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## SUPPORTING INFORMATION

### Exsolved Cu-ZnO Interfaces for Methanol Production from CO<sub>2</sub> hydrogenation at atmospheric pressure

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## Methods

### Synthesis

The catalyst was synthesized via a modified solid state method. Oxide precursors (CaCO<sub>3</sub>, TiO<sub>2</sub>, La<sub>2</sub>O<sub>3</sub>) were first dried and weighed while hot and were then mixed with the nitrate precursors (Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and Cu(NO<sub>3</sub>)<sub>2</sub>·5H<sub>2</sub>O). The powders were sonicated in acetone until achieving a homogeneous solution and were subsequently dried in the drying oven at 65 °C. The dried mixture was then transferred to alumina crucibles and calcined in air at 1000 °C for 12 hr (ramp rate, 5 °C/min). The calcined powder was then milled for 2h at 500 rpm and the milled powder was sintered at 1000 °C for 24 hr. The as-prepared perovskite oxide was reduced under H<sub>2</sub> with a 100 ml/min flow rate at 500°C for 10 hr at atmospheric pressure.

### X-ray diffraction

The crystalline phase components of all freshly prepared and reduced samples were investigated using X-ray diffraction (XRD) (X'Pert Powder from PANalytical) with Cu K $\alpha$  radiation ( $\lambda = 0.154$  nm) at 40 kV and 30 mA. For the measurements, the diffraction patterns were recorded from 10° to 90° (2 $\theta$ ) with a scanning speed of 0.011°sec<sup>-1</sup>.

Rietveld refinement of the Cu-exsolved sample was carried out using GSAS-II. Background (shifted Chebyshev polynomial, 7 terms), unit cell parameters, atomic coordinates, thermal displacement parameters, microstrain and size were gradually refined. Space groups used were *Pbnm* for the perovskite phase and *Fm-3m* for the metallic Cu phase.

## Scanning electron microscopy

Scanning electron microscope (SEM) images of the fresh and reduced samples were taken using Thermo Fischer Apreo 2 SEM. The catalyst samples were affixed to the sampling plate with carbon black tape and partially coated with silver to improve the imaging of samples. The SEM images were taken under high vacuum condition with a working distance range of 2.8–10 mm and magnification range of 100 to 1,000,000. Image processing program (ImageJ) was used to carry out the morphological analysis of the SEM images such as crystal size and exsolved particle population and size.

## Transmission electron microscopy

The samples for TEM and STEM-EDX analysis were prepared by drop-casting the powders of the reduced and post-testing samples previously dispersed and sonicated in high purity propan-2-ol (10  $\mu$ L) on holey-C coated Au TEM grids (Quantifoil, 300 mesh) which were previously plasma cleaned in Ar (20 seconds) to remove possible contamination before sample dropcasting. The analyses were performed with a Thermo Scientific Talos F200X TEM operated at a 200 kV voltage equipped with a CMOS 16 Mpx camera and an EDX detector (Gatan).

## X-ray photoelectron spectroscopy

X-ray Photoelectron Spectroscopy (XPS) spectra were recorded using a Thermo Scientific K-Alpha+ spectrometer. The system operates at a base pressure of  $8 \times 10^{-9}$  mbar. It incorporates a monochromated, micro-focused Al K $\alpha$  X-ray source ( $E = 1486.6$  eV) and a 180° double focusing hemispherical analyser. For all measurements, the X-ray source was operated at 6 mA emission current and 12 kV anode bias. The maximum spot size was 400  $\mu$ m<sup>2</sup>. Sample charging during measurement was minimised with an in-built dual-beam source, consisting of an ultra-low energy co-axial electron and Ar<sup>+</sup> ion beam. Powder samples were mounted onto a tantalum sample plate with conductive copper tape. The pass energies at which core-level and survey spectra were recorded were 20 and 200 eV, respectively. Modified auger parameters ( $\square'$ ) for Cu and Zn were obtained by summing the 2p<sub>3/2</sub> binding energy and L3M45M45 kinetic energy. Due to the complex overlapping signals constituting the core level and Auger signals of Cu and Zn, the peak position was taken as the point of highest intensity. The one exception to this is the Cu L3M45M45 Auger signal, where the complex line shape and poor signal to noise ratio necessitated the assignment of a range of energies rather than a specific energy. For all other core levels, peak fitting was performed using the Thermo Avantage software; a Shirley background was applied, and the shape of all peaks was constrained to be a convolution of Gaussian and Lorentzian line shapes (80% Gaussian-20% Lorentzian, with no asymmetry). Binding energy correction was performed by setting the C 1s peak of adventitious carbon (C-C) at 284.8 eV, with all other peaks shifted accordingly. An estimate for the B-site composition (Figure 4) was obtained with the Thermo Avantage software, using the areas of the relevant peaks (corrected with the TPP-2M algorithm) and their respective sensitivity factors.

## Operando FTIR

Operando FTIR (Invenio, Bruker) was used to achieve dynamic mechanistic characterization on-stream, using a gas flow of 3H<sub>2</sub>:CO<sub>2</sub> and 7 bar pressure. A heated cell (HT/HP cell, Specac Ltd.) was used for the operando FTIR experiment, which was carried out by first pretreating the sample in a 5% H<sub>2</sub>/N<sub>2</sub> atmosphere (60 mL/min flow rate, NTP) up to 350 °C for 50 minutes

(5 °C/min heating rate). The sample was then ramped down to 180 °C in the same pretreatment atmosphere, after which Ar was introduced until complete removal of the H<sub>2</sub> mixture. The reaction mixture was then introduced (15 mL/min, NTP) and the pressure increased gradually to 7 bar. Isothermal experiments were then carried out after increasing the T to 200 °C, then with 50 °C steps up to 350 °C. A 30-minute dwell was performed at each target T from 250 °C and spectra were recorded every 10 minutes. At the end of the test, the pressure was decreased to 1 bar at 350 °C, after which the experiment was stopped. A mass spectrometer (Hyden Analytical QGA) was used to monitor the reaction products.

### CO<sub>2</sub> TPD

The CO<sub>2</sub> temperature-programmed desorption (TPD) analysis was performed using a TPD/R/O AMI 300 Lite (Altamira) analyser equipped with a TCD detector. For the analysis, 112 mg of the sample was loaded into a quartz tube reactor and pretreated with a 5% H<sub>2</sub>/Ar flow (40 mL/min) from RT to 350 °C (10 °C/min heating rate, 30 min dwell) to remove any possible surface passivated layer. The sample was then cooled in a He flow (40 mL/min) and kept at 50 °C for 20 min before starting the CO<sub>2</sub> treatment at the same temperature for 1 h (40 mL/min flow). The TPD was then performed by ramping the sample to 500 °C using a 10 °C/min rate under He and then holding the sample at the final temperature for 1 h.

The calculated CO<sub>2</sub> desorbed % was done by performing integration of CO<sub>2</sub> pulses after the TPD analysis to obtain a calibration factor, expressed in mmol CO<sub>2</sub>/(%TCD\*min). This was then used to calculate the amount of CO<sub>2</sub> desorbed per peak after background subtraction and peak integration analysis with Origin software.

### CO<sub>2</sub> hydrogenation

After exsolution the catalyst's performance in CO<sub>2</sub> hydrogenation was evaluated in a quartz tube reactor. 0.2 g of the catalyst powder packed in the quartz tube reactor column, using quartz wool so that the catalyst is prevented from moving and reduce the free volume of the reactor. The reactor temperature was controlled using an outer mount heating jacket, and the inner temperature was monitored by a K- type thermocouple. The inlet gas flow rates to the reactor were controlled by mass flow controllers. The product gases were analysed and measured by using a Micro gas chromatograph (Agilent 490 Micro-GC) equipped with thermal conductivity detectors (TCD). The concentrations of H<sub>2</sub>, CH<sub>4</sub>, and CO were determined using the Molsieve 5Å column, while CO<sub>2</sub> concentration using the PoraPLOT Q column. The concentration of methanol was quantified using the CP-Sil CB column. The detection limit of microGC for Molsieve 5Å column and PoraPLOT Q column is 2 ppm and for CP-Sil CB column is 0.5 ppm. Prior to the catalytic reaction, catalysts were pre-reduced at 350 °C for 1 hr with a ramp of 10 °C/min under 100% hydrogen. The CO<sub>2</sub> hydrogenation experiment was carried out under atmospheric pressure with a feed composition of H<sub>2</sub>/CO<sub>2</sub> ratio of 3:1 with a total feed flow rate of 25 mL/min with a top-to-down continuous flow rate of reactants NTP. The temperature was raised from 200 to 350°C at a rate of 10 °C/min, and for each temperature 12 readings were recorded over a ~50 min dwell time. The equations utilized for calculating the CO<sub>2</sub> conversion and selectivity are provided below: <sup>1</sup>

$$C_{\text{sum}} = \sum C(\text{carbon-containing compound}) \quad (1)$$

$$\text{CO}_2 \text{ conversion}(\%) = \left(1 - \frac{CCO_2}{C_{\text{sum}}}\right) * 100 \quad (2)$$

$$\text{Selectivity}_i (\%) = \frac{C_i}{\text{Total sum of all products}} * 100 \quad (3)$$

Where  $C_{CO_2}$  is the concentration of  $CO_2$  remaining and  $C_i$  represents the detected concentration of product 'i' at each data point.

Thermodynamic simulation was performed using Chemstations' ChemCad software (CHEMCAD 7.1.8) to obtain the thermodynamic equilibrium conversions to methanol and CO during the  $CO_2$  hydrogenation reaction. The equation of state used was the Soave-Redlich-Kwong. The reactor was simulated as a Gibbs reactor in order to calculate thermodynamic equilibrium limits. The total inlet flow rate and the percentages of the reactants used in the ChemCad simulation were the same as those used in catalytic experiment above.

### Calculation of turn over frequency (TOF)

The turnover frequency was calculated by using the formula:

$$\text{TOF}_{CO_2} = \frac{[\text{conversion } CO_2 * CO_2 \text{ flow rate (mLs}^{-1} - 1) * 6.022 \times 10^{23} (m)}]}{[24400(\text{mLmol}^{-1}) * Cu \text{ active sites}]} \quad (4)$$

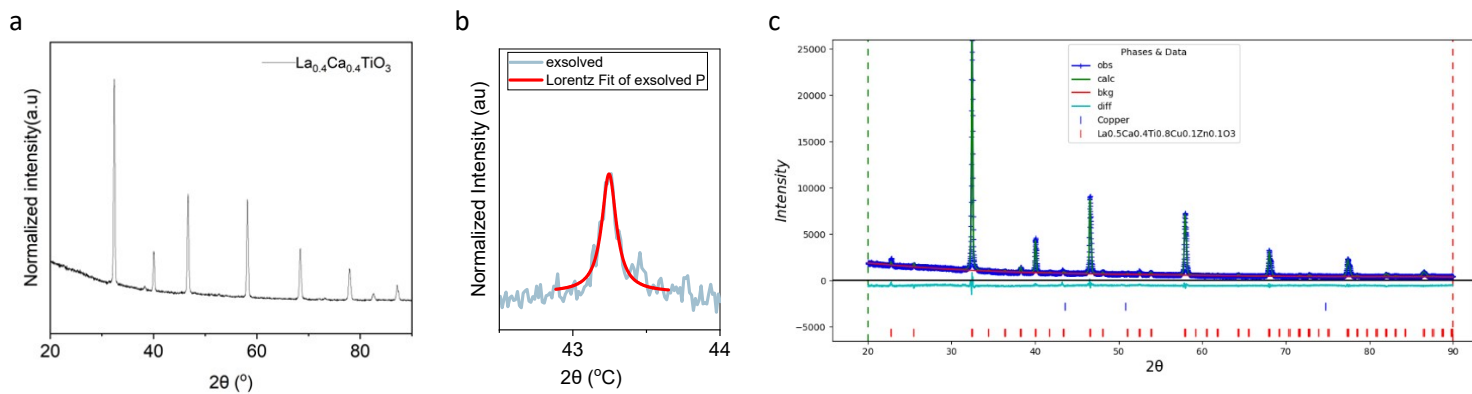
Where Cu active sites can be calculated by the formula  $(A_e \cdot A) / a^2 \cdot k$  where a is the unit cell parameter of the crystal lattice of the particles, k is the average number of metal sites per unit cell face, A is the total surface area of perovskite decorated with exsolved particles and  $A_e$  represents exposed particle area per total surface area of perovskite. Since the exsolved particle is copper and Cu metal has FCC type structure, thus  $k=4$  and  $a=0.361 \text{ nm}$ .<sup>3</sup>

$A_e$  is calculated from SEM analysis. To calculate  $A_e$ , the average particle size (diameter) of the particles and total perovskite surface decorated with exsolved particles is needed. In this case, Average particle size of Cu is  $4 \text{ nm} = 4 \times 10^{-3} \mu\text{m}$ . Assumptions has been made that the shape of the nanoparticle is a hemisphere. To calculate the metal surface area of one nanoparticle, following equation is used:

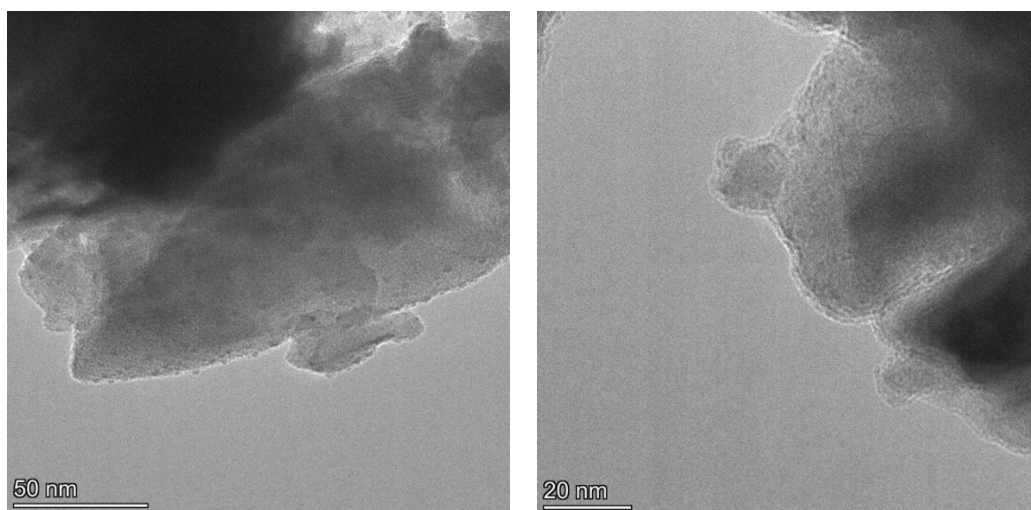
$$\text{metal surface area of one nanoparticle} = 2 \cdot \pi \cdot r^2 = 2 \cdot 3.14 \cdot \left(\frac{4 \cdot 10^{-3} \mu\text{m}}{2}\right)^2 = 0.00002512 \mu\text{m}^2$$

Then from the number of particles per  $\mu\text{m}^2$  (in this case 24450 particles/  $\mu\text{m}^2$ ) and the total surface area of perovskite decorated with exsolved particles (A in  $\mu\text{m}^2$ ) we calculate the total metal surface area of exsolved nanoparticles in  $\mu\text{m}^2$ . Dividing this number with A ( $\mu\text{m}^2$ ) allows to determine the exposed particle area per total surface area,  $A_e$  ( $\mu\text{m}^2 \mu\text{m}^{-2}$ ).

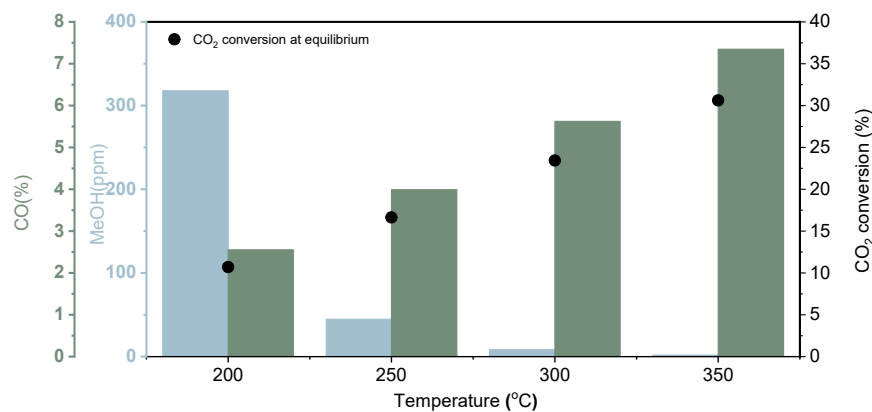
\* The total surface area of perovskite is  $1 \text{ m}^2/\text{g}$  based on published literature.<sup>4</sup> The calculated perovskite surface area is for 0.2g sample used.



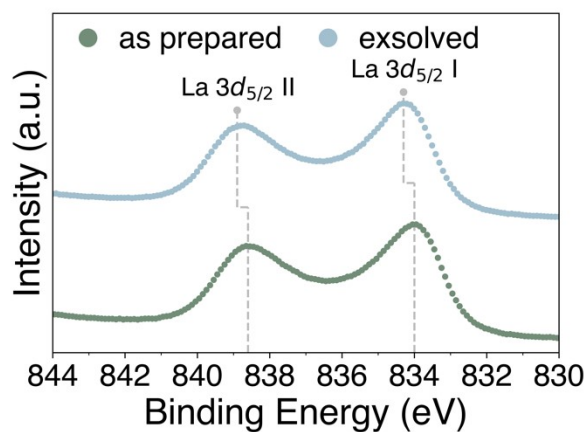
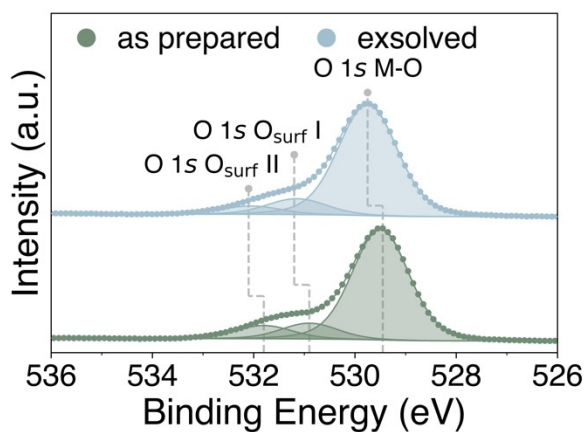
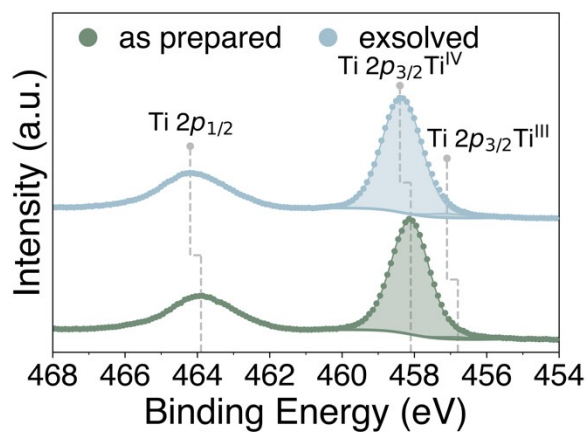
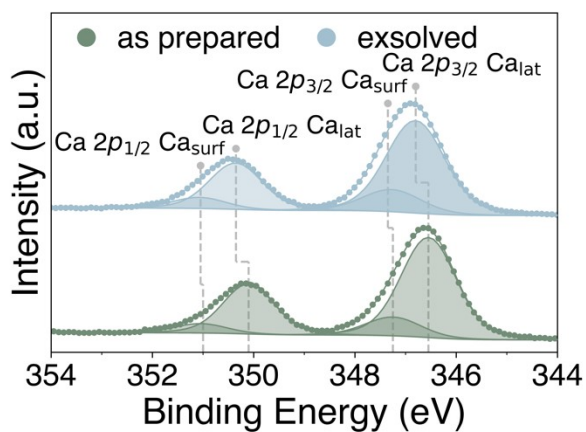
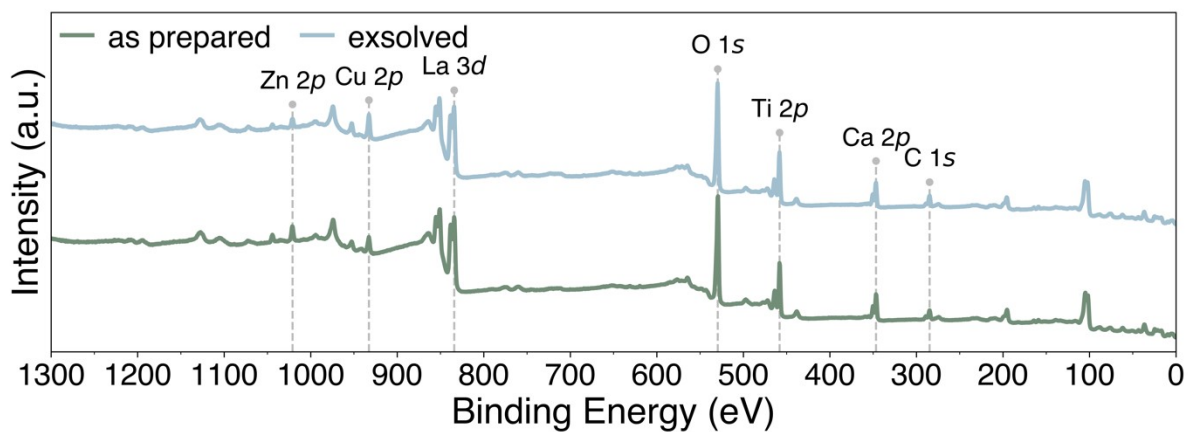
**Figure S1: a. XRD pattern of the undoped catalyst b. XRD fitting of Scherrer for Cu particles c. Rietveld Refinement verifying the amount of Cu exsolved.**



**Figure S2: TEM images of the sample reduced at 500 °C for 10 h showing small exsolved NPs on the different analysed grains.**

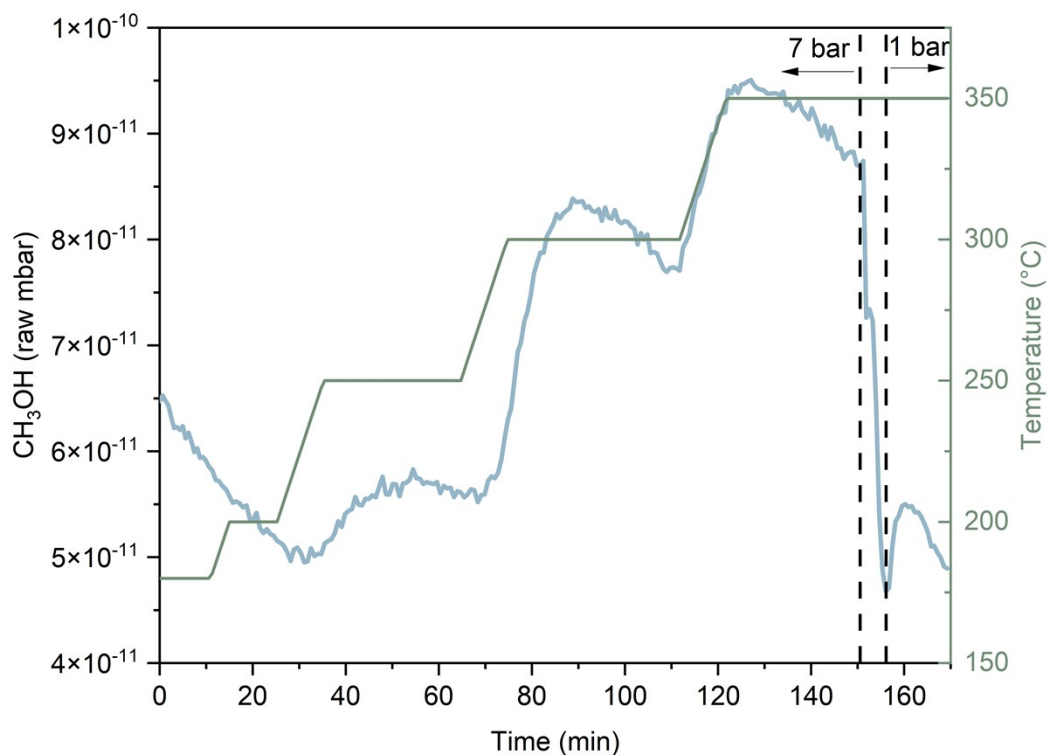


**Figure S3: Thermodynamic calculations for catalytic testing using conditions ( $P=1\text{atm}$ ;  
 $H_2/CO_2=3$ ;  $GHSV=7500\text{ml gcat}^{-1}\text{h}^{-1}$ )**

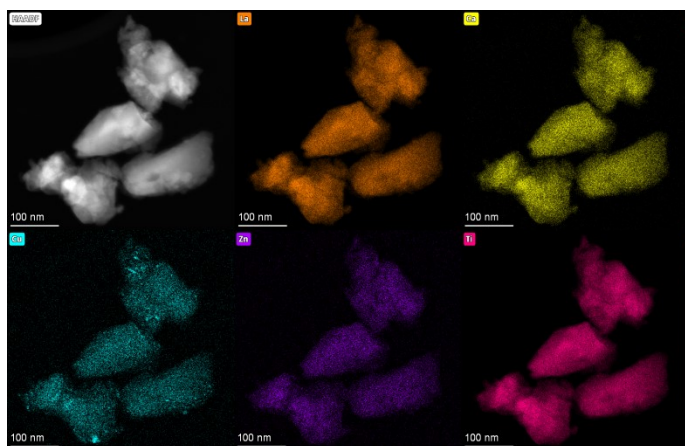


**Figure S4.** (top) survey spectra, (centre left) Ca 2p core level, (centre right) Ti 2p core level, (bottom left) O 1s core level, (bottom right) La 3d core level, focusing on La 3d<sub>5/2</sub>.

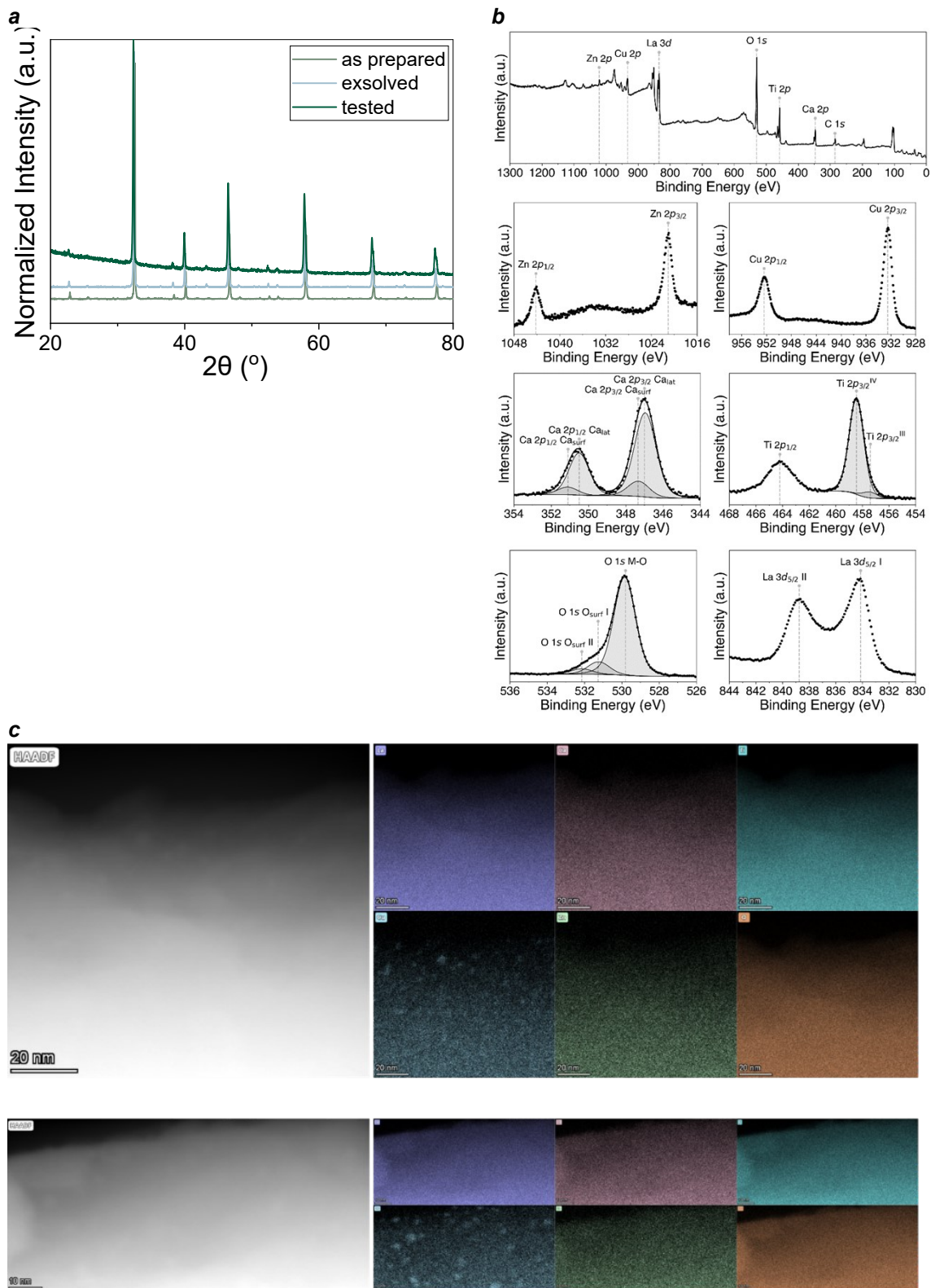




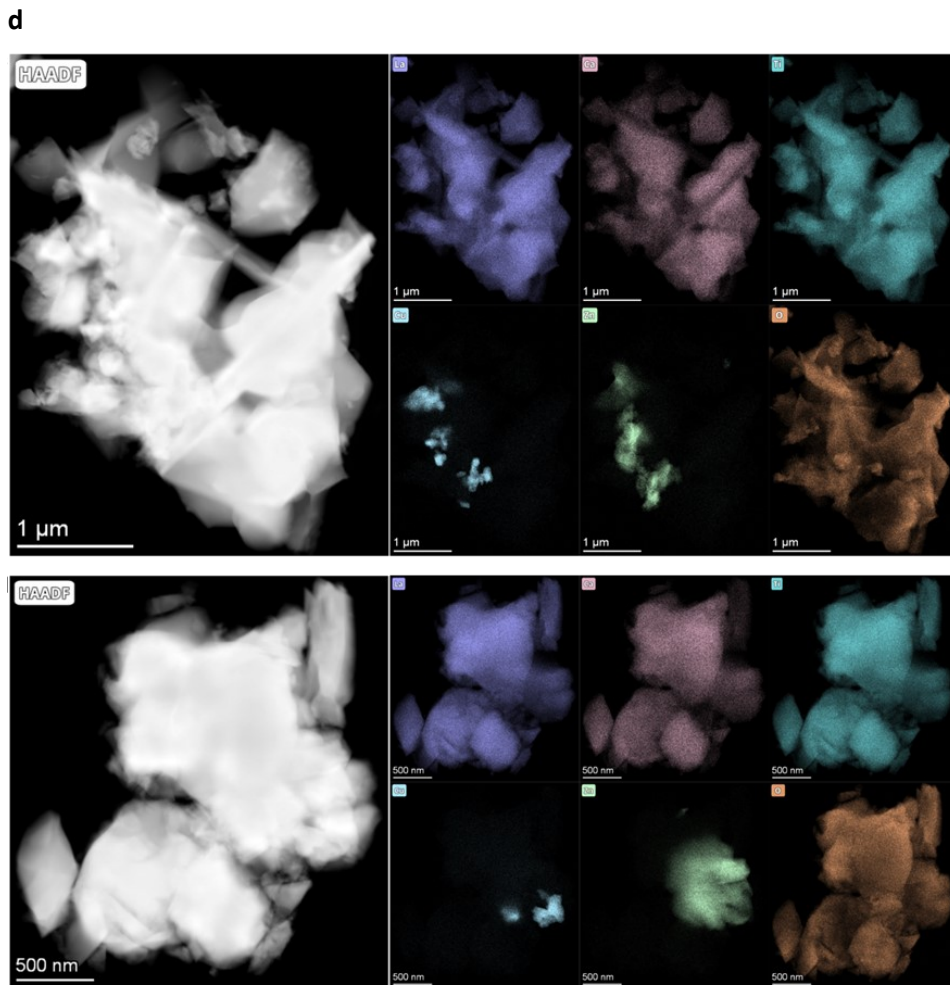
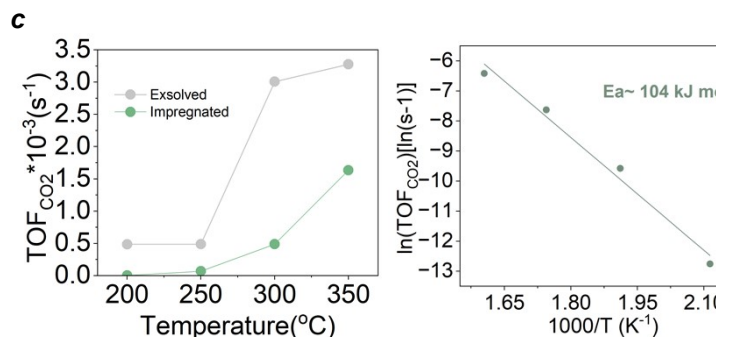
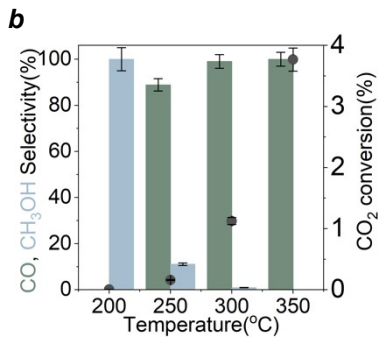
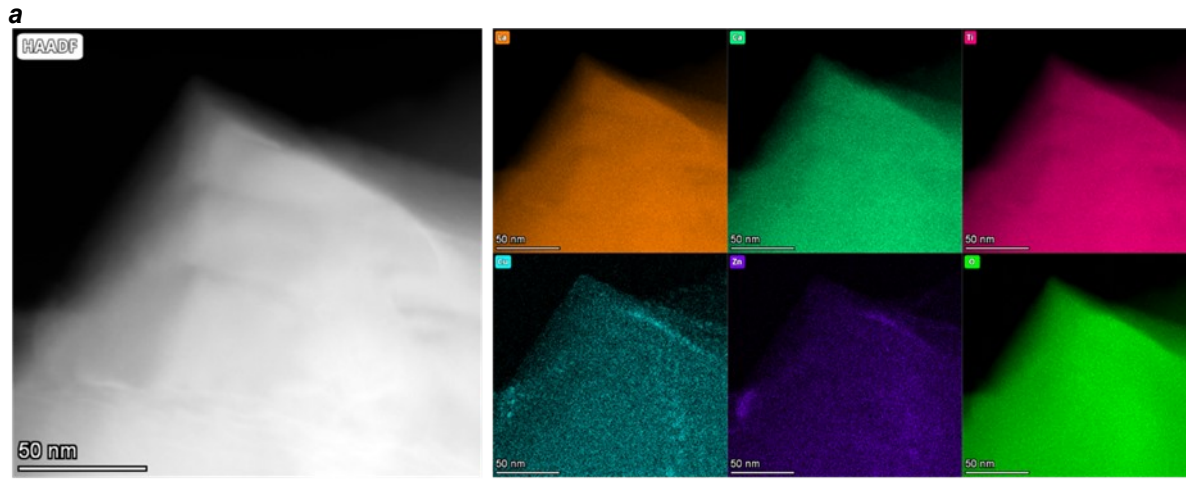
**Figure S5: Methanol signal** measure through mass spectrometry during the operando FTIR test from 180 °C to 350 °C at 7 bar, and after decreasing to 1 bar at the end of the test.



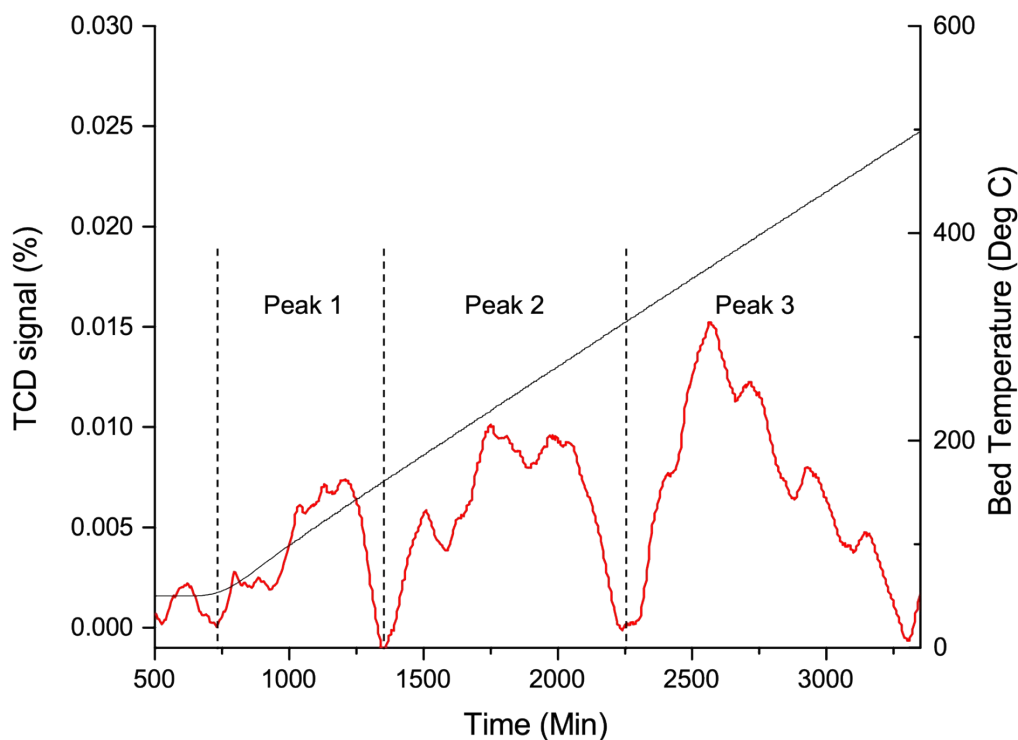
**Figure S6: Catalyst after high pressure testing**, STEM-EDX elemental maps of La, Ca, Zn, Cu, and Ti acquired on grains of the used sample at high pressures, indicating the existence of nanoscale Cu particles as well as the elemental dispersion of Zn in the material.



**Figure S7:** Characterisation of the catalyst after testing. *a.* XRD *b.* XPS (survey spectrum of the exsolved sample post-testing (top), accompanied by high-resolution core level scans of Zn 2p (upper centre left), Cu 2p (upper centre right), Ca 2p (lower centre left), Ti 2p (lower centre right), O 1s (bottom left) and La 3d (bottom right), focusing on La 3d<sub>5/2</sub>.) *c.* STEM-EDX elemental maps acquired on several areas of the Cu-Zn exsolved sample after catalytic testing showing dispersed Cu NPs of the same size as the ones found for the reduced sample.



**Figure S8: An impregnated CuZn/LaCaTiO<sub>3</sub> catalyst** a. STEM-EDX characterisation of the Cu/Zn wet-impregnated sample after 2h reduction at 350 °C. The sample shows presence of several Cu and Zn NPs, although not uniformly distributed b. Catalytic performance, conditions ( $P=1\text{atm}$ ;  $H_2/CO_2=3$ ;  $GHSV=7500\text{ml gcat}^{-1}\text{h}^{-1}$ ) c. Turn over frequency as the function of temperature d. Arrhenius plot of TOF of CO<sub>2</sub> conversion versus inverse temperature e. TEM of tested sample STEM-EDX elemental maps acquired on several areas of the impregnated sample after catalytic testing, where several agglomerated Cu/Zn areas of size ranging between 100-700 nm are evident, proving lack of control of NP dispersion and a certain degree of instability for this system with respect to the exsolved one.



**Figure S9: CO<sub>2</sub> TPD experiment showing the three desorption peaks identified after CO<sub>2</sub> desorption (red profile plotted over desorption time after background subtraction; black line refers to the T ramp from 50 to 500 °C- right Y axis).**

**Table 1.** Measured energies for the as prepared and exsolved samples in eV. XPS peaks are given in binding energy, Auger peaks are given in kinetic energy.

	Zn 2p <sub>3/2</sub>	Zn LMM	α'Zn	Cu 2p <sub>3/2</sub>	Cu LMM	α'Cu	Ti 2p <sub>3/2</sub>	La 3d <sub>5/2</sub>	Ca 2p <sub>3/2</sub>	O 1s
<b>as prepared</b>	1021.0	989.7	2011. 7	932.8	915.2 - 918.0	1845.0 - 1850.8	458.1	834.1	346.6	529.5
<b>exsolved</b>	1021.0	989.7	2011. 7	932.5	915.2	1847.7	458.3	834.3	346.8	529.8

**Table 2.** Quantitative analysis of CO<sub>2</sub> TPD measurement on the exsolved sample. The TPD profile showed three main adsorption peaks between 140-360 °C corresponding to different strength basic of the sample.

CO <sub>2</sub> TPD peak	Position (°C)	Desorbed CO <sub>2</sub> (%)
1	140	16
2	232	36
3	350-360	48

$$\text{mmol}_{\text{CO}_2}/\text{g}_{\text{sample}} = 0.02$$

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