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/CO₂ (mol%) | Pressure (bar) | GHSV (mL N₂ g⁻¹ h⁻¹) |
|--------|-----------------|---------------|----------------|---------------------|
| 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):

\[
S_{DME,CO} = \frac{2 \cdot \dot{n}_{DME,\text{out}}}{2 \cdot \dot{n}_{DME,\text{out}} + \dot{n}_{MeOH,\text{out}} + \sum n_i n_{i} + \dot{n}_{CO_2,\text{out}} - \dot{n}_{CO_2,\text{in}}} \times 100\%
\]

Where \( n_i \) represents the number of carbon atoms in the hydrocarbon \( \dot{n}_{i} \).

With positive CO₂ conversion (CO₂ is a reactant):

\[
S_{MeOH,CO} = \frac{2 \cdot \dot{n}_{DME,\text{out}} + \dot{n}_{MeOH,\text{out}} + \sum n_i n_{i} + \dot{n}_{CO_2,\text{out}} - \dot{n}_{CO_2,\text{in}}}{2 \cdot \dot{n}_{DME,\text{out}} + \dot{n}_{MeOH,\text{out}} + \sum n_i n_{i}} \times 100\%
\]

Productivity:

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

\[
P_{DME,m_{\text{cat}}} = \frac{2 \dot{n}_{DME,\text{out}}}{\text{mass}_{\text{cat}}} \left[ \text{mmol}_{C} \cdot (g_{\text{cat}} \cdot h)^{-1} \right]
\]
2. Further Characterization results

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

(6)

**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 ± 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         |

\( \sigma^2 \): Variance
Fig. S2 Selected electron microscopy images of calcined CuO/ZnO/Al$_2$O$_3$ nanoparticles produced in the batch reactor.

Table S3 Quantified EDX results from different regions of the CuO/ZnO/Al$_2$O$_3$ 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/Al$_2$O$_3$ 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 σ² = 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/Al$_2$O$_3$ 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.