SUPPLEMENTARY INFORMATION

Competition between reverse water gas shift reaction and methanol synthesis from CO₂: influence of copper particle size

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Section S1: Catalyst Synthesis and structural properties

For a typical impregnation, 1.5 g pristine graphene nanoplates (GNP500) were dried at 170 °C under dynamic vacuum for 2 hours. The vacuum was partially released and impregnated directly afterwards with a 95% pore-filling amount of precursor solution (1-3 M) consisting of Cu(NO₃)₂·3H₂O (Acros Organics, ≥99% purity) in 0.1M HNO₃ (Merck, 65% in water). The solution was added dropwise under magnetic stirring. After the addition, the powder was dried at room temperature for 24 hours under dynamic vacuum. To avoid exposure to air, the dried impregnated powder was stored in an Ar-filled glovebox (Mbraun Lab Star Glove Box supplied with pure 5.5 grade Argon, <1 ppm O₂, <1 ppm H₂O). The dried sample, loaded in a plug-flow reactor, was treated following the parameters reported in Table S1. The heat treatment was performed under N₂ flow (100 mL min⁻¹ g⁻¹), while the reduction step was performed under 10% H₂/N₂ or 20% H₂/N₂ flow (100 mL min⁻¹ g⁻¹). After allowing cooling down to room temperature, the obtained sample was transferred to an Ar-filled glovebox. Finally, after characterization of the metallic phase, the catalyst was slowly passivated by exposure to air. The catalysts were pressed and sieved to a grain size of 75-150 μm.
Table S1 (a) Nominal copper weight loading. (b) Temperatures adopted for the heat treatment ($T_{HT}$) and the reduction ($T_R$) steps during the synthesis of the catalysts. Surface-averaged Cu particle sizes (in nm) of Cu/C catalysts in the fresh, activated and used state determined by (c) XRD and (d) TEM.

| Name   | Cu loading (wt. %) | $T_{HT}$ (°C) | $T_R$ (°C) | Fresh Catalysts (nm) | Activated catalysts (nm) | Used catalysts (nm) |
|--------|--------------------|---------------|------------|-----------------------|--------------------------|---------------------|
|        |                    |               |            | $d_{Cu}^0$ $\pm \sigma_{ds}^d$ | $d_{Cu}^0$ $\pm \sigma_{ds}^d$ | $d_{Cu}^c$ $\pm \sigma_{ds}^d$ |
| 4.7_Cu/C | 5.2              | -             | 250        | 3.9 ± 0.9             | 4.7 ± 1.2               | 4.9 ± 1.3           |
| 5.8_Cu/C | 9.9             | 250           | 200        | 4.3 ± 1.0             | 5.8 ± 1.6               | 5.6 ± 1.5           |
| 11.2_Cu/C | 9.9              | -             | 250        | 7.5                   | 11.2 ± 3.6              | 11.9 ± 3.7          |
| 12.8_Cu/C | 9.9              | 300           | 200        | 9.6                   | 12.8 ± 4.1              | 13.3 ± 4.2          |
| 19.4_Cu/C | 14.1             | 260           | 200        | 12.4                  | 16.8                    | 16.2                |
Supplementary Information

| Fresh catalysts | Activated catalysts | Used catalysts |
|-----------------|---------------------|----------------|
| ![Image](76x342 to 519x756) | ![Image](50 nm) | ![Image](50 nm) |
| ![Image](50 nm) | ![Image](50 nm) | ![Image](50 nm) |
| \( d_1 = 3.9 \pm 0.9 \text{ nm} \) | \( d_2 = 4.7 \pm 1.2 \text{ nm} \) | \( d_3 = 4.9 \pm 1.3 \text{ nm} \) |
| ![Image](76x342 to 519x756) | ![Image](50 nm) | ![Image](50 nm) |
| ![Image](50 nm) | ![Image](50 nm) | ![Image](50 nm) |
| \( d_1 = 4.3 \pm 1.0 \text{ nm} \) | \( d_2 = 5.8 \pm 1.6 \text{ nm} \) | \( d_3 = 5.6 \pm 1.5 \text{ nm} \) |
Figure S1  Transmission electron micrographs with corresponding particle size distributions of the Cu/C catalysts in the fresh (a, d, g, j, m), activated (b, e, h, k, n) and used (c, f, l, o) state.
Section S2: Catalytic performance

The activity of the catalyst was given as CO$_2$ conversion ($X_{CO_2}$), copper-time yield (CTY) and turnover frequency (TOF). The CO$_2$ conversion was calculated by the difference in CO$_2$/Ar ratio between chromatograms taken during reaction through a catalyst-filled reactor and chromatograms taken during reaction through a SiC-filled reference reactor. The TOF was based on CTY and the number of copper surface atoms, according to the equation: $CTY \times M_{Cu} / D_{Cu}$. Where CTY is expressed in mol$_{CO_2}$ g$_{Cu}$ s$^{-1}$, $M_{Cu}$ is the molar mass of Cu and $D_{Cu}$ is the dispersion of surface Cu atoms. The value of $D_{Cu}$ was calculated as $D_{Cu} = 6 \times V_{Cu} / A_{Cu} \times d_s$. Therefore, considering the molar volume ($V_m$) of 7.09*10$^{21}$ nm$^3$, the molar area of the particles ($A_{m}$) of 4.10*10$^{22}$ nm$^2$ and mean diameter ($d_s$) of the activated catalyst, as determined by TEM.

The value of the apparent activation energy ($E_a$) in the Arrhenius model was obtained from the slope of the linear fit through the ln(CTY (mmol$_{CO_2}$ g$_{Cu}$ s$^{-1}$)). The pre-exponential factor (A) was obtained in the Arrhenius model from the intercept of the linear fit through the ln(surface-normalized CTY (mmol$_{CO_2}$ m$^2_{Cu}$ s$^{-1}$)).

$$S_i = 100 \times \frac{C_i}{\sum n \times C_i}$$

with $C_i$ as the concentration of the product $i$ in the effluent gas mixture and $n$ the corresponding carbon number. The TOF$_{MeOH}$ and TOF$_{CO}$ were based on the MeOH and CO outflows and the number of copper surface atoms, using the $d_s$ of the activated catalysts (determined by TEM measurements). The values of the apparent activation energy ($E_a$) in the Arrhenius model for MeOH and CO were obtained from the slope of the linear fit through the ln(CTY (mmol$_{Product}$ g$_{Cu}$ s$^{-1}$)). All calculations were performed considering the data at the end of each isothermal step in order to evaluate the catalysts activity and selectivity under steady-state conditions.
Figure S3 CO$_2$ TOF as function of Cu particle size at temperature between 200°C and 260°C for the series of Cu/C catalysts. Lines are drawn to guide the eye. Reaction conditions: 40 bar(g), 600 mL min$^{-1}$ g$^{-1}$, H$_2$/CO$_2$/He = 67.5/22.5/10 vol%.

Figure S4 CO$_2$ conversion as a function of temperature for the Cu/C catalysts with different copper particle size. Equilibrium CO$_2$ conversion has been reported as well. Reaction conditions: 40 bar(g), 600 mL min$^{-1}$ g$^{-1}$, H$_2$/CO$_2$/He = 67.5/22.5/10 vol%.
Figure S5 Comparison of CO$_2$ hydrogenation TOF of this work (yellow symbols) and values reported in literature.

Table S2 Experimental parameter with corresponding literature references for the data reported in Figure S5.

| Catalyst                  | T (°C) | bar | H$_2$/CO$_2$ ratio | Reference |
|----------------------------|--------|-----|--------------------|-----------|
| Cu(0.5-15 wt.%)/ZnO       | 180    | 7   | 9                  | 1         |
| Cu/ZrO/Al$_2$O$_3$        |        |     |                    |           |
| Cu/MgO                    | 230    | 30  | 3                  | 2         |
| Cu(111)                   | 230    | 30  | 3                  | 2,3       |
| Poly-Cu                   | 230    |     |                    | 2,4       |
| Cu(5 wt.%)/SiO$_2$        | 220    | 30  | 3                  | 5         |
| Cu(5 wt.%)/Al$_2$O$_3$    |        |     |                    |           |
| Cu/SiO$_2$                | 230    | 25  | 3                  | 6         |
| Cu/SiO$_2$                | 225-275| 7.2 | 3.3                | 7         |
| Cu/SiO$_2$                | 260    | 8   | 3                  | 8         |
Figure S6 (a) Arrhenius plot with the rate expressed as weight-normalized copper time yield for the whole series of Cu/C catalysts. (b) Apparent activation energy ($E_a$). Error bars were obtained from the linear fit of the Arrhenius plot. The error on the average $E_a$ was calculated from the standard deviation of the mean with a 95% confidence interval. Reaction conditions: 40 bar(g), 600 mL min$^{-1}$ g$_{Cu}$, H$_2$/CO$_2$/He = 67.5/22.5/10 vol%.

Figure S7 Arrhenius plot (a) for MeOH and (b) CO with the rate expressed as weight-normalized copper time yield for the whole series of Cu/C catalysts.

Table S3 Apparent activation energy for CO$_2$ conversion, CH$_3$OH and CO formation.

| Name      | $E_a$ CO$_2$ (kJ mol$^{-1}$) | $E_a$ CH$_3$OH (kJ mol$^{-1}$) | $E_a$ CO (kJ mol$^{-1}$) |
|-----------|-------------------------------|--------------------------------|--------------------------|
| 4.7_Cu/C  | 67 ± 1                         | 55 ± 10                         | 108 ± 3                  |
| 5.8_Cu/C  | 80 ± 7                         | 60 ± 9                          | 123 ± 8                  |
| 11.2_Cu/C | 67 ± 2                         | 61 ± 10                         | 116 ± 6                  |
| 12.8_Cu/C | 73 ± 3                         | 63 ± 14                         | 115 ± 7                  |
| 19.4_Cu/C | 83 ± 3                         | 76 ± 9                          | 126 ± 10                 |
| Average   | 74 ± 7                         | 63 ± 7                          | 118 ± 6                  |
Section S3: DFT calculations

Based on the computed electronic energies, reaction energies and free energies were calculated at 503 K and 1 bar reference pressure using the results of published calculations.[2] Based on the data on *HCOO/Cu(211) in the supporting information of ref [2], we obtain the following energy differences for the formation of *CHOO/Cu(211) from CO₂(g) and H₂(g): Correction to DFT-energies to improve gas-phase energetics (-0.455 eV), ZPVE contribution (0.169 eV) and finally the Gibbs free energy contribution, including ZPVE (1.238 eV). Based on these contributions, corrected energies and Gibbs free energies for the formation of formate were obtained for all facets by adding -0.286 eV (E) and -0.783 eV (G) to the electronic reaction energies.

Table S4. Unit cell sizes, coverages of different adsorbates on slabs and k-point grids of each calculated systems are depicted.

| Surfaces | HCOO | cis-COOH | CO |
|----------|------|----------|----|
|          | Unit cell | Coverage (ML) | k-point sampling | Unit cell | Coverage (ML) | k-point sampling | Unit cell | Coverage (ML) | k-point sampling |
| Cu(100)  | (4x4)   | 0.12      | 3x3×1 | (4x4)   | 0.12      | 3x3×1 | (3x3)   | 0.11      | 4x4×1 |
|          | (3x3)   | 0.22      | 4x4×1 | (2x2)   | 0.5       | 6x6×1 | (2x2)   | 0.25      | 6x6×1 |
|          | (2x2)   | 0.66      | 6x6×1 | (2x2)   | 0.66      | 4x4×1 | (2x2)   | 0.5       | 6x6×1 |
|          | (2x2)   | 1         | 6x6×1 | (2x2)   | 1         | 6x6×1 | (1x1)   | 1         | 12x12×1 |
| Cu(110)  | (4x4)   | 0.12      | 3x3×1 | (4x4)   | 0.12      | 3x3×1 | (3x3)   | 0.11      | 4x4×1 |
|          | (3x3)   | 0.22      | 4x4×1 | (3x3)   | 0.22      | 4x4×1 | (2x2)   | 0.25      | 6x6×1 |
|          | (2x2)   | 0.5       | 6x6×1 | (2x2)   | 0.5       | 6x6×1 | (2x2)   | 0.5       | 6x6×1 |
|          | (2x2)   | 1         | 6x6×1 | (2x2)   | 1         | 6x6×1 | (1x1)   | 1         | 12x12×1 |
| Cu(111)  | (4x4)   | 0.12      | 3x3×1 | (4x4)   | 0.12      | 3x3×1 | (3x3)   | 0.11      | 4x4×1 |
|          | (3x3)   | 0.22      | 4x4×1 | (3x3)   | 0.22      | 4x4×1 | (3x3)   | 0.22      | 4x4×1 |
|          | (2x2)   | 0.5       | 6x6×1 | (2x2)   | 0.5       | 6x6×1 | (2x2)   | 0.25      | 6x6×1 |
|          | (3x2)   | 0.66      | 4x4×1 | (3x3)   | 0.66      | 4x4×1 | (2x2)   | 0.5       | 6x6×1 |
|          | (3x2)   | 0.66      | 4x4×1 | (3x3)   | 0.66      | 4x4×1 | (2x2)   | 0.5       | 6x6×1 |
|          | (1x2)   | 1         | 12x6×1 | (1x2)   | 1         | 12x6×1 | (1x1)   | 1         | 12x12×1 |
| Cu(211)  | (3x6)   | 0.33      | 4x2×1 | (3x6)   | 0.33      | 4x2×1 | (3x3)   | 0.33      | 4x4×1 |
|          | (3x4)   | 0.5       | 4x3×1 | (3x4)   | 0.5       | 4x3×1 | (3x2)   | 0.5       | 4x5×1 |
|          | (3x3)   | 0.66      | 4x4×1 | (3x3)   | 0.66      | 4x4×1 | (3x3)   | 0.66      | 4x4×1 |
|          | (3x2)   | 1         | 4x5×1 | (3x2)   | 1         | 4x5×1 | (3x2)   | 1         | 4x5×1 |

Table S5. Total energies of each of the calculated systems. All energies in eV. (a) in x and y direction.
| surfaces      | size $^a$ | E      |
|--------------|----------|--------|
| Cu(100)      | 4×4      | -22.1111 |
|              | 3×3      | -18.003 |
|              | 2×3      | -12.4363 |
|              | 2×2      | -5.5257 |
|              | 1×1      | -1.3813 |
| Cu(110)      | 4×4      | -12.2079 |
|              | 3×3      | -6.8656 |
|              | 2×4      | -6.1029 |
|              | 2×2      | -3.0506 |
|              | 1×1      | -0.7625 |
| Cu(111)      | 4×4      | -26.2532 |
|              | 3×3      | -14.7605 |
|              | 3×2      | -9.8388 |
|              | 2×2      | -6.5573 |
|              | 1×2      | -3.2789 |
|              | 1×1      | -1.6392 |
| Cu(211)      | 3×6      | -28.1207 |
|              | 3×4      | -18.7475 |
|              | 3×3      | -14.0618 |
|              | 3×2      | -9.3660 |

**adsorbates**

|                          | size $^a$ | E      |
|--------------------------|----------|--------|
| Cu(100) - formate        | 4×4      | -44.7658 |
|                          | 3×3      | -35.09306 |
|                          | 2×2      | -28.10359 |
|                          | 2×3      | -53.37807 |
|                          | 2×2 (2×HCOO) | -49.3798 |
| Cu(110) - formate        | 4×4      | -35.1978 |
|                          | 3×3      | -29.8633 |
|                          | 2×4 (2×HCOO) | -52.12319 |
|                          | 2×2 (2×HCOO) | -49.0243 |
| Cu(111) – formate        | 4×4      | -48.6733 |
|                          | 3×3      | -37.1371 |
|                          | 2×2      | -28.9057 |
|                          | 3×2 (2×HCOO) | -54.34907 |
|                          | 3×3 (3×HCOO) | -81.5849 |
|                          | 1×2      | -49.5454 |
| Cu(211) – formate        | 3×6      | -51.0394 |
|                          | 3×4      | -41.6697 |
|                          | 3×3      | -36.98902 |
| Surface | Reconstruction | Formation Energy (eV) |
|---------|----------------|----------------------|
| Cu(100) – cis-COOH | 3×2 | -32.2313 |
| | 4×4 | -43.8454 |
| | 3×3 | -34.1766 |
| | 2×2 | -27.2331 |
| | 3×3 (3×COOH) | -77.6105 |
| | 2×3 (2×COOH) | -51.5739 |
| | 2×2 (2×COOH) | -48.3009 |
| Cu(110) – cis-COOH | 4×4 | -34.1882 |
| | 3×3 | -28.8539 |
| | 2×4 (2×COOH) | -50.14508 |
| | 2×2 (2×COOH) | -47.0684 |
| Cu(111) – cis-COOH | 4×4 | -47.6981 |
| | 3×3 | -36.1292 |
| | 2×2 | -28.0289 |
| | 3×2 (2×COOH) | -52.7968 |
| | 3×3 (3×COOH) | -79.2094 |
| | 1×2 | -24.0853 |
| Cu(211) – cis-COOH | 3×6 | -50.0979 |
| | 3×4 | -40.7196 |
| | 3×3 | -36.0104 |
| | 3×2 | -31.2294 |

Cu(100) - CO

| Surface | Reconstruction | Formation Energy (eV) |
|---------|----------------|----------------------|
| Cu(100) - CO | 1×1 | -13.4862 |
| | 3×3 | -25.1395 |
| | 2×2 | -18.2001 |
| | 2×2 (2×CO) | -30.9429 |

Cu(110) - CO

| Surface | Reconstruction | Formation Energy (eV) |
|---------|----------------|----------------------|
| Cu(110) - CO | 1×1 | -13.3442 |
| | 3×3 | -19.6398 |
| | 2×2 | -15.8243 |
| | 2×2 (2×CO) | -28.7625 |

Cu(111) – CO

| Surface | Reconstruction | Formation Energy (eV) |
|---------|----------------|----------------------|
| Cu(111) – CO | 1×1 | -13.1757 |
| | 3×3 | -27.3015 |
| | 3×3 (2×CO) | -39.8089 |
| | 2×2 | -19.1069 |
| | 2×2 (2×CO) | -31.5247 |

Cu(211) – CO

| Surface | Reconstruction | Formation Energy (eV) |
|---------|----------------|----------------------|
| Cu(211) – CO | 1×1 | -13.1757 |
| | 3×3 | -26.8508 |
| | 3×2 | -22.1513 |
| | 3×3 (2×CO) | -39.6126 |
| | 3×2 (2×CO) | -34.3138 |
Table S6. Zero-point energy corrections (ZPE), entropy contributions and total energies of gas-phase species and intermediates. (a) All values in eV. (b) $\text{H}_2(\text{g})$ and $\text{CO}_2(\text{g})$ are corrected by +0.09 eV and +0.41 eV, respectively, as described in reference [2]. (c) All values from reference [2], that is data based on Cu(211) and the BEEF-vdW functional.

| Intermediates | E    | ZPEc  | $S^c$  | $C_p^c dT^c$ |
|---------------|------|-------|--------|-------------|
| HCOO*         | see Table S5 | 0.624 | 0.000751 | 0.105       |
| CO*           | see Table S5 | 0.192 | 0.000452 | 0.085       |
| **Gas-phase species** | | | | |
| $\text{H}_2(\text{g})^{b}$ | -7.072 | 0.270 | 0.001380 | 0.091       |
| $\text{CO}_2(\text{g})^{b}$ | -18.003 | 0.320 | 0.002263 | 0.098       |
| $\text{CO}(\text{g})$ | -12.074 | 0.130 | 0.02092 | 0.091       |

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