

# Supporting Information

## **Operando Spectroscopic Monitoring of Active Species in CO<sub>2</sub> Hydrogenation at Elevated Pressure and Temperature: Steady-State versus Transient Analysis**

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## 1. Experimental

### 1.1. Materials.

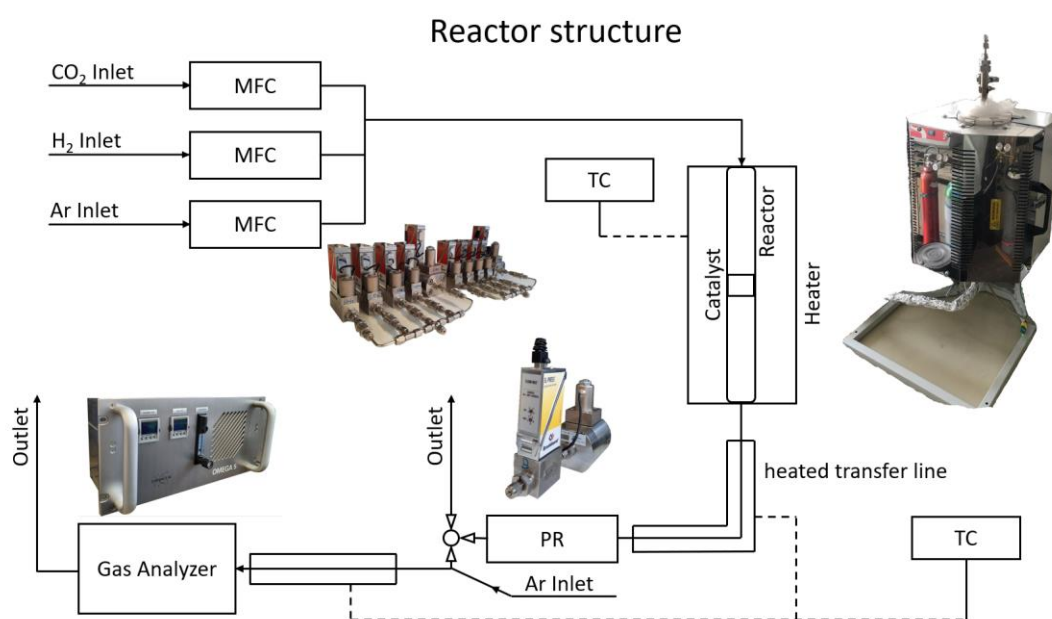
Ultrapure water (Elga Purelab Chorus 1, typ 1+, 18.2 M $\Omega$ \*cm), copper (II) nitrate trihydrate (Sigma-Aldrich, 99-104 %), zinc nitrate hexahydrate (Sigma-Aldrich, reagent grade, 98 %), zirconium(IV) oxynitrate hydrate (Sigma-Aldrich, 99 %), barium nitrate (Acros Organics, 99+ %) and gamma-alumina (Sigma-Aldrich, nanopowder < 50 nm) were used as received without any further treatment or purification. Hydrogen 4.5 (PanGas,  $\geq 99.995$  %), carbon dioxide 3.0 (PanGas,  $\geq 99.9$  %) and argon (Pangas,  $\geq 99.996$  %) were also utilized without any further purification.

### 1.2 Synthesis

Catalysts were prepared by a conventional wet-impregnation method as follows. All metal precursors were added to a beaker with ca. 50 mL of water and stirred with a magnetic stirrer (IKA, RCT standard) at room temperature until all the metal complexes were completely dissolved. The bluish solution was then added into a flask containing dry alumina powder. The resulting suspension was vigorously stirred at room temperature for 1 h. The suspension was then transferred to a rotary evaporator (Büchi, Rotavapor R-210) and stirred for another 1 h at 60 °C. Afterward, the water solvent was slowly evaporated at 30 mbar and 35 °C. The obtained blue solid was dried overnight at 80 °C in an oven (Mettler GmbH, UE400). The dried solid was then calcined in air at 400 °C for 3 h (a ramping rate of 10 °C/min). The calcined samples were transferred into a quartz-glass reactor for hydrogenation. The reactor was first flushed with a nitrogen flow of 200 ml/min for 30 min to remove the remaining oxygen. Then the sample was heated to 400 °C in a 200 ml/min of hydrogen flow at a ramping rate of 10 °C/min. The temperature was kept at 400 °C for 3 h. The sample was cooled in the same hydrogen flow.

### 1.3 Catalytic performance test

First of all, the gas analyser (Bruker, OMEGA 5) was flushed with argon and a background spectrum was recorded. 1.0 g of catalyst powder was loaded into a stainless-steel tubular reactor. To do this, the reactor was opened and a placeholder was placed inside. The reactor was flushed with carbon dioxide and hydrogen at a flow rate of 200 mL/min ( $\text{H}_2/\text{CO}_2 = 3.0$ ), and then pressurized to 30 bar by a back-pressure controller (Bronkhorst, PL-Flow). The outlet gas lines were heated by ribbon heaters at 110 °C to avoid the condensation of water and methanol. Figure 1 shows the schematic structure of the conversion reactor. The entire gas pipe system was built with Swagelok components.



**Figure S1.** A schematic illustration of the reactor set-up

### 1.4 Infrared spectroscopy

Adsorbed species at solid-gas catalytic interfaces during  $\text{CO}_2$  hydrogenation were monitored by operando FT-IR spectroscopy (Bruker, INVEIO-R) equipped with a liquid-nitrogen cooled mercury-cadmium-telluride (Bruker, DC313/IB) detector operated at -196 °C (see Figure 1a in the main manuscript). Diffuse-reflectance IR

Fourier transform spectroscopy (DRIFTS) was chosen to maximize IR absorption bands particularly from the material surfaces. 20 mg of catalyst powder was placed into an in situ DRIFTS cell with a high pressure dome with ZnSe windows (ST Japan, DiffusIR Type-1000°C). IR spectra were acquired at a spectral resolution of 4 cm<sup>-1</sup> and 32 scans/spectrum, aperture size of 8 mm, signal gain of x16 and scanning velocity of 60 kHz in a spectral range of 650-3800 cm<sup>-1</sup>. The rapid scan option (S129/IR) was employed to operate modulation excitation spectroscopy (MES) as in the following section. The optical compartment was continuously flushed with dried air (200 L/h). The sample compartment being flushed with pure nitrogen generated by a nitrogen generator (Schmidlin-DBS AG, N2-Mistral-4) to remove the water vapor whose IR absorption overlaps with IR bands of our interests in the range of 1300-1800 cm<sup>-1</sup>. The gas phase compositions were analyzed by a mass spectrometer (Pfeiffer Vacuum, Omnistar)

### 1.5 Modulation excitation spectroscopy

A state-of-the-art spectroscopic technique, i.e., MES was coupled with DRIFTS. MES operates under unsteady-state transient conditions where an external perturbation such as concentration, pH and Temperature is enforced to periodically modulate the concentration of active species on material surfaces.<sup>1-3</sup> The periodic oscillation of the concentration of surface species is exploited to enhance the signal-to-noise (S/N) ratio and time resolution. Further mathematical treatment by phase-sensitive detection (PSD) additionally provides kinetic information of each species.<sup>1-3</sup> The details of MES and PSD can be found in literatures.<sup>1-3</sup> In this study, only the concentration of CO<sub>2</sub> was modulated in 136 s between 0 vol% and 20 vol% for 24 cycles. The first 4 cycles were used to obtain stable responses, and the next 20 cycles were employed for MES analysis.

## 2. Catalytic performance of different materials

All the catalysts tested in this study showed enhanced selectivity to methanol at low temperatures with lower CO<sub>2</sub> conversion. By adding barium to Cu-Zn catalyst, high selectivity with a higher conversion can be achieved at low temperatures. By adding

zirconium to Cu-Zn-Zr catalyst, the 100 % selectivity to methanol was achieved at 130 °C. Based on these measurement results, a combination of copper, zinc, barium and zirconium was selected as a model catalytic material for operando MES-DRIFTS study.

**Table S1.** Catalytic performance of three different materials during hydrogenation of CO<sub>2</sub> (30 bar, H<sub>2</sub>/CO<sub>2</sub> = 3.0, 200 mL/min, H<sub>2</sub>: 150 mL/min, CO<sub>2</sub>: 50 mL/min)

<b>20% Cu-10 % Zn/<math>\gamma</math>-Al<sub>2</sub>O<sub>3</sub></b>					
Temperature (°C)	Concentration (ppm)		Selectivity (%)		Conversion (%)
	MeOH	CO	MeOH	CO	
250	775	0	100.0	0.0	0.3
275	852	227	79.0	21.0	0.4
300	864	2555	25.3	74.7	1.4

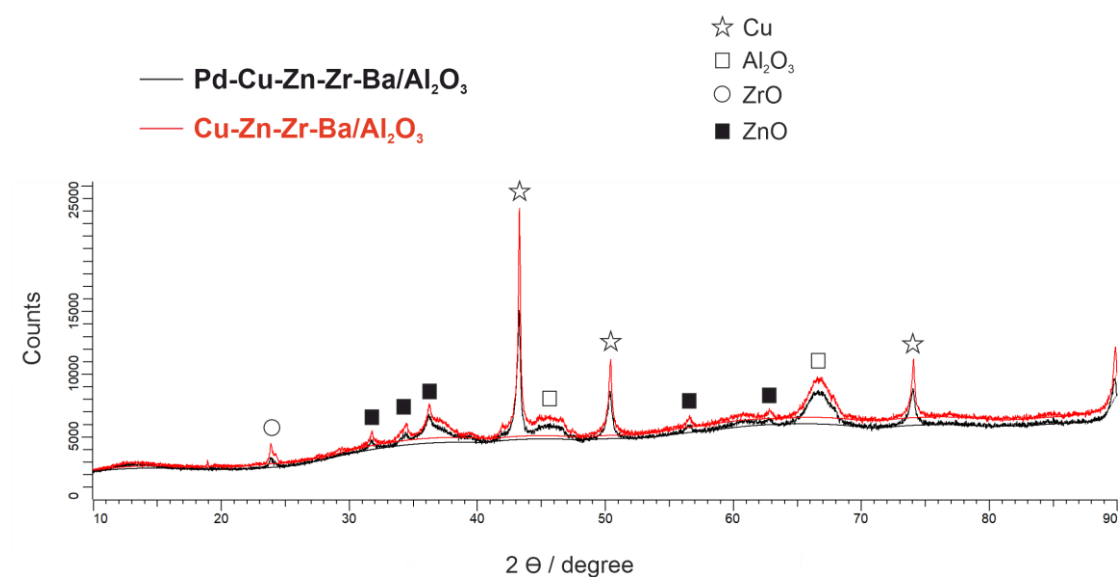
  

<b>15% Cu-7.5% Zn-7.5% Ba/<math>\gamma</math>-Al<sub>2</sub>O<sub>3</sub></b>					
Temperature (°C)	Concentration (ppm)		Selectivity (%)		Conversion (%)
	MeOH	CO	MeOH	CO	
150	1726	154	91.8	8.2	0.8
175	3135	1837	63.1	36.9	2.0
200	3812	7698	33.1	66.9	4.6
225	5202	29177	15.1	84.9	13.8
250	5186	29247	15.1	84.9	13.8

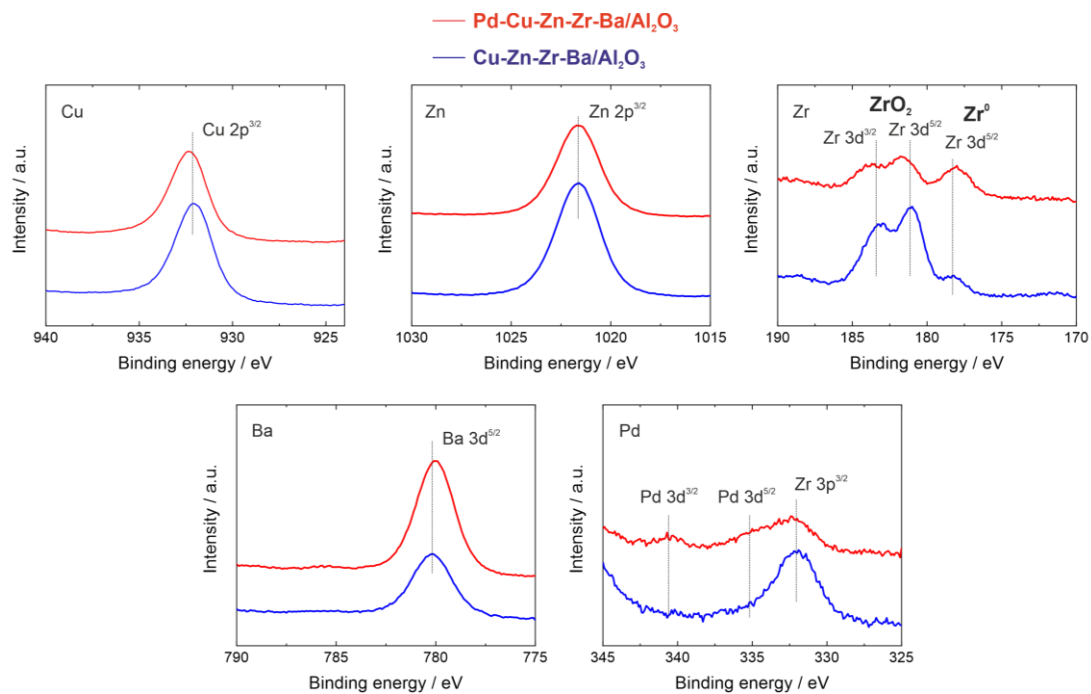
<b>20% Cu-10% Zn-7.5% Ba-2.5% Zr/<math>\gamma</math>-Al<sub>2</sub>O<sub>3</sub></b>					
Temperature (°C)	Concentration (ppm)		Selectivity (%)		Conversion (%)
	MeOH	CO	MeOH	CO	
130	1922	0	100.0	0.0	0.8
150	2811	407	87.4	12.6	1.3
175	4749	2729	63.5	36.5	3.0
200	6085	17063	26.3	73.7	9.3
225	7231	49218	12.8	87.2	22.6
250	7006	86006	7.5	92.5	37.2

### 3. XRD Patterns



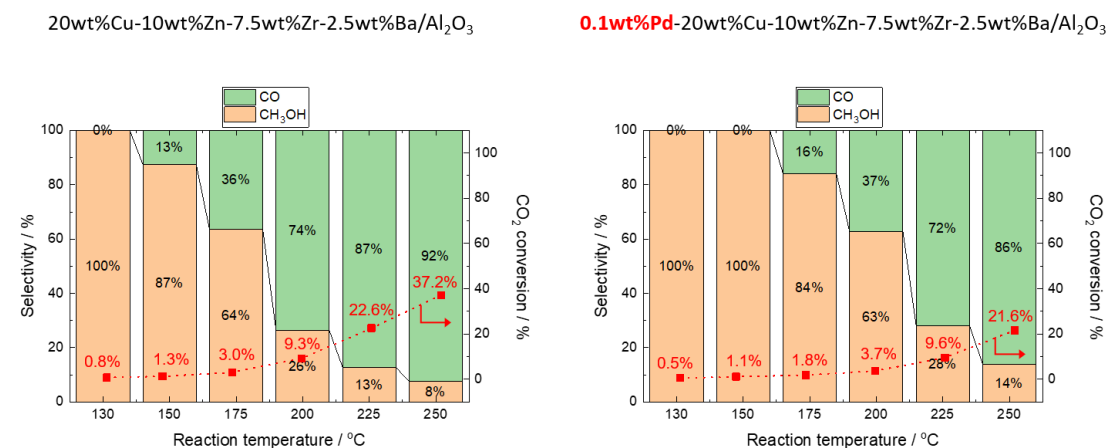
**Figure S2.** XRD patterns of 0.1wt% Pd-20 wt% Cu-10 wt% Zn-7.5 wt% Zr-2.5 wt% Ba/ $\text{Al}_2\text{O}_3$  and Cu-10 wt% Zn-7.5 wt% Zr-2.5 wt% Ba/ $\text{Al}_2\text{O}_3$  after pretreatment with pure hydrogen at 400 °C for 3 h.

#### 4. XPS spectra



**Figure S3.** XPS spectra of 0.1wt% Pd-20 wt% Cu-10 wt% Zn-7.5 wt% Zr-2.5 wt% Ba/Al<sub>2</sub>O<sub>3</sub> and Cu-10 wt% Zn-7.5 wt% Zr-2.5 wt% Ba/Al<sub>2</sub>O<sub>3</sub> after pretreatment with pure hydrogen at 400 °C for 3 h.

## 5. Catalytic performance of 0.1 wt% Pd-Cu-Zn-Zr-Ba/Al<sub>2</sub>O<sub>3</sub> catalyst



**Figure S4.** Catalytic performance of materials with and without 0.1 wt% Pd during hydrogenation of CO<sub>2</sub> (30 bar, H<sub>2</sub>/CO<sub>2</sub> = 4.0, 200 mL/min, H<sub>2</sub>: 160 mL/min, CO<sub>2</sub>: 40 mL/min).

## References

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