Tailored Catalytic Properties Induced by 3D Printing in Hybrid Monolith Structures for the One-step Synthesis of DME via CO_2 Hydrogenation

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G. Bonura[1], S. Todaro[1], E. Abbenhuis[2], G. Gerritsen[2], V. Middelkoop[3], Y. De Vos[3], C. Cannilla[1], F. Frusteri[1*]

1 CNR-ITAE, Istituto di Tecnologie Avanzate per l'Energia "Nicola Giordano", Via S. Lucia sopra Contesse 5, 98126, Messina, Italy

2 Hybrid Catalysis B.V., Helix STW-4.43, Den Dolech 2, 5612 AZ Eindhoven, The Netherlands

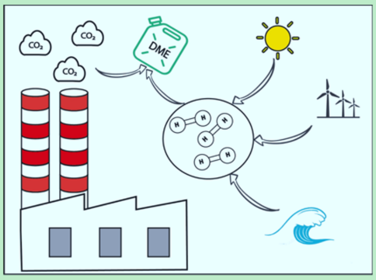
3 VITO NV, Vlaamse Instelling Voor Technologisch Onderzoek, Boeretang 200, BE-2400 Mol, Belgium

*Email address: francesco.frusteri@itae.cnr.it

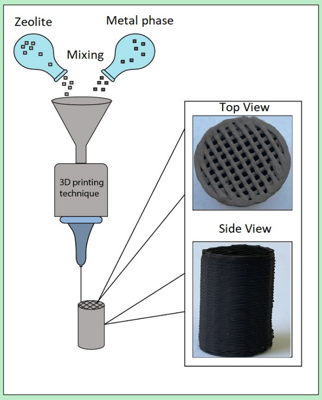
Introduction

The CO_2 conversion into high value products is an useful way to reduce greenhouse emissions [1].
In particular, the direct catalytic conversion of CO_2 into dimethyl ether (DME), represents an interesting solution in this sense due to its environmentally friendly properties as a substitute for conventional diesel fuel [2-3]. A *bi*-functional catalyst is necessary for the process, in which there are two active phases, a metallic phase for MeOH formation and an acidic functionality for MeOH dehydration into DME. In this work, Cu-ZnO-ZrO_2/HZSM-5 catalysts have been prepared by 3D printing in order to obtain novel systems characterized by controllable and precise architecture and reproducibility.

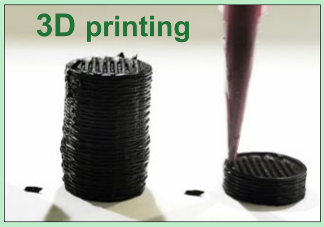
Factors affecting activity, selectivity and productivity of 3D catalysts in the direct hydrogenation of CO_2 to DME have been evaluated.



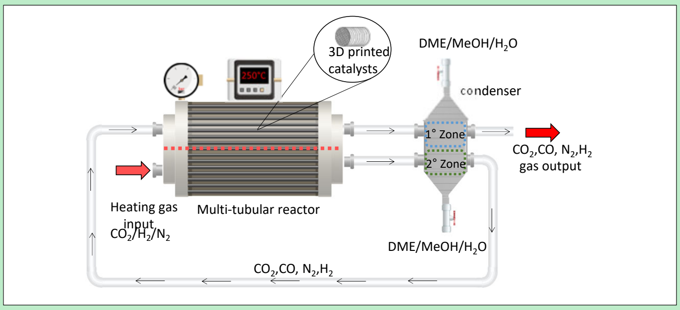
Catalyst Design



An ink paste based on Cu, Zn and Zr precursor and HZSM-5 zeolite was extruded through a thin nozzle and deposited layer-by-layer (external diameter, 13.0 mm; length, 50 mm; porosity voidage, 30%). The 3D printed structures were dried and then thermally treated for mechanical strength.

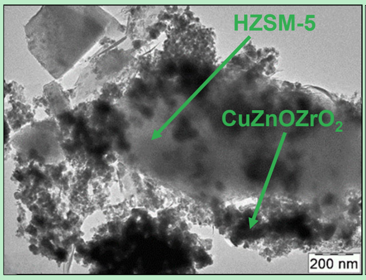


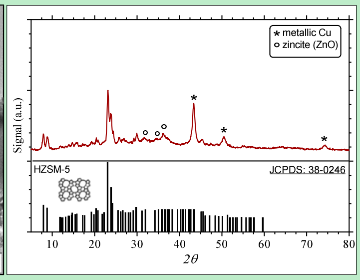
Plant Concept



The concept idea was to realize a multi-tubular reactor with a recirculation of stream at high rate and low pressure drop. The reaction mixture is flowed through the 1° zone of the reactor and then the product mixture reaches a condenser. The condensed phase can be drained and sent to the DME recovery section, the gas phase containing also CO can be recycled to a second inlet of the reactor for a passage in a second zone of reactor to complete the reaction, again condensing the DME-rich phase in a second zone of the condenser prior to be sent to the separation.

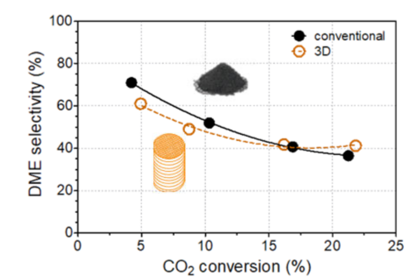
Morphology and Structure

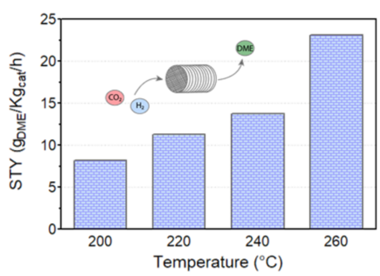


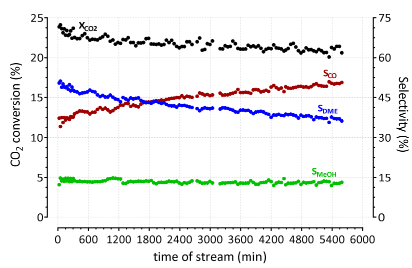


The printing procedure favours a quite uniform distribution of mixed oxides on the zeolite framework, ensuring an intimate surface contact among the phases and predicting minor restrictions in terms of transport phenomena during reaction. The intensities of the diffraction peaks at low angles (<20°) and ascribed to HZSM-5 are diagnostic of a zeolite structure well-preserved after printing and chemical interaction with metal precursors.

Catalytic Results







The catalytic behaviour of the 3D catalysts in the direct CO_2-to-DME hydrogenation reaction (GHSV: 1,000 *NL*/g_{cat}/h; $CO_2/H_2/N_2$: 3/9/1 v/v) was investigated at 30 bar and 200-260°C, in a tubular fixed bed reactor (i.d., 14 mm; l., 250 mm)

On the whole, the catalytic data suggest the effectiveness of the printing technique in the synthesis of materials with tailored features, allowing a good control and reproducibility of physico-chemical properties as well as a huge potential for future commercial exploitation.

Conclusions

- The development of hybrid catalysts allows a cost-efficient valorisation of CO_2 sources, so opening new pathways for producing DME. Key to an effective CO_2 recycling and utilization is the use of "green" hydrogen.
- The 3D printing technique represents a very powerful tool to realize multi-material components, characterized by tailored architectures and formulations, tuneable properties and a repeatability at a major extent than conventional materials.
- Physico-chemical measurements and catalytic data clearly demonstrate how Carbon Capture and Utilization technologies (CCU) can significantly benefit from the use of finessed 3D catalyst materials.

References

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