Supporting Information for Stability of Mesocellular Foam Supported Copper Catalysts for Methanol Synthesis

C.E. Pompe[a,c], D.L. van Uunen[a], L.I. van der Wal[a], J.E.S. van der Hoeven[a,b], K.P. de Jong[a], P.E. de Jongh[a,*]

[a]*Inorganic Chemistry and Catalysis, Debye Institute for Nanomaterials Science, Utrecht University, Universiteitsweg 99, 3584 CG Utrecht, the Netherlands*

[b]*Soft Condensed Matter, Debye Institute for Nanomaterials Science, Utrecht University, Princetonplein 5, 3584 CC Utrecht, The Netherlands*

[c] *Current address: RIVM, National Institute for Public Health and the Environment, Antonie van Leeuwenhoeklaan 9, 3721 MA Bilthoven, the Netherlands*

*Corresponding author: P.E. de Jongh, P.E.deJongh@uu.nl

Calculation activity, Turn-over-Frequency (TOF), number-averaged particle size and surface-averaged particle size

The conversion (*X*) of CO and CO_2 are calculated using Equation S1 and S2:

$$X_{\mathrm{CO}} = \frac{\frac{CO_{feed}}{Ar_{feed}} - \frac{CO_{reaction}}{Ar_{reaction}}}{\frac{CO_{feed}}{Ar_{feed}}} \qquad \text{Eq. S1}$$

$$X_{\mathrm{CO2}} = \frac{\frac{CO2_{feed}}{Ar_{feed}} - \frac{CO2_{reaction}}{Ar_{reaction}}}{\frac{CO2_{feed}}{Ar_{feed}}} \qquad \text{Eq. S2}$$

Where the CO_{feed}, $CO2_{feed}$ and Ar_{feed} indicate the peak area of the corresponding gas in the chromatogram before catalysis and $CO_{reaction}$, $CO2_{reaction}$ and $Ar_{reaction}$ the peak area in the chromatogram during catalysis.

The number of converted moles CO and CO_2 is calculated by multiplying the conversion by the number of moles of the corresponding gas in the feed:

$$n_{X\mathrm{CO+CO2}} = X_{\mathrm{CO}} * n_{\mathrm{CO}} + X_{\mathrm{CO2}} * n_{\mathrm{CO2}} \qquad \text{Eq. S3}$$

The number of moles CO and CO_2 in the feed stream are calculated using Equation S4 and S5 respectively.

$$n_{\mathrm{CO}} = \frac{Q_{\mathrm{CO}} p_{ref}}{\mathrm{R} T_{ref}} * \varphi \qquad \text{Eq. S4}$$

$$n_{\mathrm{CO2}} = \frac{Q_{\mathrm{CO2}} p_{ref}}{\mathrm{R} T_{ref}} * \varphi \qquad \text{Eq. S5}$$

Where Q_{CO} or $Q_{CO2}$is the fraction CO or CO_2 in the feed, R the gas constant (8.3145 J/(K*mol)), p_{ref} (in Pa) the pressure at which the mass flow controllers are calibrated, T_{ref} the temperature (in K) at which the mass flow controllers are calibrated and φ the total gas flow (in m^3/h).

The activity of the catalyst is expressed as moles CO and CO_2 converted per hour per kg of catalyst ($mol_{CO+CO2}/(kg_{cat}*h)$:

$$a = \frac{n_{X\mathrm{CO+CO2}}}{m_{\mathrm{cat}}} \qquad \text{Eq. S6}$$

Where $n_{XCO+CO2}$ is the number of moles CO and CO_2 converted per hour (mol_{CO+CO2}/h) and m_{cat} the catalyst mass in the reactor in kg.

The turn-over-frequency (TOF) is calculated using Equation S7:

$$\mathrm{TOF} = \frac{a * M_{\mathrm{Cu}}}{D_{\mathrm{Cu}} * wt\%\ \mathrm{Cu}} \frac{100}{3.6 * 10^6} \qquad \text{Eq. S7}$$

Where M_{Cu} is the molar mass of Cu (63 g/mol) and D_{Cu} the dispersion of Cu as expressed in Equation S8. The factor $100/3.6*10^6$ corrects for the used units and to obtain the unit of s^{-1} for the calculated TOF.

Dispersion of Cu:

$$D_{\mathrm{Cu}} = \frac{6\, V_m}{A_m d_s} \approx \frac{1.04}{d_S} \qquad \text{Eq. S8}$$

V_m is the molar volume of Cu which is $7.09*10^{21}$ nm^3 and A_m is the molar surface area of Cu and is $4.10*10^{22}$ nm^2. d_s is the surface-averaged particle size and is calculated as depicted in Equation S10 (the number-averaged particle size is in contrast calculated using Equation S9). This calculation assumes that the particles are spherical and every surface atom takes part in the reaction.

Number-averaged particle size:

$$d_N = \frac{1}{N} \sum_{n=1}^{N} d_i \qquad \text{Eq. S9}$$

Surface-averaged particle size:

$$d_S = \sqrt{\frac{1}{N}\sum_{n=1}^{N} d_i^2} \qquad \text{Eq. S10}$$

Dependence of turn-over-frequency on particle size

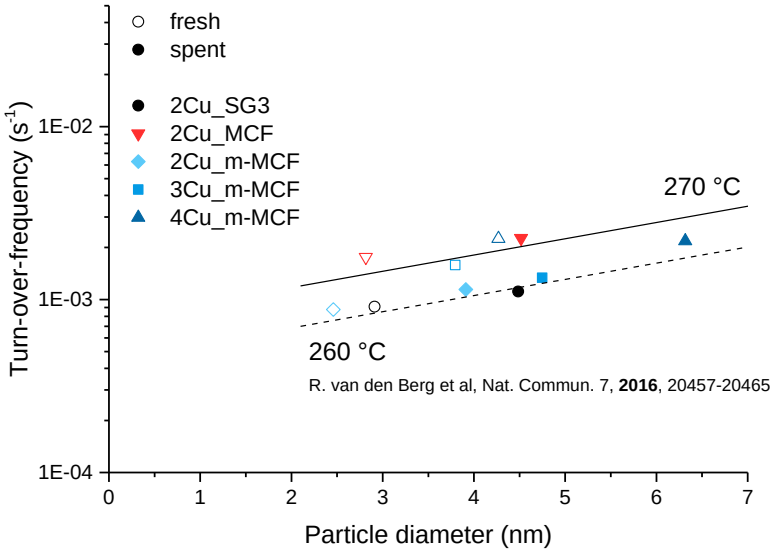

Figure S1: Turn-over-frequency (TOF) versus the particle size for the five catalysts (open symbols represent the TOF of the fresh catalysts and the closed symbols the TOF of the spent). The dashed line indicates the relation between the particle size and TOF taken from by [1] for Cu/SiO_2 at 260 °C. The slightly higher TOF for these samples is explained by the fact that the activity for these five samples was measured at 270 °C instead of 260 °C in reference [1]. The solid line indicates he TOF versus the particle diameter for the more active samples, where the Cu particles are likely not embedder in the SiO_2.

TEM images of spent catalysts

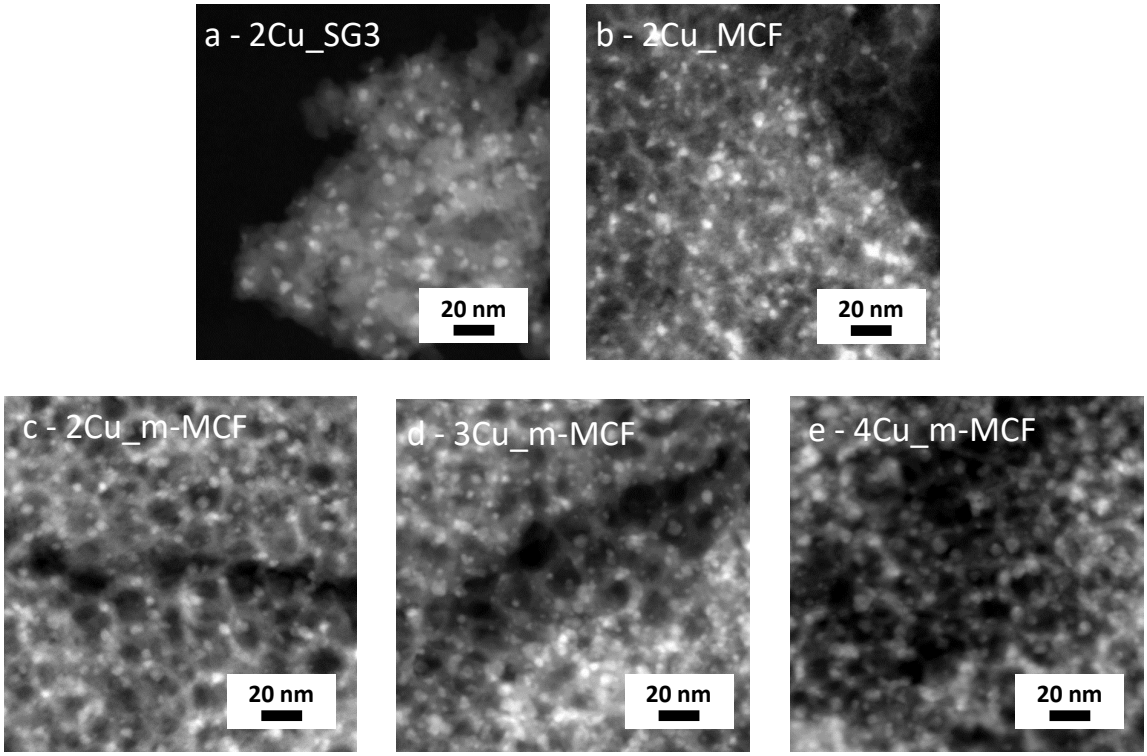

Figure S2: HAADF-STEM images of the spent catalyst.

Particle size distributions of fresh and spent catalysts

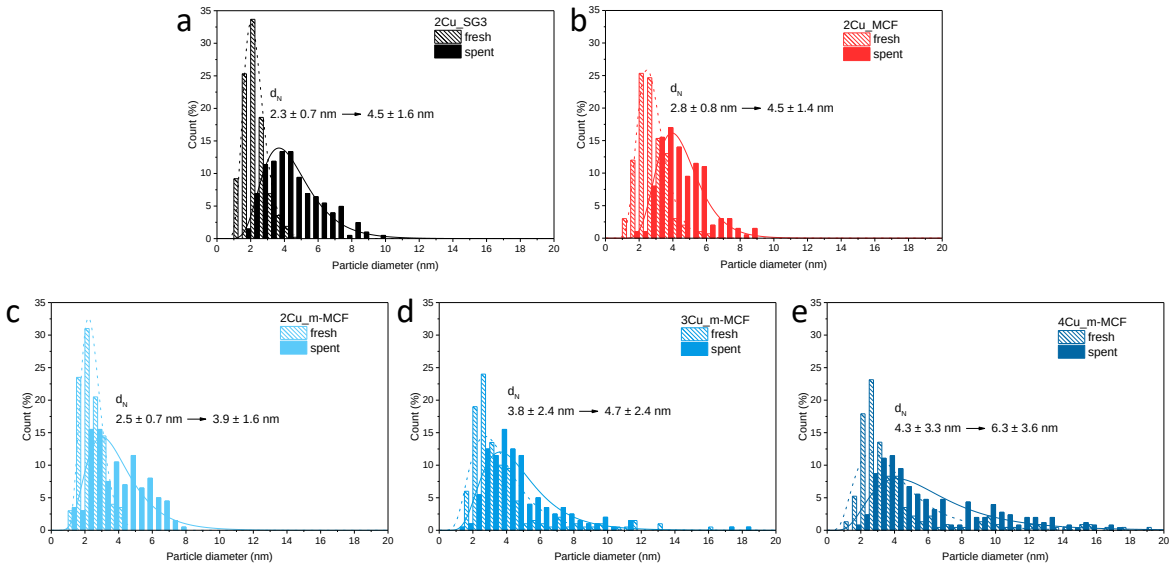

Figure S3: Particle size distributions of the fresh and spent samples. a) 2Cu_SG3, b) 2Cu_MCF, c) 2Cu_m-MCF, d) 3Cu_m-MCF and e) 4Cu_m-MCF. The lines represent lognormal distributions.

References:

[1] R. van den Berg, G. Prieto, G. Korpershoek, L.I. van der Wal, A.J. van Bunningen, S. Lægsgaard-Jørgensen, P.E. de Jongh, K.P. de Jong, Structure sensitivity of Cu and CuZn catalysts relevant to industrial methanol synthesis, Nat. Commun. 7 (2016) 20457–20465. doi:10.1038/ncomms13057.