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INTENSIFICATION EFFECT ON CATALYTIC CO₂ HYDROGENATION TO DME PROMPTED BY WATER-ADSORBENT SYSTEMS

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Speaker: Dr. Serena Todaro

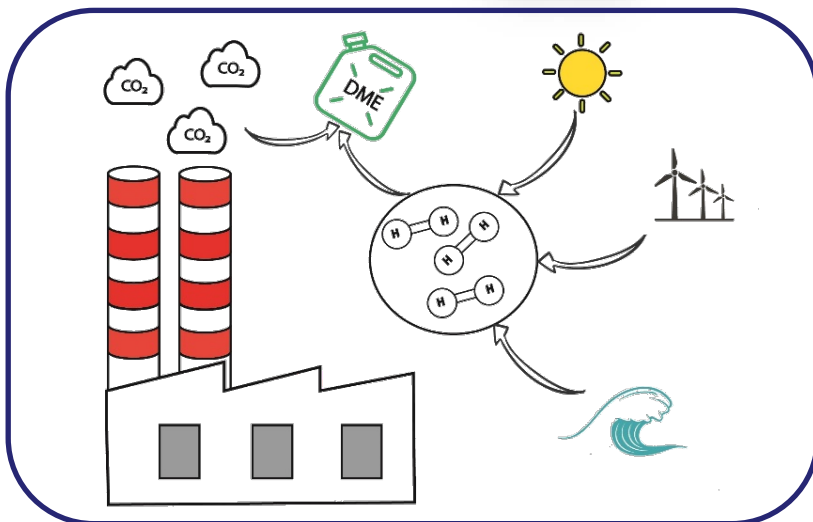
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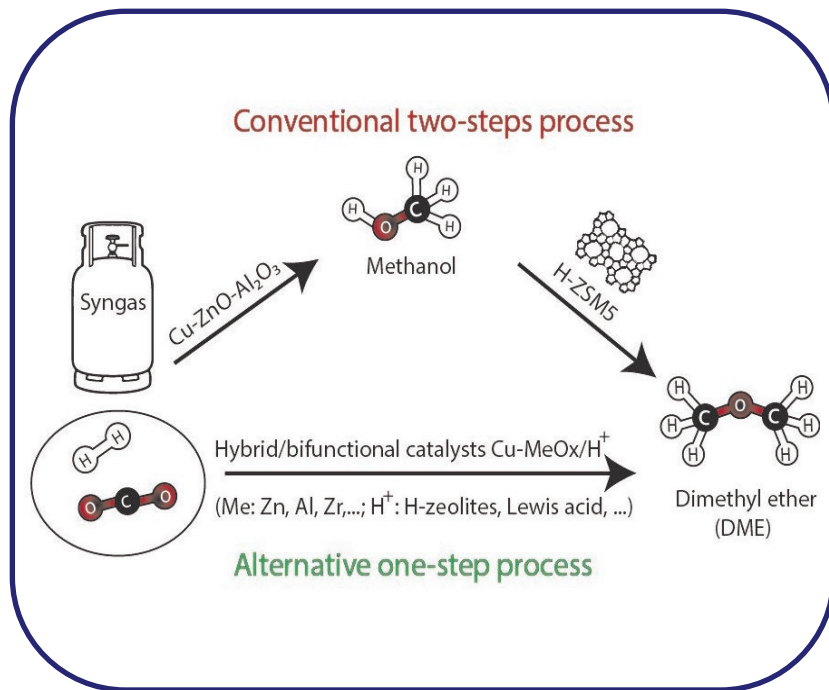
DME

Properties

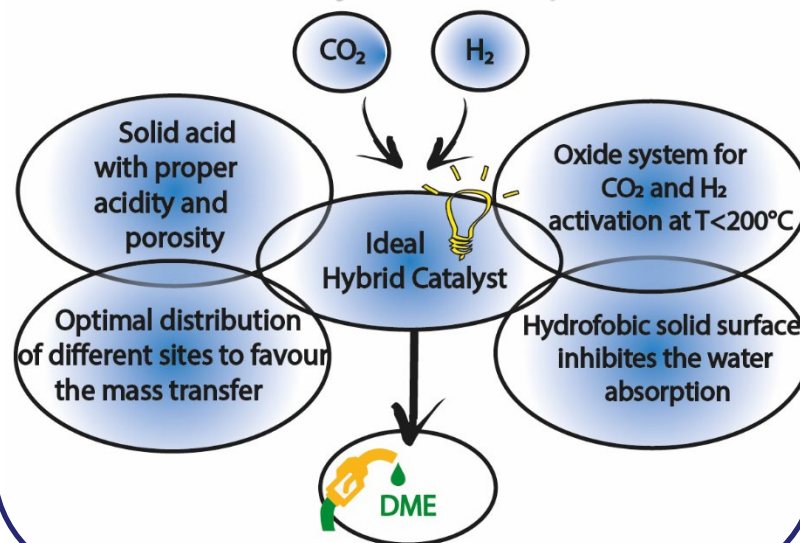
- High cetane number
- High efficiency of combustion
- Low-emission of NO_x, SO_x and CO

Applications

- LPG alternative
- Transportation fuel
- Power generation



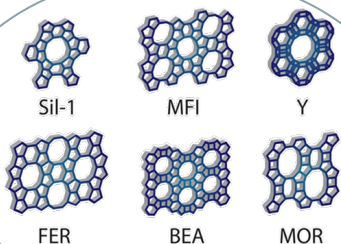
Catalyst Concept



Catalyst Preparation

- Hybrid catalyst: $\text{CuZnOZrO}_2@$ zeolite (metal-oxides):zeolite (1:1 wt/wt)

Cu, Zn and Zr
nitrate
precursors



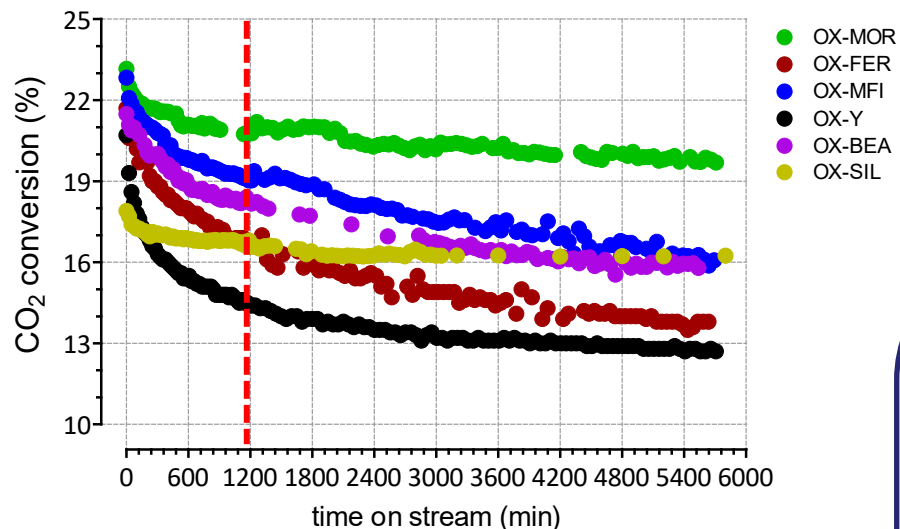
*Gel-oxalate
coprecipitation
method*

Catalyst Testing

- Reduction *in situ* at 300°C (1 h)
- Testing : ($T_R=200-300^\circ\text{C}$; $P_R= 30$ bar)
GHSV= 8,800-18,000 NL/g_{cat}/h.
CO₂/H₂/N₂, 23/69/8 v/v



Catalytic behaviour of hybrid systems



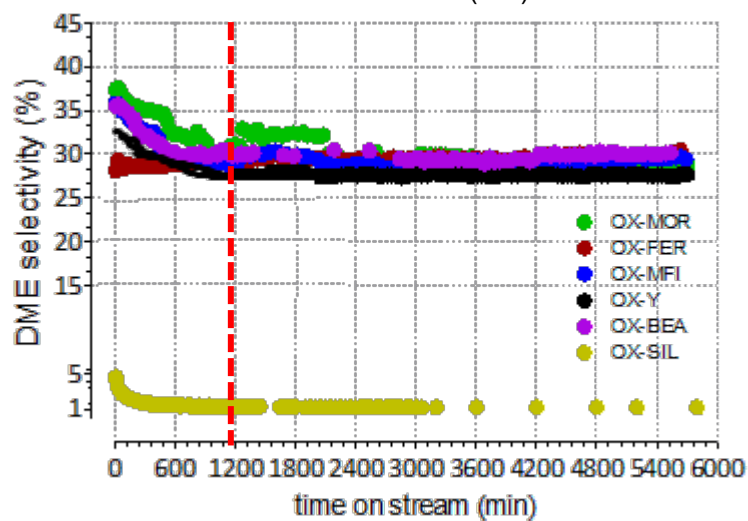
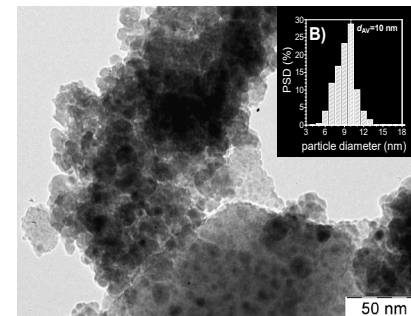
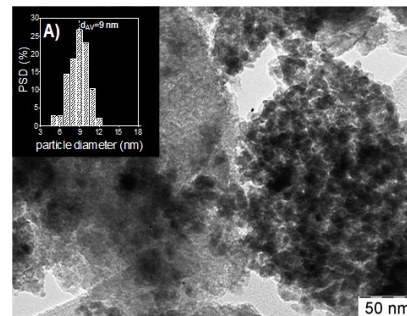
Experimental conditions:

T_R : 260 °C; P_R : 30 bar;
 $GHSV$: 8,800 NL·(kg_{cat}·h)⁻¹
 $H_2:CO_2$ 3:1 (vol)

Investigation on coke formation & metal sintering

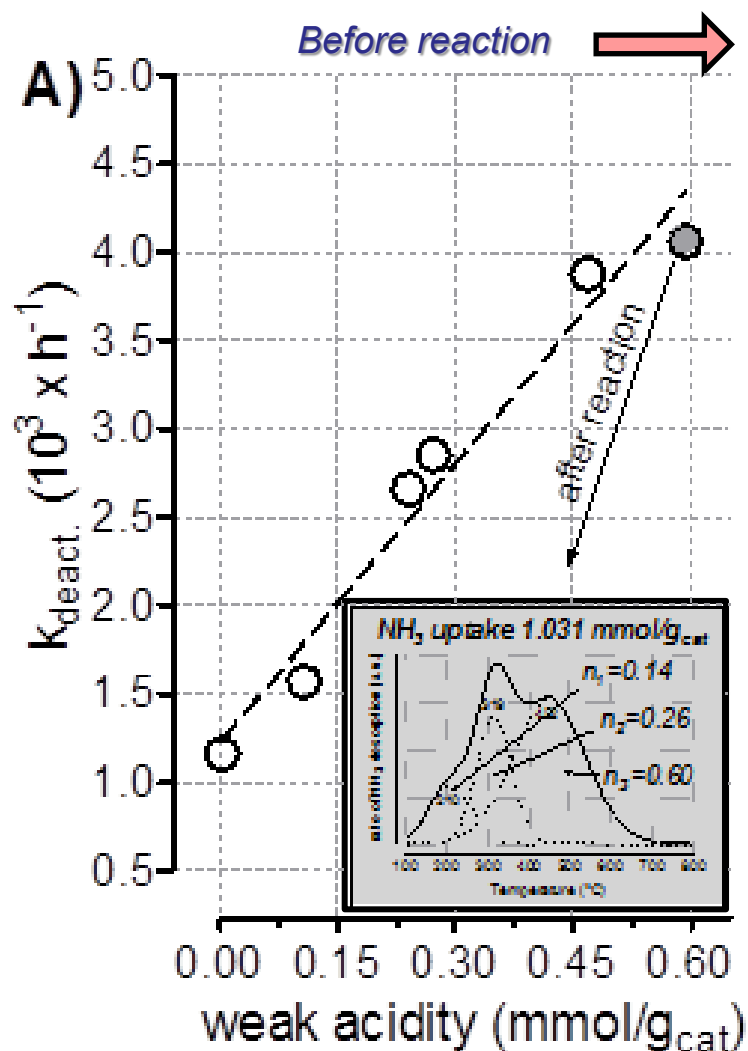
fresh

used



Neither coke or metal sintering can be invoked as responsible for the decay of activity

The influence of water on the catalytic stability



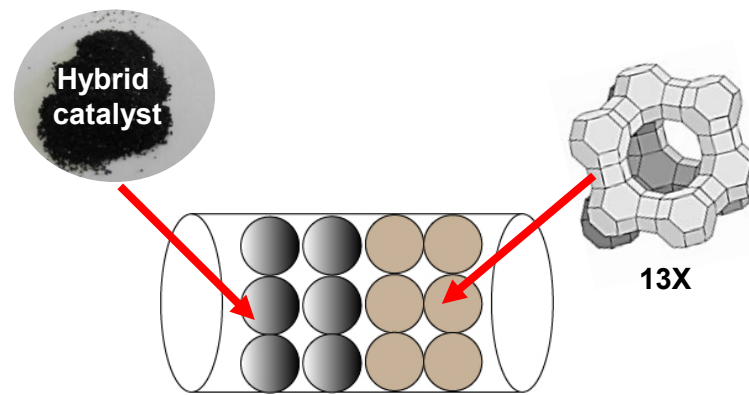
Loss of acid capacity mainly attributable to a decrease in weak acidity.

Deactivation constant (k_{deact}), determined for the various systems as independent on the coke accumulation, increases with weak acidity

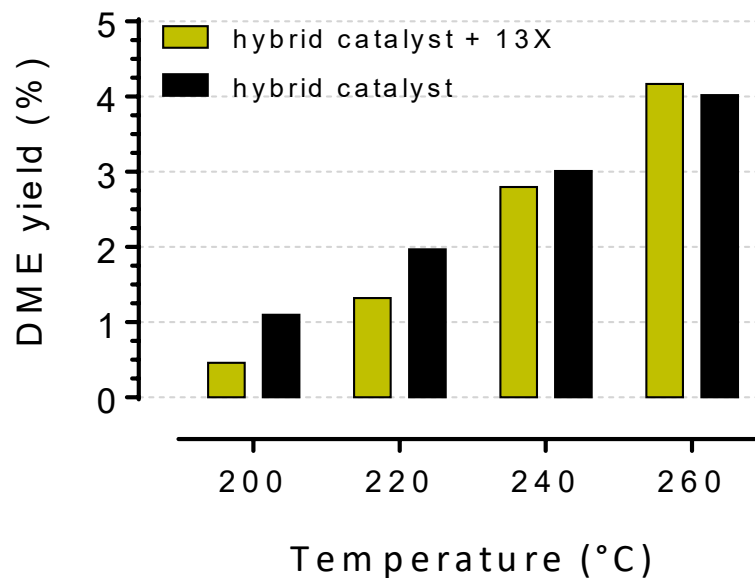
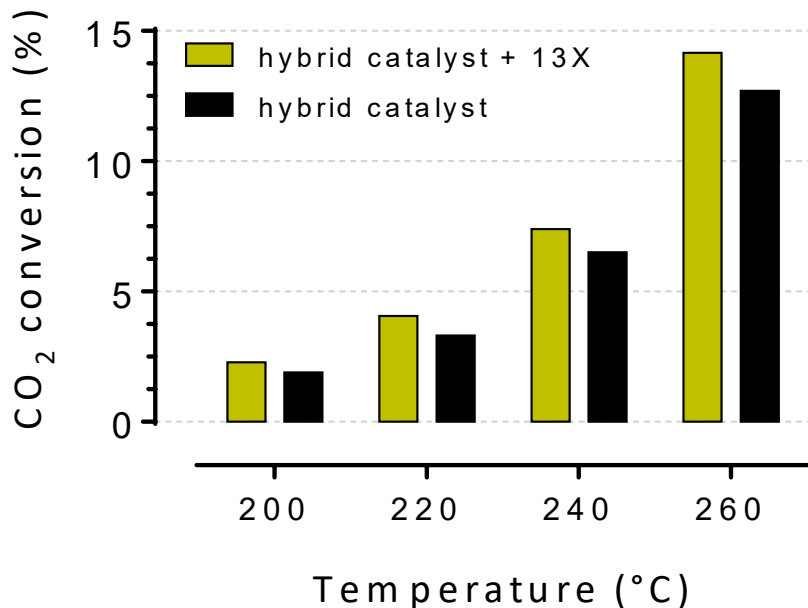
The weak acid sites generated on the hybrid catalysts during co-precipitation exhibit a significant mobility, being more prone to migrate in presence of water.

The effect of adding 13X zeolite

Experimental conditions:
 T_R : 200-260 °C; P_R : 30 bar;
 $GHSV$: 18,800 NL·(kg_{cat}·h)⁻¹
 H_2 :CO₂ 3:1 (vol)

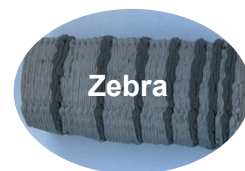


configuration of the bed reactor



Conclusions

- In line with the current policies on CCU, the development of a catalytic process for the direct hydrogenation of CO₂ to DME over hybrid systems is feasible.
- The hybridization of active sites of different nature is fundamental to deliver a process with no limitation in terms of mass transfer.
- The intensification of the synthesis process of dimethyl ether (DME) represents a promising approach to overcome the thermodynamic limitations of the conventional DME process.
- The use of hydrophilic zeolitic matrix systems combined with the hybrid catalyst effectively allows water to be absorbed even at high pressure and temperature.



Future challenges

- 3D printed catalyst obtained alternating layers of hybrid system and water adsorbers (e.g. LTA zeolite).

Acknowledgements

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