3D-Printed Raney-Cu POCS as Promising New Catalysts for Methanol Synthesis

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Supporting Information

Determination of elemental composition by inductively-coupled plasma optical emission spectroscopy

The elemental composition of the catalysts or the composition of the caustic were determined by optical emission spectroscopy with inductively coupled plasma. The solid samples were digested with condensed water. The gas used is usually argon, and a plasma is generated via a high-frequency current. The sample was sprayed into the hot plasma and a detector was used to measure the ion lines. The intensity can be quantified with a calibration standard.

Measuring of active copper surface area by nitrous oxide decomposition

The active copper surface area of the tested catalysts was measured by using the isothermal nitrous oxide flow experiment, also known as nitrous oxide reactive frontal chromatography (N2O-rfc). The experiment was performed in an Autochem II 2920 (s. Figure S2) automated catalyst characterization system from Micromeritics. A sample mass of 200 mg was weight in. For a uniform starting point, a drying and a temperature programmed reduction (TPR) experiment was performed before the N2O-rfc. Therefore, the catalyst is heated up in 50 cm^3 min^{-1} Ar flow to 150 °C (20 K min^{-1}) and hold for 30 min. After cooling down to room temperature, the sample is heated with 5 K min^{-1} in 20 vol.% H2 in Ar mixture(50 cm^3 min^{-1}) to 250 °C. After cooling down to 45 °C, the sample is flushed in 50 cm^3 min^{-1} He to get a stable TCD signal. The gas flow is switched to 0.5 vol.% N2O in Helium. Not reacted N2O is condensed out in a cold trap and the amount of the released N2 is measured with a thermal conductivity sensor (TCD) (s. Figure S1). Nitrous oxide decomposes at the active copper sites according the equation.

$$N_2O + 2\,Cu \leftrightarrow Cu - O - Cu + N_2 \qquad \text{(S1)}$$

At low temperature the nitrous oxide oxidizes the copper surface in a monolayer, so it is possible to calculate the copper surface area with the following assumptions:

$$A_{N_2,Peak} \rightarrow n_{N_2}$$
$$N' = 1{,}47 \cdot 10^{19}\ \left[N_{Cu,surf} \cdot m^{-2}\right]$$
$$S_{Cu,act} = \frac{2 \cdot n_{N_2} \cdot N_A}{N' \cdot m_{cat}} \qquad \text{(S2)}$$

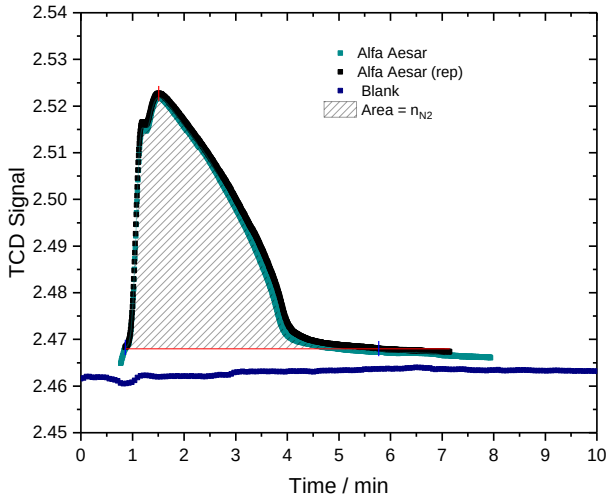

Figure S1: Nitrous oxide flow experiment with a Cu/ZnO/Al_2O_3 (Alfa Aesar) catalysts (2 times) and a blank experiment. Conditions: T=318.15 K, p=0.1 MPa, V=50 mlN min^{-1}, 0.5 vol% N_2O in He, m_{cat}=0.2 g.

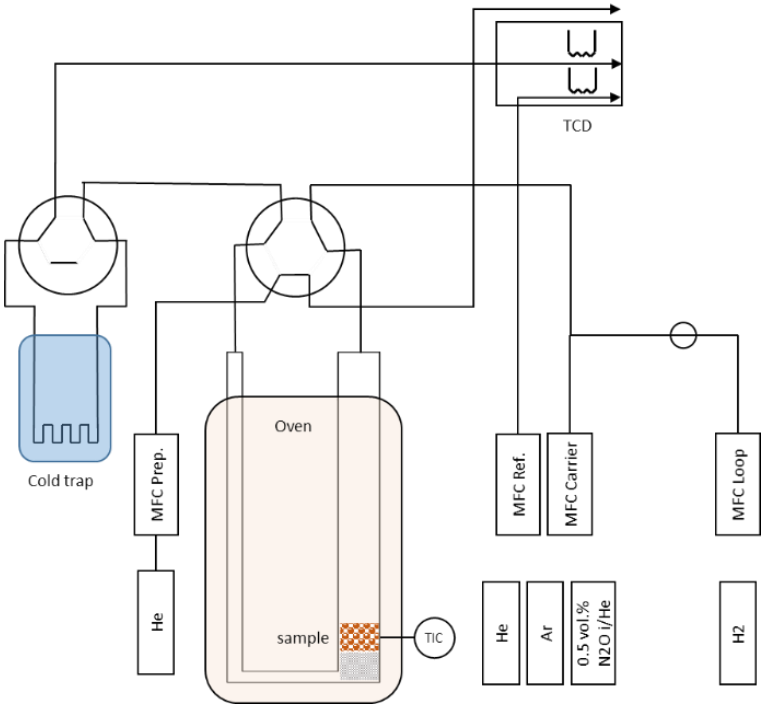

Figure S2: Schematic flowsheet of the Autochem 2920 (Micromeritics).

For the calculation of the methanol productivity related to the surface area, the active copper surface area of the fresh catalyst was used. The active copper surface after methanol synthesis was also measured to investigate possible changes in the catalyst structure. Figure S3 shows the active surfaces of the measured catalysts before (fresh) and after (used) the methanol synthesis reaction. As the catalyst surface is changing during the reaction, a trend of decreasing active copper surface area after the reaction can be observed for all tested catalysts.

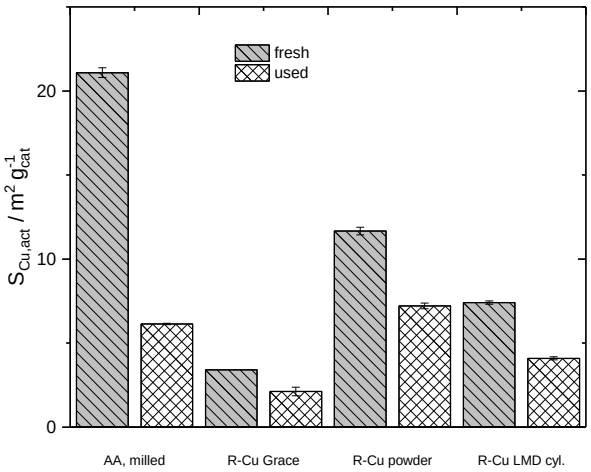

Figure S3: Active copper surface area of the tested catalyst before (fresh) and after methanol synthesis (used) for the tested catalysts (s. Table 1)

Calculation of Zn/Cu ratio

For the characterization of the catalytic activity, the Zn/Cu ratio is calculated in the nanoporous layer using equation (S3):

$$Zn/Cu = \frac{w_{\mathrm{Zn}}^{\mathrm{Kat}}}{\eta_{\mathrm{L}} \cdot w_{\mathrm{Cu}}^{\mathrm{Kat}}} \qquad \text{(S3)}$$

Since the composition of the nanoporous layer depending on the leaching depth can only be determined by time-consuming surface measurements, the ratio of zinc to nanoporous copper in the catalytically active layer is estimated. The composition of the catalysts was determined by ICP-OES measurements. Since the Zn(OH)2 is only present in the nanoporous copper layer and not in the unreacted Cu50Al50 core, the Zn/Cu ratio can be determined by equation above.