Supporting Information

Iso-Potential Operando Microwave Cavity Perturbation - Spatial Conductivity Changes of a Cu/ZnO/Al_2O_3 Catalyst inside a Fixed-Bed Reactor during Reverse Watergas Shift Reaction

Diego Espinoza [a], *Neda Kazemi* [a], *Zoran Bondzio* [c], *Oliver Korup* [a,b], *Thomas Risse* [c, *],
Raimund Horn [a,b, *]

[a] Department of Chemical Reaction Engineering, Hamburg University of Technology, Hamburg 21073, Germany.

[b] Reacnostics GmbH, Hamburg 20457, Germany.

[c] Institute of Chemistry and Biochemistry, Freie Universität Berlin, Berlin 14195, Germany.

1. Elemental characterization (ICP-OES)

Metal concentrations (Cu, Zn, Al) were quantified by Inductively Coupled Plasma – Optical Emission Spectroscopy (ICP-OES). In this regard, the original CZA catalyst sample was measured on the NCHS analyzer. For the aluminum (Al) determination, the original sample was digested with inverted aqua regia/HF/Boric Acid. Whereas, for zinc (Zn) and copper (Cu) detection, the original sample was digested with inverted aqua regia/ HBF4.

Accordingly, Perkin Elmer ICP-OES AVIO 550 Max was used. The sample was weighed and analyzed by an NCHS analyzer with an internal thermal conductivity detector (TCD) in order to measure nitrogen (N), hydrogen (H), sulfur (S), and total carbon (C). Furthermore, the residue of the sample was dried (80.7%) to evaluate the humidity of the sample. Due to precipitation during HBF4 digestion, which is probably due to aluminum, further digestion with inverted hydrocarbons/HF/boric acid was carried out for Al. Table S1 presents the results of the chemical composition analysis by ICP-OES. As shown, Al, Zn, and Cu were the main metal elements composing the catalyst sample, with a small amount of carbon also present. Other elements, including N, H, and S, may appear due to humidity.

Table S1. Quantitative results of the ICP-OES characterization for CZA catalyst

Element	**Value (g Kg^{-1})**
Al	32.5
Zn	91.7
Cu	504
N	< 1
C	20
H	3.4
S	< 2

2. XRD characterization

The high-energy X-ray total scattering experiments were performed in the experimental hutch of the Beamline P21.1 at PETRA III, DESY, Hamburg, Germany. The samples were mounted in a 0.5 mm inner diameter glass capillary. A 1×1 mm2 beam was used at 101.5 keV. Scattering data were collected on a Pilatus3 CdTe detector positioned at a sample-to-detector distance (SDD) of 1100 mm. In order to calibrate the SDD and remaining detector geometry parameters, a capillary with LaB6 powder was measured as the standard sample. Azimuthal integration of the 2D diffraction patterns and calibration were carried out using the pyFAI package.

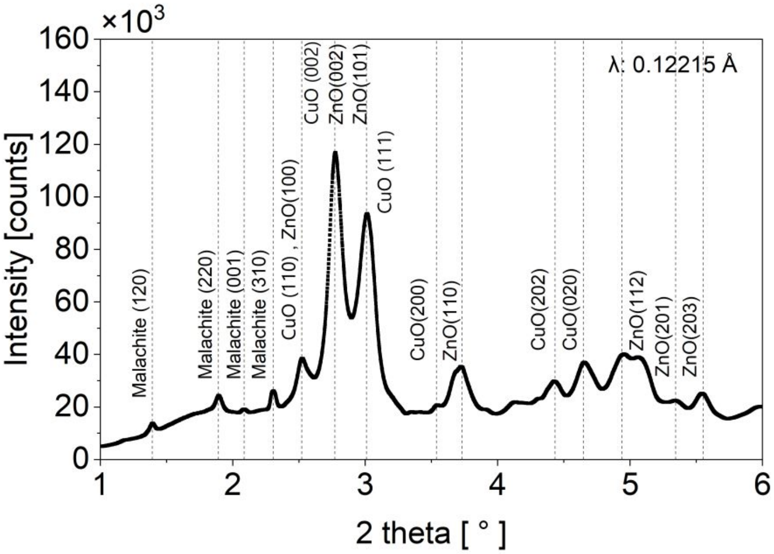

Figure S1 Powder ex-situ X-ray diffraction pattern of fresh CZA catalyst

3. IPO-MCP temperature profiles

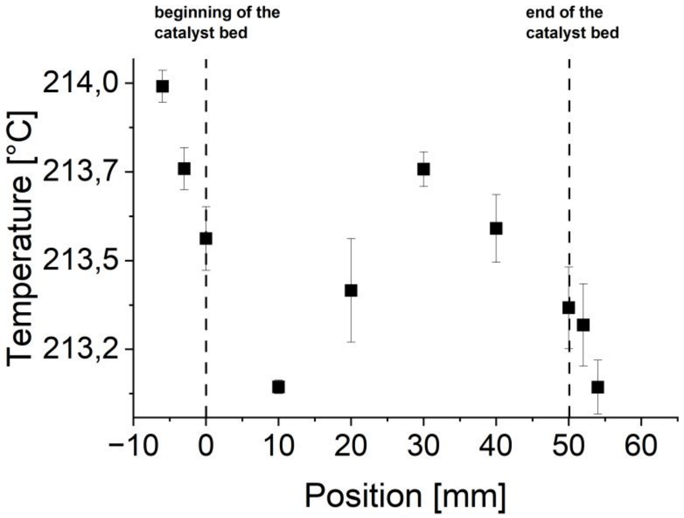

Figure S2. IPO-MCP temperature profiles with standard deviation obtained during r-WGS reaction over an industrial CZA catalyst. Reaction conditions: Feed composition $CO_2/H_2/N_2$ =10/10/80, 213 ˚C, 100 mL min^{-1} (25 °C, 1 atm), 1 bar, 4 replicates, and 50 mm catalyst bed.

4. Equilibrium conversion

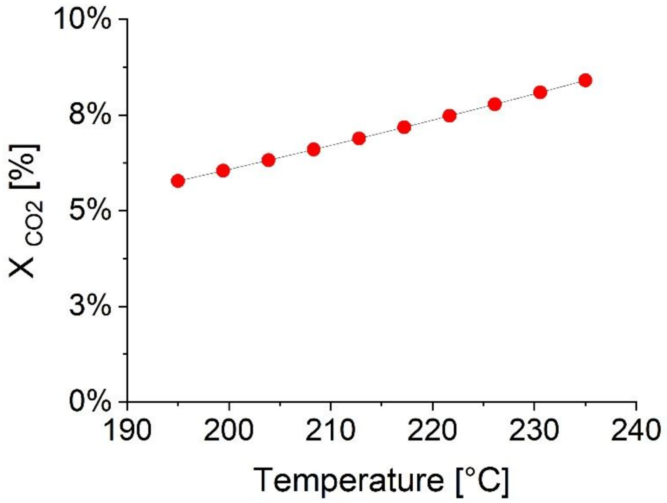

Figure S3. CO_2 equilibrium conversion for the rWGS system as a function of temperature under for a feed ratio $CO_2/H_2/$ = 1:1 at atmospheric conditions.

5. Chemical Potential Criteria for CPR vs. CPR-MCP at z = 0 mm and z = 50 mm

Assumptions: ideal gas, T = 500 K, $p^{CPR} = 1.6$ bar, $p^{MCP} = 1.4$ bar, $p^{\circ} = 1.013$ bar, entrance of reactor at z = 0 mm.

Equations used:

$$\mu_{mix}(T,p) = \sum_i x_i \mu_i \tag{1}$$

$$\mu_i = \mu_i^o(T) + RT\, ln\left(x_i \frac{p}{p^o}\right) \tag{2}$$

$$\mu_{mix}(T,p) = \sum_i x_i \mu_i = \sum_i x_i \left(\mu_i^o(T) + RT\, ln\left(x_i \frac{p}{p^o}\right)\right) \tag{3}$$

Species	i	$\frac{\boldsymbol{\mu_i^o(500\,K)}}{\boldsymbol{J.mol^{-1}}}$	$\boldsymbol{x_{i,z=0\,mm}^{CPR}}$	$\frac{\boldsymbol{RT\,ln\left(x_i \frac{p}{p^o}\right)^{CPR}}}{\boldsymbol{J.mol^{-1}}}$	$\boldsymbol{x_{i,z=0\,mm}^{CPR-MCP}}$	$\frac{\boldsymbol{RT\,ln\left(x_i \frac{p}{p^o}\right)^{CPR-MCP}}}{\boldsymbol{J.mol^{-1}}}$
Ar	1	0	0.8	973	0.8	417
CO_2	2	-394914	0.1	-7672	0.098	-8311
H_2	3	0	0.1	-7672	0.098	-8311
CO	4	-155412	0	$-\infty$	0.002	-24489
H_2O	5	-219050	0	$-\infty$	0.002	-24489

$$\mu_{mix}(T,p)_{z=0\,mm}^{CPR} = -40248\ \frac{J}{mol} \tag{4}$$

$$\mu_{mix}(T,p)_{z=0\,mm}^{CPR-MCP} = -40843\ \frac{J}{mol} \tag{5}$$

According to Equations 4 and 5, and at the inlet of the packed bed reactor (CPR) where the deviations are greatest, a deviation of 1.04% is obtained, which indicates that the system can be considered Iso-Potential.