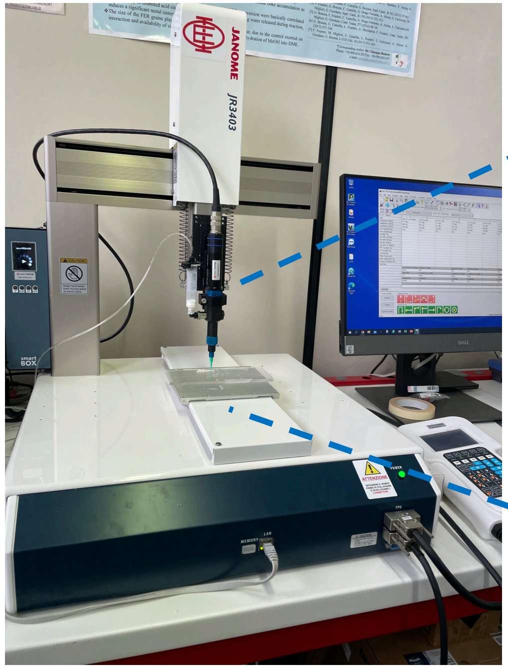
catalytic ink/paste

Robocasting extrusion-based 3D-printing

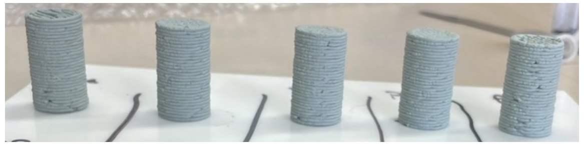
3D modeling



Cylinder shape



3D-printing step

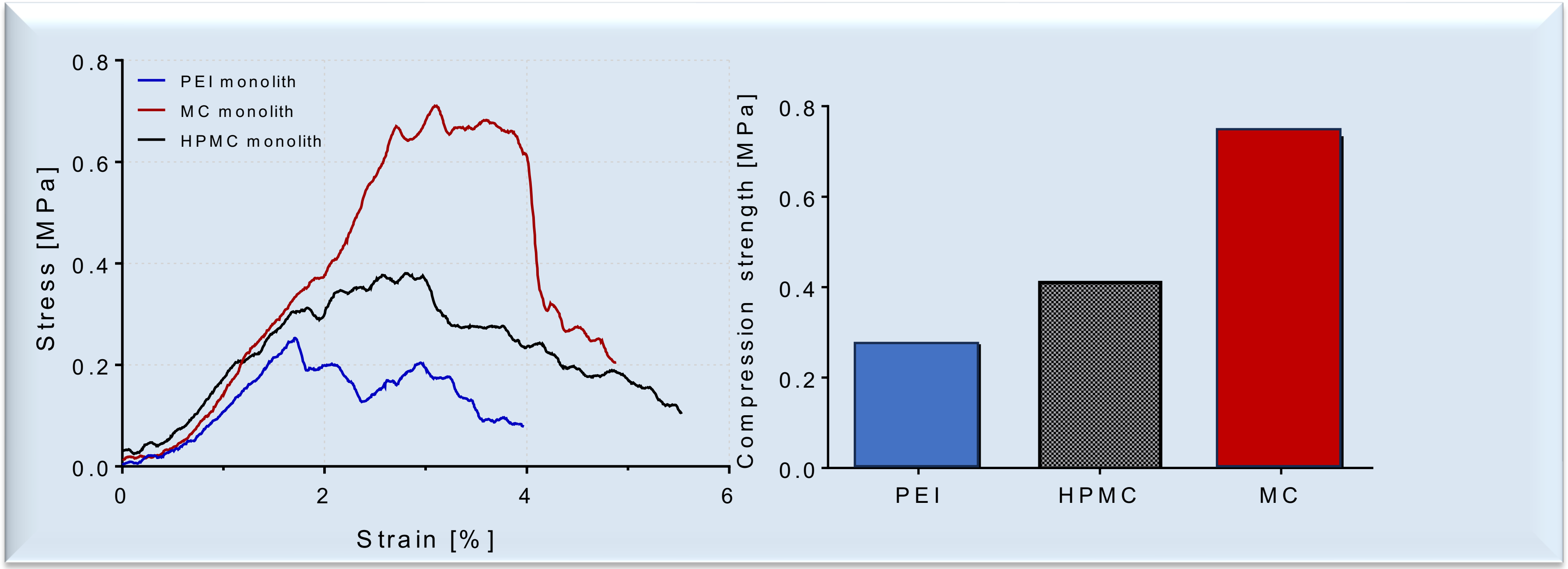


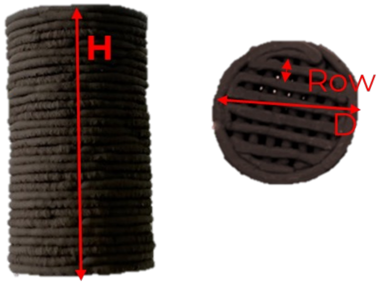
After calcination

3D catalysts

Mechanical strength of 3D monolith

Compression testing machine





Young's modulus

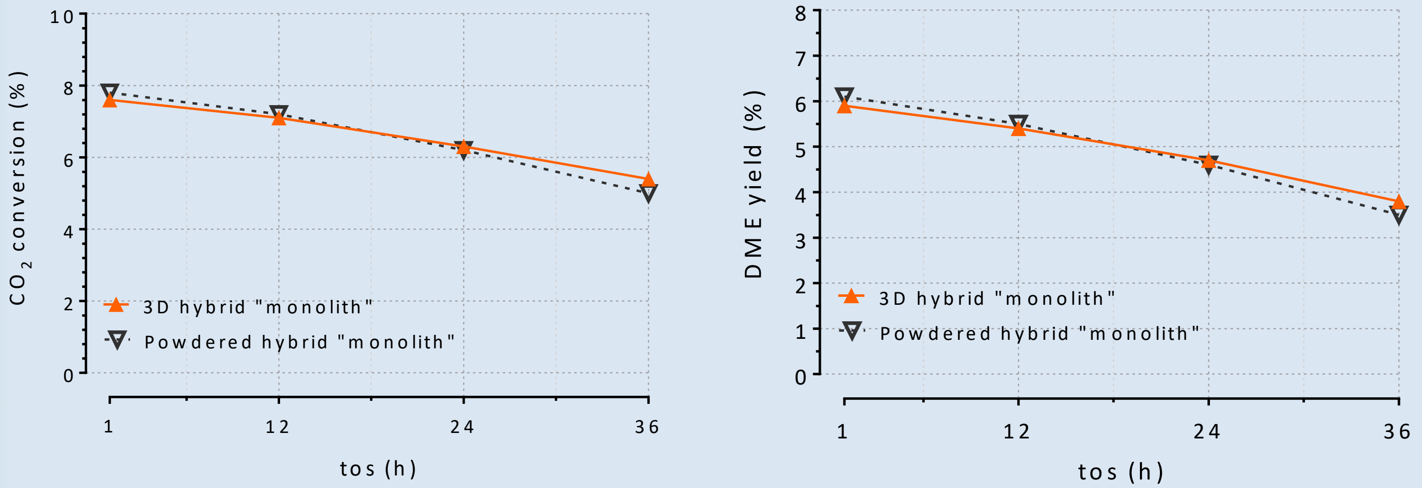
Sample	E (MPa)	σ_{max} (MPa)
CZA-Z PEI	0.125 ± 0.002	0.25
CZA-Z HPMC	0.169 ± 0.002	0.31
CZA-Z MC	0.201 ± 0.001	0.67

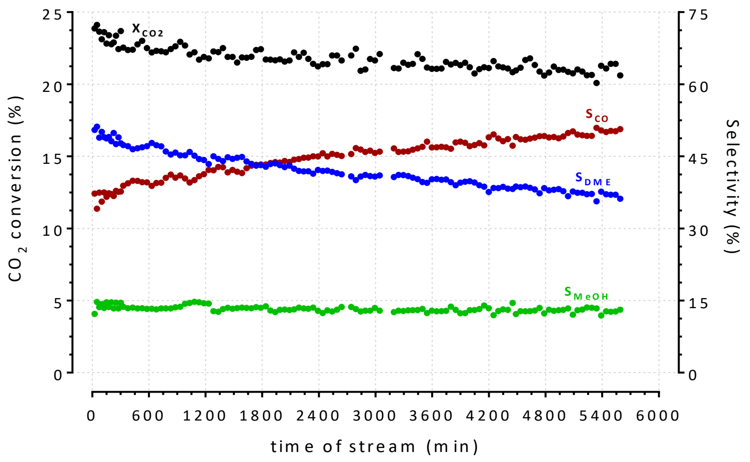
Catalytic Testing

CO_2 Hydrogenation plant

- Reduction *in situ* at 300°C (1 h)
- Testing : (T_R=200-300°C; P_R= 30 bar)
  CO_2/H_2 feed ratio: 1:3 v/v (GHSV: 1,000 $NL/kg_{cat}/h$)

220 °C @ 30 bar





Stability test @ 260 °C and 30 bar on CZA/MFI

Conclusions

- In line with the current policies on CCU, the development of a catalytic process for the direct hydrogenation of CO_2 to DME over hybrid systems is feasible.
- Hybrid catalysis holds the potential to integrate equilibrium-limited cascade reactions in one single reactor, so to deliver new process chains at higher conversion rate and productivity than conventional multi-step processes
- Once found the proper combination among ink-paste composition, 3D model and annealing treatments, the robocasting technique shows all its effectiveness, offering an alternative, cost effective and facile approach to fabricate structured catalysts
- The tunability of structural, chemical and morphological properties was seen to comprehensively mirror the features of conventional powdered catalysts used in CO_2 utilization technologies.

Open issues

- Operation at lower temperature (< 200 °C) for high selectivity to DME
- Need for novel active phases alternative to Cu
- Optimization of 3D design (number of layers, thickness of layers, …)
- Reactor design (multi-tubular configurations, recycle set-up, …)

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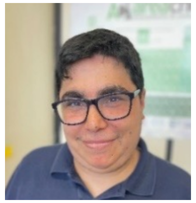

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