

Supporting Information

Continuous Synthesis of Cu/ZnO/Al₂O₃ Nanoparticles in a Co-precipitation Reaction Using a Silicon Based Microfluidic Reactor

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1. Additional information on the catalytic testing

Table S1 Reaction conditions in a plug flow reactor (PFR) test

ToS h	Temperature °C	CO/CO ₂ mol%	Pressure bar	GHSV mL _N g ⁻¹ h ⁻¹ cat
2	230	15/0	50	24000
4	230	14/1	50	24000
6	250	15/0	50	24000
8	250	14/1	50	24000

Catalytic performance

Selectivity:

The selectivity formula is defined according to whether CO₂ is a product or a reactant

For negative CO₂ conversion (CO₂ is a product):

$$S_{DME,CO} = \frac{2 * \dot{n}_{DME,out}}{2 * \dot{n}_{DME,out} + \dot{n}_{MeOH,out} + \sum_i n_{C_i} n_i + \dot{n}_{CO_2,out} - \dot{n}_{CO_2,in}} * 100\%$$

$$S_{MeOH,CO} = \frac{\dot{n}_{MeOH,out}}{2 * \dot{n}_{DME,out} + \dot{n}_{MeOH,out} + \sum_i n_{C_i} n_i + \dot{n}_{CO_2,out} - \dot{n}_{CO_2,in}} * 100\%$$

Where n_{C_i} represents the number of carbon atoms in the hydrocarbon n_i .

With positive CO₂ conversion (CO₂ is a reactant):

$$S_{DME,CO_x} = \frac{2 * \dot{n}_{DME,out}}{2 * \dot{n}_{DME,out} + \dot{n}_{MeOH,out} + \sum_i n_{C_i} n_i} * 100\%$$

$$S_{MeOH,CO_x} = \frac{\dot{n}_{MeOH,out}}{2 * \dot{n}_{DME,out} + \dot{n}_{MeOH,out} + \sum_i n_{C_i} n_i} * 100\%$$

Productivity:

The productivity of DME and MeOH is based on the number of carbon atoms in the respective hydrocarbon

$$P_{DME,m_{cat}} = \frac{2 \dot{n}_{DME,out}}{mass_{cat}} [mmol_C \cdot (g_{cat} * h)^{-1}] \quad (5)$$

$$P_{MeOH,m_{cat}} = \frac{\dot{n}_{MeOH,out}}{mass_{cat}} [mmol_C \cdot (g_{cat} * h)^{-1}] \quad (6)$$

2. Further Characterization results

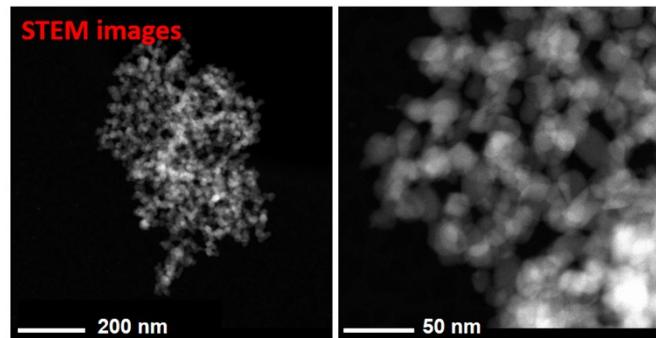


Fig. S1 STEM images of calcined CuO/ZnO nanoparticles produced in the batch reactor.

Table S2 Quantified EDX results from different regions of the CuO/ZnO catalyst produced in the batch reactor ($Cu/Zn = 2.2 \pm 1.2$ and $\sigma^2 = 1.4$).

Particle No.	O (at.%)	Cu (at.%)	Zn (at.%)	Cu:Zn ratio
1	41.5	47.1	11.4	4.1
2	56.9	23.6	19.4	1.2
3	59.8	22.2	17.9	1.2
4	43.9	33.1	22.9	1.4
5	58.5	30.2	11.3	2.7
6	49.0	37.7	13.3	2.8

σ^2 : Variance

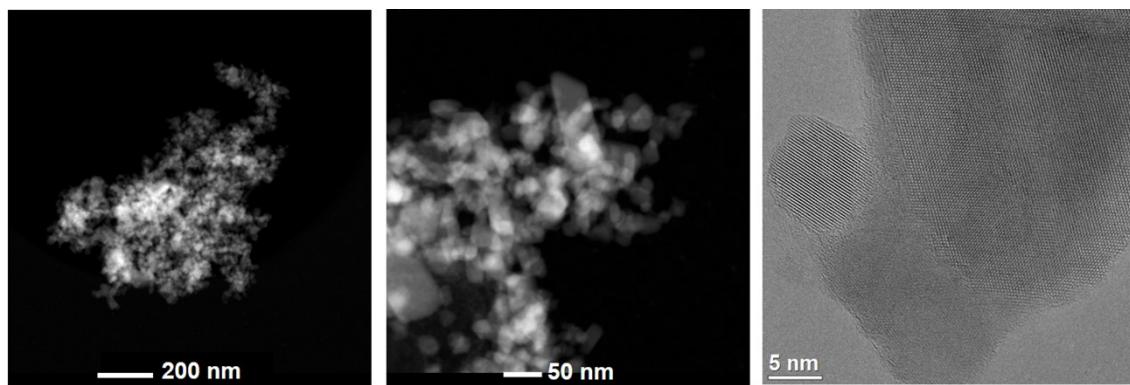


Fig. S2 Selected electron microscopy images of calcined CuO/ZnO/Al₂O₃ nanoparticles produced in the batch reactor.

Table S3 Quantified EDX results from different regions of the CuO/ZnO/Al₂O₃ catalyst produced in the batch reactor, (Cu/Zn = 20.1 ± 3.5 and $\sigma^2 = 12.6$).

No.	O (at.%)	Al (at.%)	Cu (at.%)	Zn (at.%)	Cu:Zn ratio
1	61.4	1.4	34.9	2.2	15.9
2	58.3	1.0	39.2	1.6	24.5
3	54.3	0.6	43.2	1.8	24.0
4	53.1	0.8	43.9	2.2	20.0
5	57.9	1.4	39.6	2.0	19.8
6	58.6	2.2	36.9	2.2	16.8

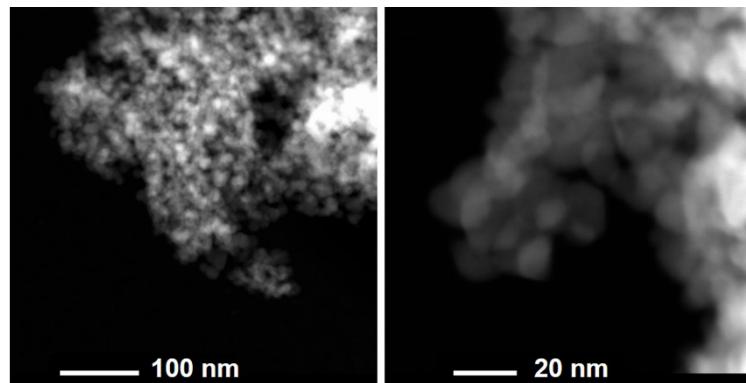


Fig. S3 Selected electron microscopy images of calcined CuO/ZnO/Al₂O₃ nanoparticles produced in the microfluidic reactor.

Table S4 Quantified EDX results from different regions of the CuO/ZnO/Al₂O₃ catalyst produced in the microfluidic reactor (Cu/Zn = 8.2 ± 2.1 and $\sigma^2 = 4.6$).

No.	O (at.%)	Al (at.%)	Cu (at.%)	Zn (at.%)	Cu:Zn ratio
1	67.2	1.7	28.0	3.1	9.0
2	57.8	2.4	36.7	3.2	11.5
3	62.1	9.4	23.9	4.6	5.2
4	52.3	5.9	36.5	5.4	6.8
5	59.3	1.1	35.2	4.4	8.0
6	59.3	3.2	33.6	3.8	8.8

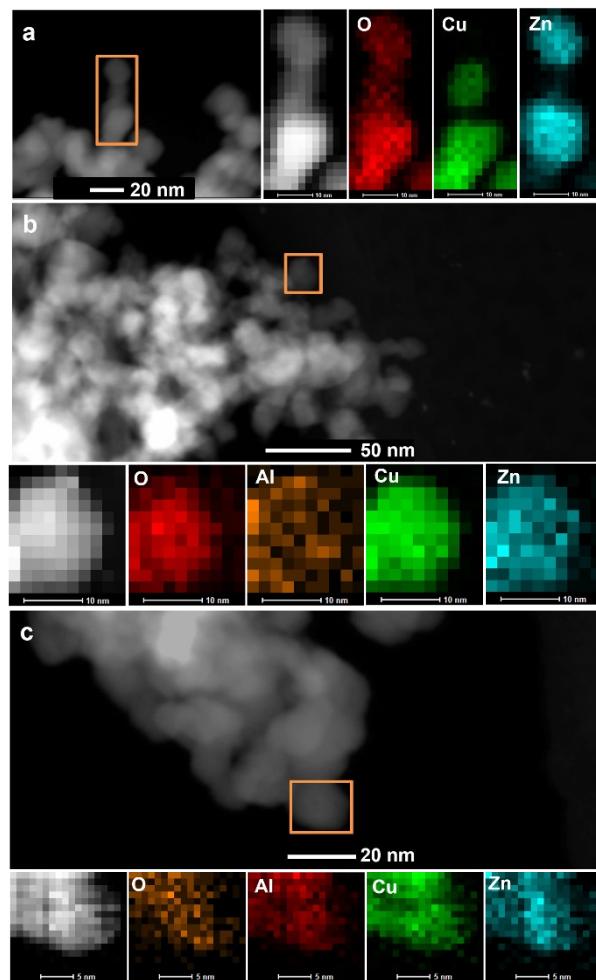


Fig. S4 STEM images and the corresponding elemental maps obtained from STEM-EDX spectrum imaging in the areas marked by the orange box of calcined (a) Cu/ZnO, (b) Cu/ZnO/Al₂O₃ nanoparticles produced in the batch reactor and (c) Cu/ZnO/Al₂O₃ nanoparticles produced in the microfluidic reactor. Scale bars for the elemental maps are 10 nm (parts a,b) and 5 nm (part c).

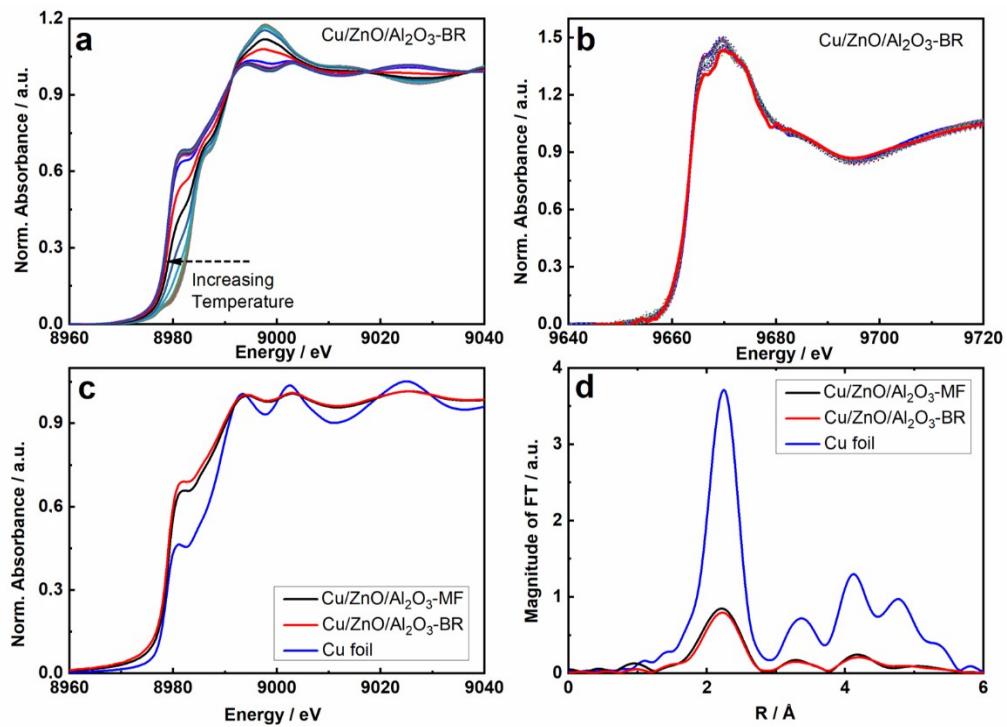


Fig. S5 *In situ* XANES spectra at (a) Cu K and (b) Zn K-edges of Cu/ZnO/Al₂O₃ produced in the batch reactor measured during the TPR (from 20 °C up to 260 °C), (c) comparison of XANES data of the reduced catalysts produced in microfluidic and batch reactor at 260 °C along with (d) their corresponding magnitude of the k^3 -weighted Fourier transformed EXAFS data at Cu K-edge.