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Catalytic vs electrocatalytic reduction of CO_2 to added-value products

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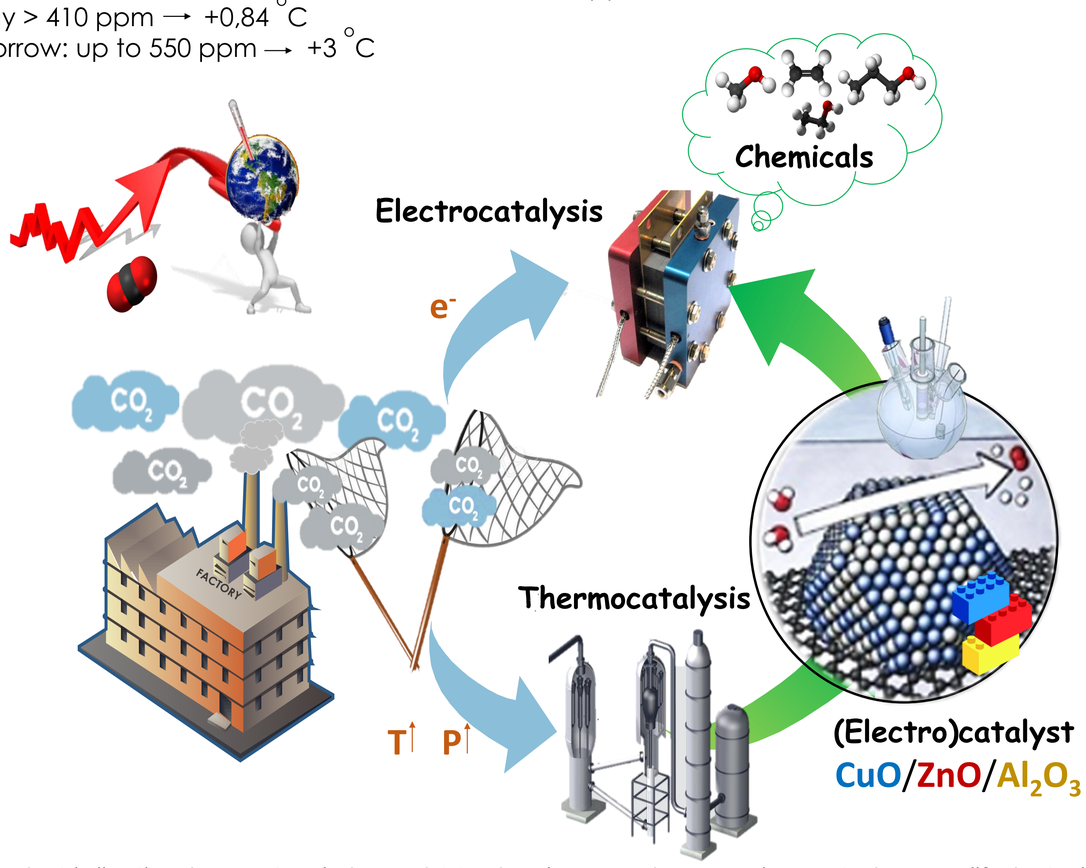
Overview

CO_2 concentration before industrial revolution = 270 ppm
Today > 410 ppm → +0,84 °C
Tomorrow: up to 550 ppm → +3 °C



The industrialization has not only brought technology and convenience to human life but also the increase in the concentration of CO_2 in the atmosphere over 400 ppm causing the raising of global temperature [1].
Nowadays, exploiting CO_2 as a raw material to synthesize high added-value products via electrochemical reduction reaction is a sustainable interesting process to capture and store energy renewable and CO_2 in the form of chemicals or fuels [2]. In such context, we are exploiting the basic knowledge of thermochemical catalysis to understand the synergies between these two processes and make faster progress in the development of an optimal electrocatalyst [3].

Methods and Materials

A **commercial** material composed of CuO, ZnO, Al_2O_3 and a small amount of magnesium oxide (CZA CC) was studied as catalyst in Thermocatalytic and Electrocatalytic tests (See Fig, 1 and 2)

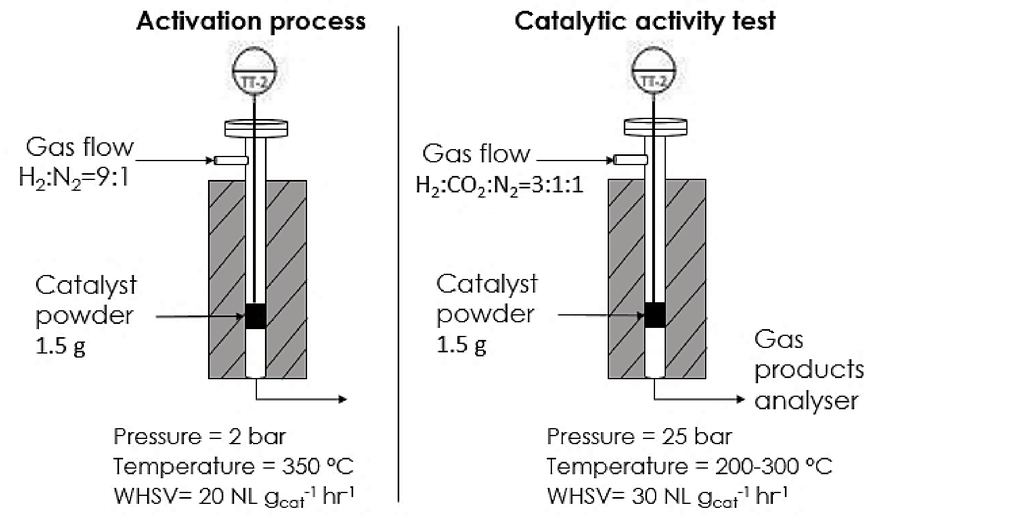


Fig. 1 Thermocatalytic Experimental Setup

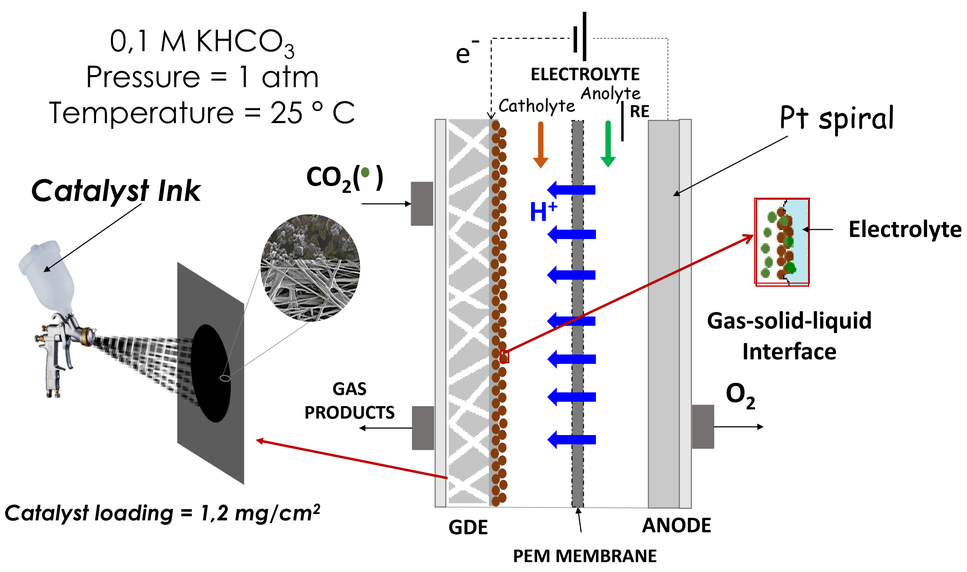
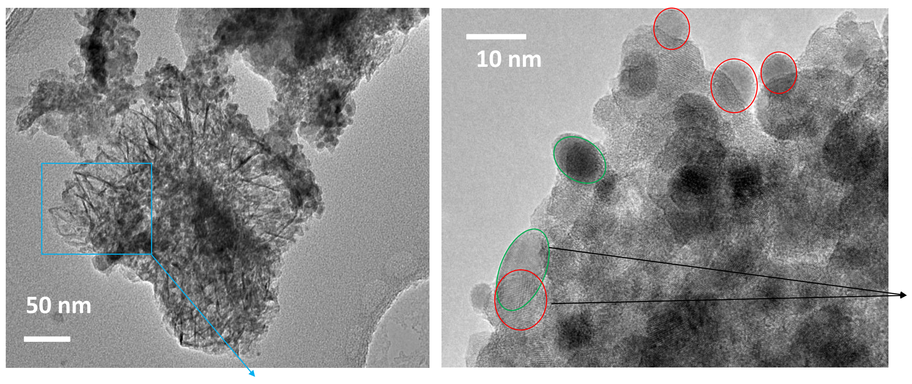


Fig. 2 Electrocatalytic Experimental Setup

Investigation Highlights

Fig. 3 *TEM images: CZA morphology*



There are **two distinct** morphologies:
1. **Spherical** (5-10 nm diameter)
2. **Elliptical** (10-15nm major axis)

Table 1 *Physicochemical properties*

Catalyst	Mass percentage, wt%	BET surface area, $m^2\ g^{-1}$	Total pore Volume, $cm^3\ g^{-1}$	Mesopore volume, $cm^3\ g^{-1}$
CZA CC	CuO 63,5 % ZnO 25 % Al_2O_3 10 % MgO 1,5 %	92	0,182	0,164

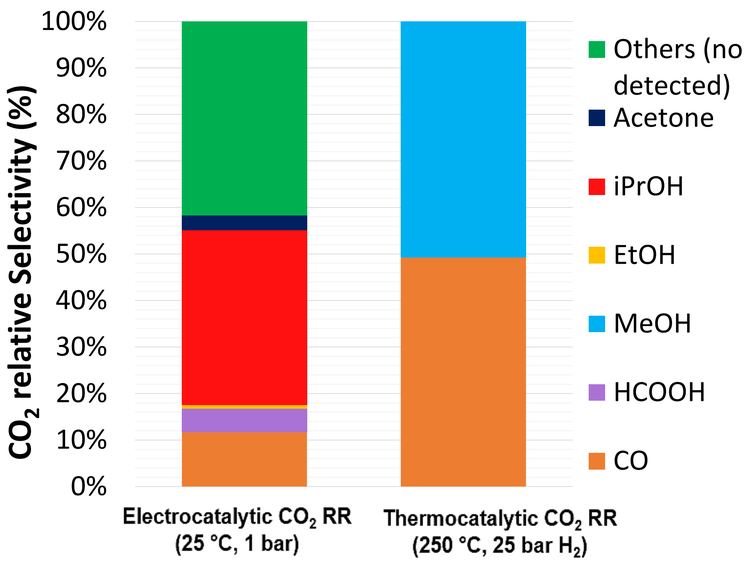


Fig. 4 CO_2 relative selectivity for different products in Thermocatalytic and Electrocatalytic process.

- CZA CC can produce ≥C_2 products at ambient T, via CO_2 electroreduction.
- CZA can also produce methanol at higher T and P, via CO_2 hydrogenation.
- The selectivity ratio of oxygenates/CO is about 8 times higher in the Electrocatalytic test than in the Thermocatalytic one.

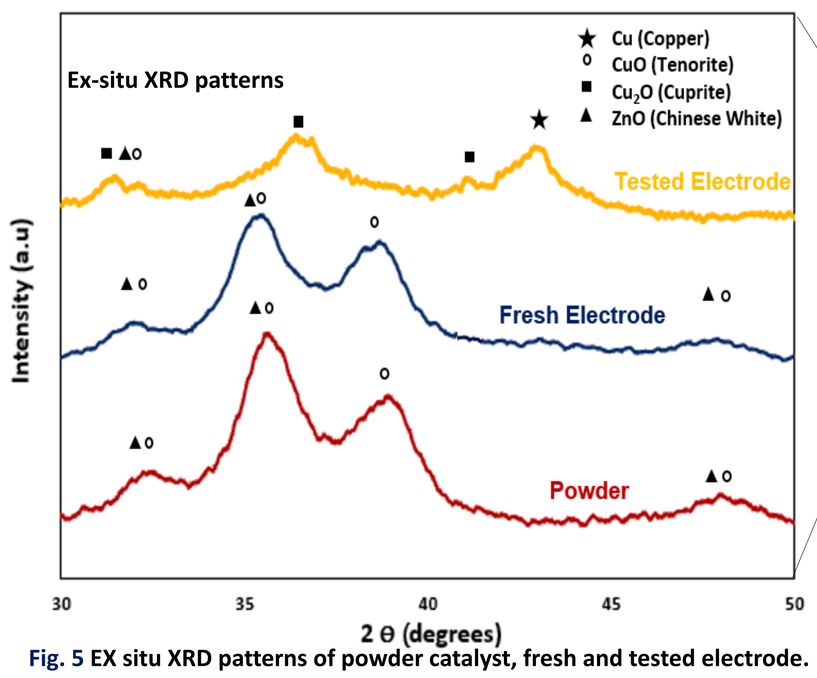


Fig. 5 EX situ XRD patterns of powder catalyst, fresh and tested electrode.

- The powder catalyst and fresh electrode are quite similar.
- The fresh and Tested electrodes evidenced the reduction from Cu^{+2} to Cu^{+1} and Cu^0 during the **Electrochemical reaction**.
- Exhausted catalyst (**not shown**) from **Thermocatalytic reaction** evidenced a complete reduction from Cu^{+2} to Cu^0 .

Recent studies have shown that the interface between Cu^{1+} and Cu^0 contributes to the dimerization of CO adsorbed on the electrode surface to generate products ≥ C_2.

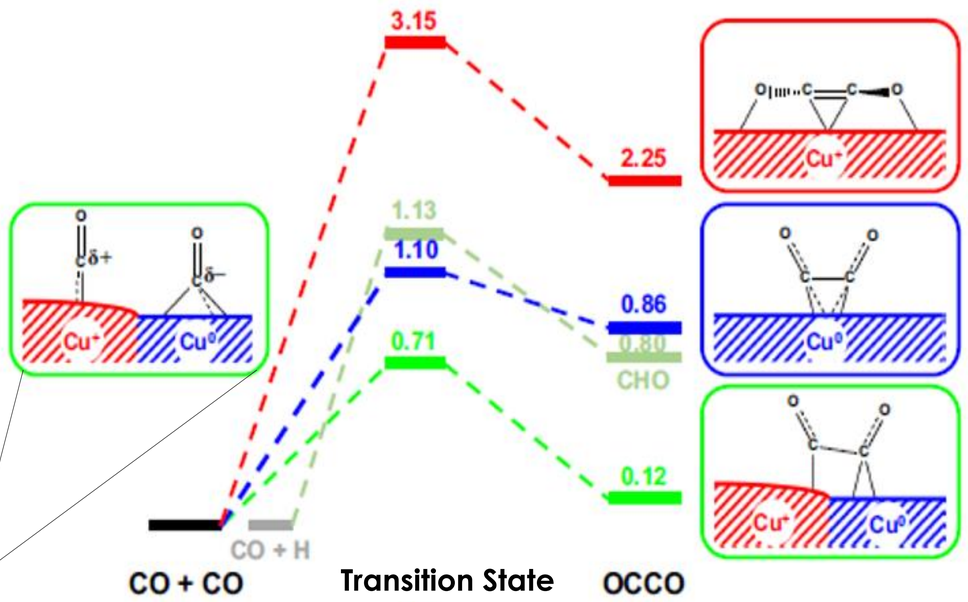


Fig. 6 Free energy profiles of CO dimerization for CO hydrogenation to form surface CHO species taken from reference [4].

Ongoing Work

We are developing a benchmarking protocol to study the activity, stability and Faradaic efficiency of synthesized materials with the same components. The activity of these material will be tested in a home-made prototype of electrochemical reactor created by using 3D printing process and technology.

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