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# *Supporting Information*

# Methanol synthesis via $CO_2$ hydrogenation over CuO-$ZrO_2$ prepared by a Two-Nozzle Flame Spray Pyrolysis.

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## 1. Experimental

### 1.1 Characterization

Specific surface area of each catalyst was measured by $N_2$ adsorption at 77 K using a MicrotracBEL BELSORP-mini II apparatus.

The crystalline phase of catalysts was determined by powder X-ray diffraction (PXRD, Bruker D8 Advance diffractometer, 40 kV, 40 mA, Cu Kα). Average crystallite sizes for $ZrO_2$ were estimated using TOPAS Rietveld method.

HAADF-STEM imaging was performed using a Hitachi HDCS2700CS microscope.

The loading of Cu in the as-prepared catalysts, except for **CuO (FSP)** and **CuO-$ZrO_2$ (PM)**, were measured by an Inductively Coupled Plasma (ICP) atomic emission spectrometry (Mikroanalytisches Labor Pascher, Germany).

$N_2O$ titration was carried out according to the methods developed by Evans *et al.* [S1] About 50 mg of catalysts were placed in a quartz U-shaped reactor connected to a flow system (MicrotracBEL, BELCAT-B apparatus) and treated at 300 °C for 30 min in 50% $H_2$/He. He gas was used as a carrier gas at 30 mL $min^{-1}$. Successive doses of 10 wt% $N_2O$/He gas were subsequently introduced into the He stream by means of a calibrated injection valve (27 $\mu L_{N2O}$(STP) $pulse^{-1}$) at 90 °C. The amount of outlet $N_2O$ and $N_2$ was analyzed by a thermal conductive detector. The number of accessible Cu surface atoms was estimated according to **Eq. (S1)**.

$$2Cu_S + N_2O \rightarrow Cu_{S2}O + N_2 \qquad \text{(S1)}$$

Temperature programmed reduction by $H_2$ ($H_2$-TPR) was carried out using AutoChem II unit (Micromeretics). 20 mg of sample powder was heated from room temperature to 450 °C at a heating rate of 10 °C $min^{-1}$ under flowing 5% $H_2$ in He (50 ml $min^{-1}$). The off-gases were measured with a mass spectrometer (Pfeiffer-vacuum, ThermoStar GSD T2).

In situ X-ray absorption spectra at the Cu K-edge were measured at the SuperXAS beamline at the Swiss Light Source. The SLS is operating in top-up mode at a 2.4-GeV electron energy and a current of 400 mA. The beam was collimated using a Si-coated collimating mirror, monochromatized by a Si (111) channel-cut monochromator and focused using a Rh-coated toroidal mirror to a size at the sample position of 5 mm by 200 micrometers (horizontal x vertical). Calibration of the monochromator energy position was performed by setting the inflection point of a Cu foil spectrum recorded simultaneously with the sample to 8979 eV. Spectra were collected in transmission mode using 20 cm long ionization chambers filled with 1 atmosphere of $N_2$. The powder samples were pressed into a glass capillary, which was connected with a high-pressure gas flow system. The catalysts were reduced under pure $H_2$ (1 bar) at 300 °C for 15 min, and then cooled down to reaction temperature (230 °C). The $H_2$ gas was then changed to the reaction gas mixture ($CO_2/H_2/N_2$ = 1/3/1, 20 bar). Spectra were background corrected and normalized using the iFeffit software suite. [S2]

## 1.2 Reaction test

The $CO_2$ hydrogenation was conducted in a fixed-bed tubular reactor at 20 bar (PID Eng&Tech). The reaction temperature in the catalyst bed was measured by a K-type thermocouple. For each experiment, 10-300 mg of a catalyst was mixed with 3 g of SiC. The catalysts were pre-treated under a flow of 17% $H_2/N_2$ (60 mL $\text{min}^{-1}$) at 300 °C for 30 min at 1 bar. After cooling down to 270 °C, the reaction gas flow ($CO_2/H_2/N_2$ = 1/3/1, 12.4 mL $\text{min}^{-1}$) was passed through the catalyst bed at 20 bar for 7 h, to ensure to have reached steady state conditions. The products were analyzed by an online gas chromatograph (Agilent 7890A) equipped with flame ionization detector (for methane and methanol separated by a DB-1 column) and thermal conductivity detector (for $N_2$, $CO_2$, CO, and $CH_4$ separated by MS5A and PPQ columns). In all experiments, the measured $CH_4$ concentration were negligible. The carbon mass balance was estimated from the concentrations of $CO_2$, CO, and methanol, using $N_2$ as the internal standard. The $CO_2$ conversion, methanol selectivity, methanol production rate, and turnover frequency of methanol production were calculated as follows:

$$\mathrm{CO_2\ conversion} = \frac{F_{\mathrm{out,CO}} + F_{\mathrm{out,methanol}}}{F_{\mathrm{out,CO_2}} + F_{\mathrm{out,CO}} + F_{\mathrm{out,methanol}}} \tag{S2}$$

$$\mathrm{Methanol\ selectivity} = \frac{F_{\mathrm{out,methanol}}}{F_{\mathrm{out,CO}} + F_{\mathrm{out,methanol}}} \tag{S3}$$

$$\mathrm{Methanol\ production\ rate} = \frac{F_{\mathrm{out,methanol}}}{w \times a} \tag{S4}$$

$$\mathrm{TOF\ of\ methanol\ production} = \frac{\mathrm{Methanol\ production\ rate}}{n_{\mathrm{N2O}} \times Y} \tag{S5}$$

where $F_{\mathrm{in},x}$ is the inlet flow rate of $x$ species (mL(stp) $\text{min}^{-1}$), $F_{\mathrm{out},x}$ is the outlet flow rate of species $x$ (mL(stp) $\text{min}^{-1}$), $w$ is the amount of catalyst in the catalyst bed ($g_{\mathrm{cat}}$), $a$ is the Cu loading ($g_{\mathrm{Cu}}\ g_{\mathrm{cat}}^{-1}$), $n_{\mathrm{N2O}}$ is the stoichiometry of Cu to $N_2O$ (2 $\mathrm{mol_{Cu}}\ \mathrm{mol_{N2O}}^{-1}$), [S1] and $Y$ is the $N_2O$ consumption measured by $N_2O$ titration ($\mu\mathrm{mol_{N2O}}\ g_{\mathrm{Cu}}^{-1}$). The MeOH selectivity was examined at different ratio of catalyst weight to the total flow rate (W/F ratio, 10 to 1450 $\mathrm{mg_{cat}}$ $\mathrm{mL}^{-1}$ s). The W/F ratio was controlled by changing the total flow rate.

## 2. Results

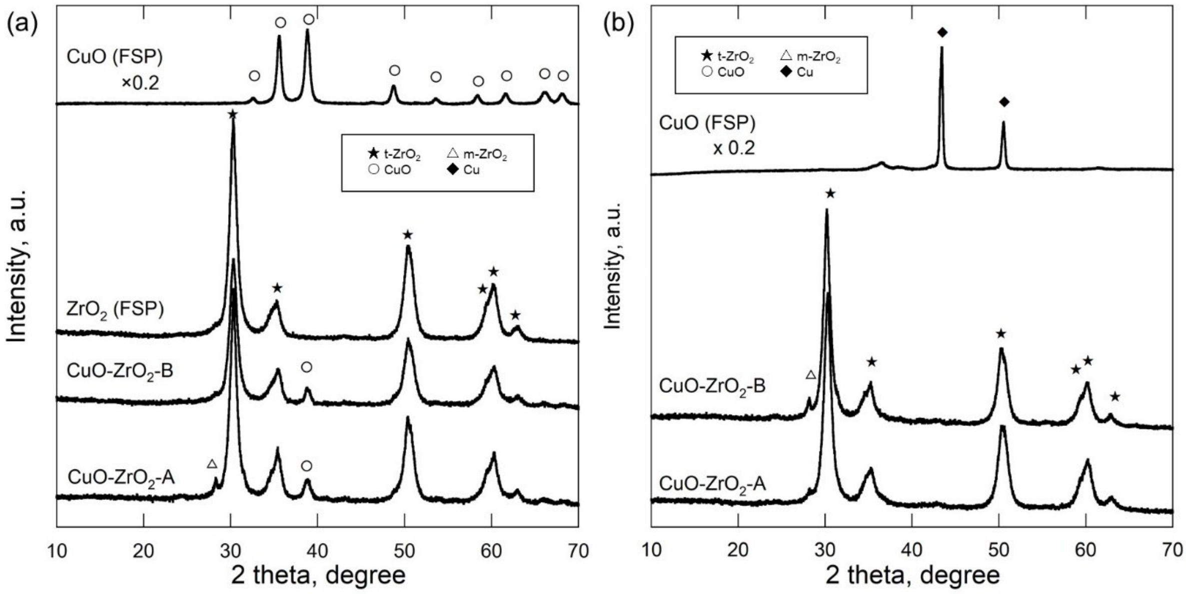

**Figure S1** PXRD patterns for (a) fresh and (b) spent catalysts. Tetragonal-$ZrO_2$ ($t$-$ZrO_2$, stars, PDF 01-079-1769), monoclinic-$ZrO_2$ ($m$-$ZrO_2$, triangles, PDF 01-083-0936), CuO (circles, PDF 01-073-6023), and metallic Cu (circles, PDF 01-089-2838) are marked in the spectra.

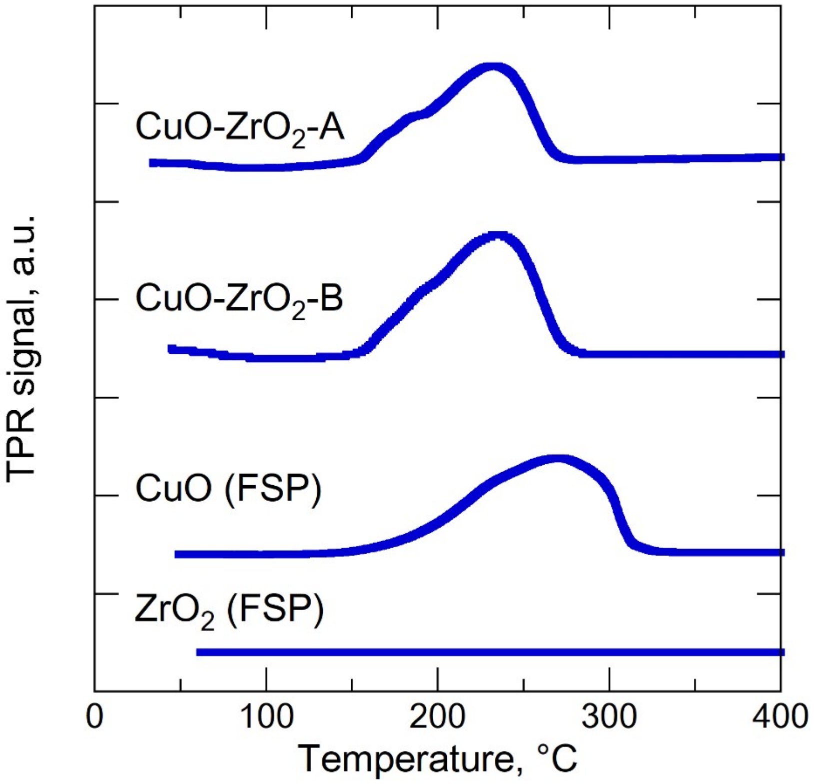

**Figure S2** Temperature programmed reduction with $H_2$ for preapred catalysts. While in pure $ZrO_2$ nothing is reduced, for $ZrO_2$ supported CuO reduction starts about 160 °C and is complete at 250 °C. Pure CuO needs higher temperature to be completely recuded at 320 °C because the CuO clusters are bigger.

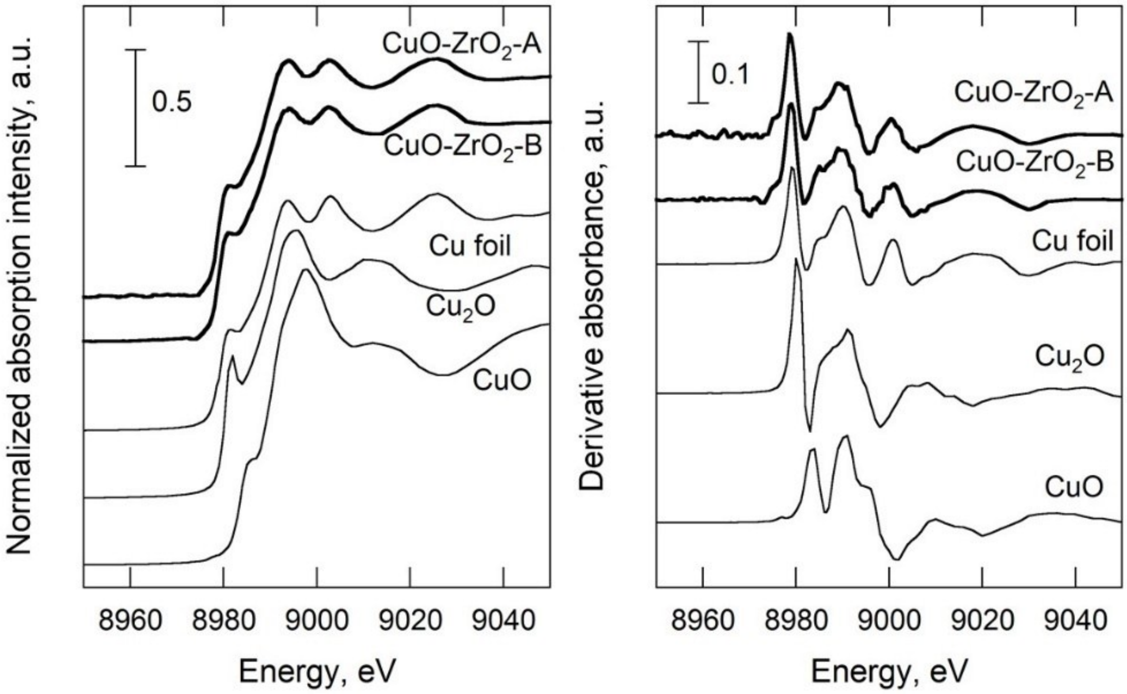

**Figure S3** Cu K-edge XANES spectra of CuO-$ZrO_2$-A and CuO-$ZrO_2$-B during $CO_2$ hydrogenation. Reaction condition: $CO_2/H_2/N_2$ = 1/3/1, 20 bar, 230 °C.

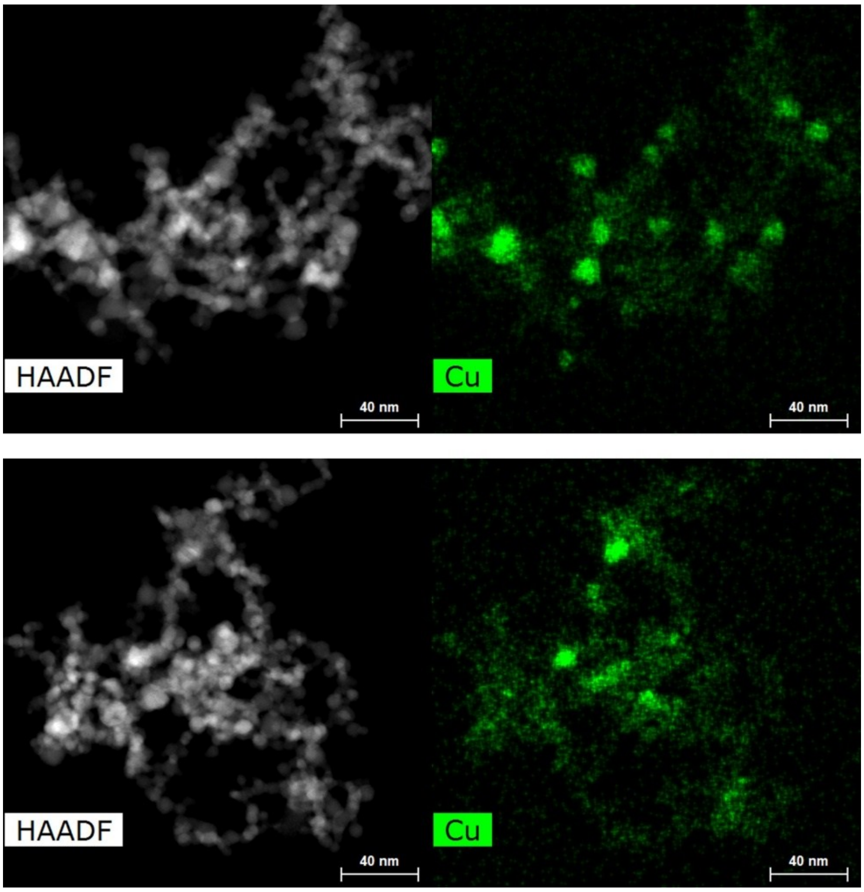

**Figure S4** STEM images of spent **CuO-$ZrO_2$-B** with Cu mapping. Highlighted areas are Cu-rich zones from EDX mapping.

## REFERENCES

S1 J. W. Evans, M. S. Wainwright, A. J. Bridgewater, D. J. Young, *Appl. Catal.*, 1983, **7**, 75-83.

S2 B. Ravel, M. Newville, *J. Synchrotron Radiat.*, 2005, **12**, 537-541.