

Additively manufactured Raney-type Copper catalyst for methanol synthesis

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Supporting Information

Description of LMD process

The samples were produced using InssTek's DMT[®] mode utilizing two cameras (visual spectrum) to observe the deposition height and adjust the laser power according to a set value for the detected height. In this study, laser powers from 215 to 300 W were applied. The DMT[®] mode results in a closed loop laser power regulation with a frequency below 100 ms, aiming to counter deviations from the nominal height. To achieve uniform geometries according to the reactor dimensions, the LMD-built cylinders were mechanically post-processed to dimensions of 9.5 mm diameter and 6 mm height.

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 cm³ 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 cm³ min⁻¹) to 250 °C. After cooling down to 45 °C, the sample is flushed in 50 cm³ 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.



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:

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

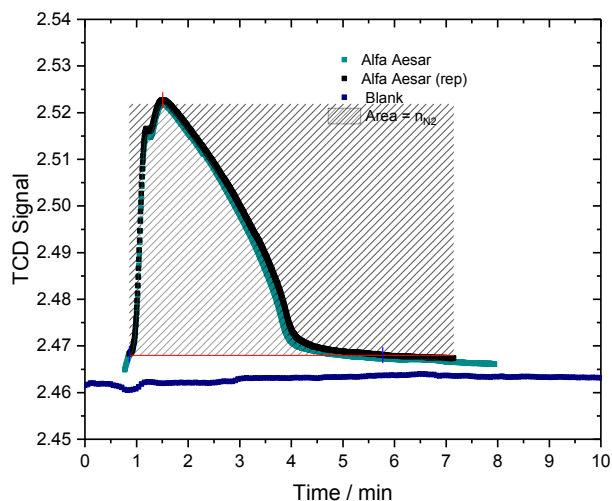


Figure S1: Nitrous oxide flow experiment with a $Cu/ZnO/Al_2O_3$ (Alfa Aesar) catalysts (2 times) and a blank experiment. Conditions: $T=318.15\text{ K}$, $p=0.1\text{ MPa}$, $V=50\text{ mL min}^{-1}$, $0.5\text{ vol\% } N_2O\text{ in He}$, $m_{cat}=0.2\text{ g}$.

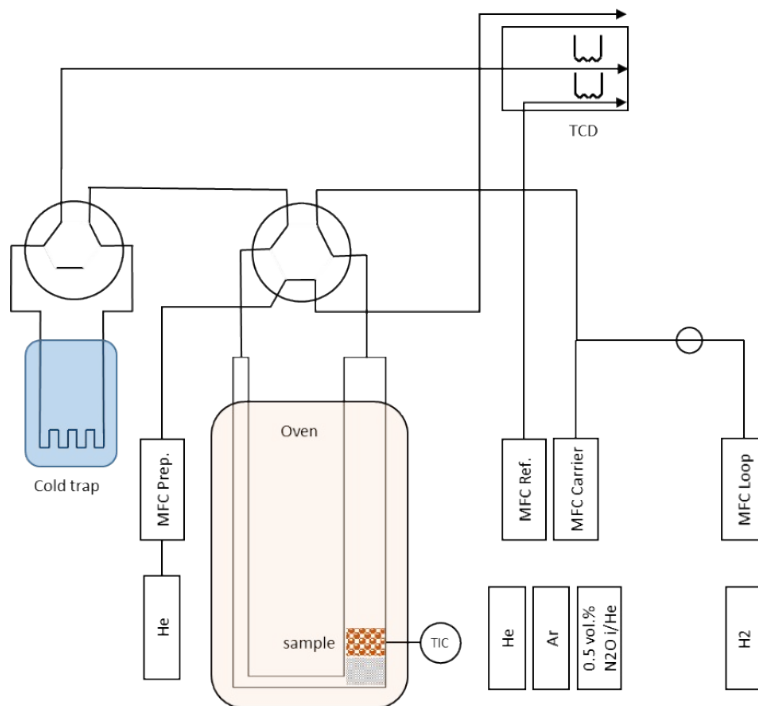


Figure S2: Schematic flowsheet of the Autochem 2920 (Micromeritics).

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.

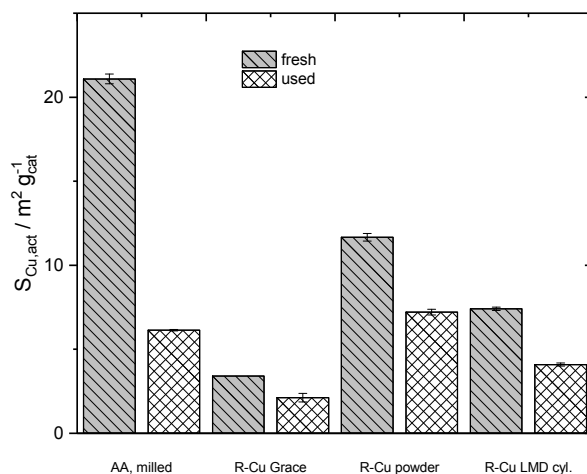


Figure S3: Active copper surface area of the tested catalyst before (fresh) and after methanol synthesis (used) for the tested catalysts (s. Table 1).

Reactor Set-Up

In Figure S4 the flowsheet of the reactor set-up for the CO hydrogenation experiments is shown. The gas volume flows were adjusted with mass flow controllers (Bronkhorst). After passing the static mixer and the heated pipe (150°C), the gas reached the reactor inlet. A stainless steel tubular reactor was used (Inner diameter $d=9.7$ mm, length $L=45$ mm), equipped with a thermocouple at the end of the catalyst bed. The reactor was heated with a heating jacket to a maximal temperature of 300°C. The pressure in the reactor was adjusted with a back pressure regulator (BPV-3.1). After the BPV-3.1 the gas was depressurised to atmospheric pressure. A part of the gas was sent over a heated capillary ($T=150^{\circ}\text{C}$) to the online GC (Agilent 7820). Prior to the catalytic testing, the catalyst was dried in $100\text{ mL N}_2\text{ min}^{-1}$ at atmospheric pressure. After 1 h of drying at 80°C the catalyst was heated in 5 K/min to 250°C . Subsequently, a reduction in $100\text{ mL N}_2\text{ min}^{-1}$ H_2 was performed for one hour at atmospheric pressure. The reaction was conducted at 75 bar and 250°C with a total volume flow of $300\text{ mL N}_2\text{ min}^{-1}$. The molar ratio of the reactants H_2/CO was set to 2. The product gas was analyzed with online gas chromatography (Agilent 7280) equipped with two columns (Plot U, Molsieve) and two thermal conductivity sensors. As the methanol synthesis is a volume reducing reaction, the outlet molar stream had to be calculated separately (see ESI equations S4-S5). To terminate the catalytic test, the reactor pressure was slowly reduced to atmospheric pressure and cooled down to 100°C under a $100\text{ mL N}_2\text{ min}^{-1}$ N_2 stream. The tested catalysts were passivated at 100°C with $100\text{ mL N}_2\text{ min}^{-1}$ in 1 vol.% N_2O in He for 1 hour.

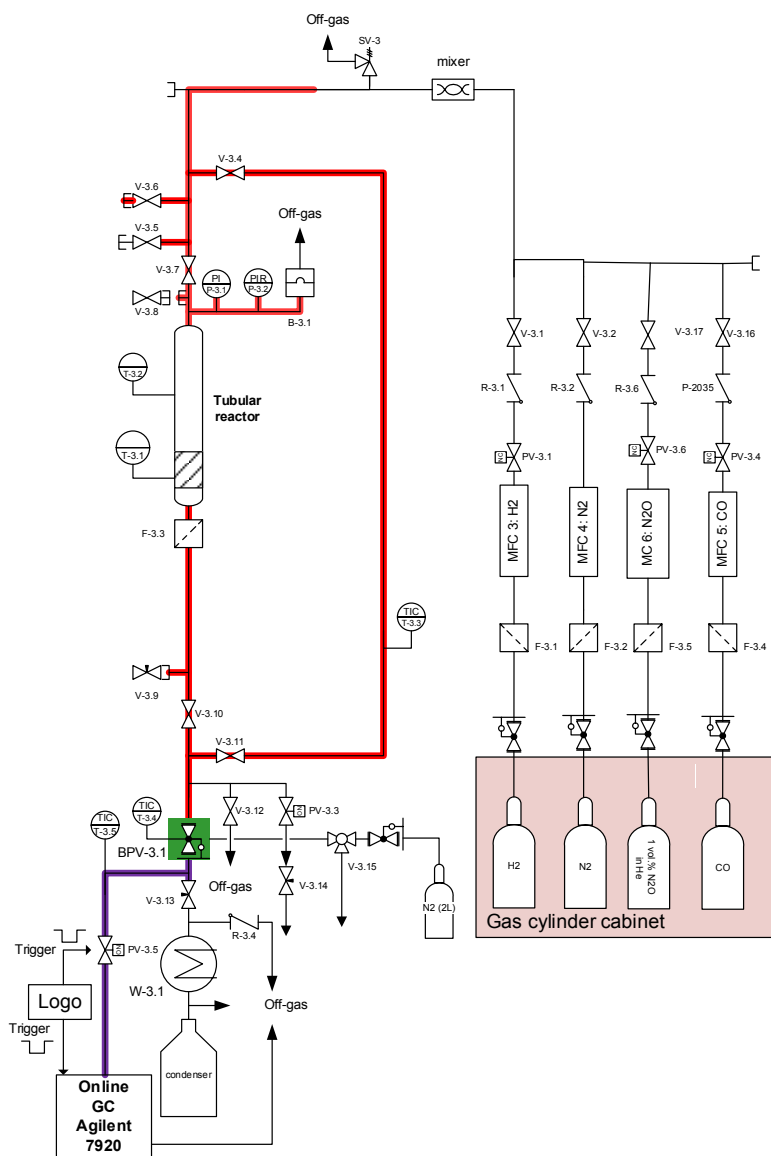


Figure S4: Flowsheet of laboratory rig for CO hydrogenation experiments.

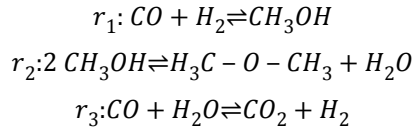
Calculations

Calculation of the outlet mole stream

In the following equations the indices 0 stands for the inlet, whereas 1 stands for the outlet conditions. The inlet mole flow $\dot{n}_{i,0}$ of the different components was determined with the ideal gas law.

$$\dot{n}_{i,0} = \frac{p \cdot V_{i,0}}{R \cdot T} \quad (S3)$$

While the inlet flow is set-up by the mass-flow controllers, the outlet mole-flow has to be calculated due to the mole changing reactions. For calculating the outlet mole flow the following reaction equations were taken into account.



With the following equations the different extent of reactions were calculated under minimization of the least square sum of the measured GC values $y_{i,1}^{GC}$ and the calculated outlet mole fractions $y_{i,1}^{calc}$ (s. equation S4). With the indices i for the different components and j for the reaction indices, the

$$\min_{(r_j)} (y_{i,1}^{GC} - y_{i,1}^{calc})^2$$

following equation could be solved.

$$\text{s.t. } y_{i,1}^{calc} = \frac{n_{i,0} + \sum_j v_{i,j} r_j}{\sum_k (n_{k,0} + \sum_j v_{k,j} r_j)}$$

$$(S4) \quad n_{ges,1} = \sum_k (n_{k,0} + \sum_j v_{k,j} r_j)$$

$$(S5)$$

With $n_{ges,1}$ it is possible to calculate the typical reaction engineering parameters.

$$X_i = \frac{\dot{n}_{i,0} - \dot{n}_{i,1}}{\dot{n}_{i,0}} \tag{S6}$$

$$S_{i,l} = \frac{\dot{n}_{i,1} - \dot{n}_{i,0}}{\dot{n}_{l,0} - \dot{n}_{l,1}} \cdot \frac{|v_l|}{v_i} \tag{S7}$$

Determination of methanol productivity for different reference quantity

The catalysts were compared with respect to their methanol activity. The methanol productivity is often related to the mass of the catalyst, as this is the easiest accessible value (s. equation S8).

$$P_{CH_3OH}(m_i) = \frac{\dot{m}_{CH_3OH}}{m_i} = \frac{\dot{m}_{CH_3OH}}{m_{cat}} \tag{S8}$$

As Raney® catalyst are bulk metal catalysts, the mass of the catalyst is quiet large compared to supported catalyst. For a fair comparison of the methanol productivity of the different catalysts, it is common to relate the product mass flow to the active species. In our case just the nanoporous copper is taking part in the reaction. We assumed that for the powder catalysts, all of the copper is nanoporous or supported as nanoparticles (Alfa Aesar). In case of the Raney-Cu LMD cylinder, we have an unreacted CuAl70 core. Therefore we estimate the nanoporous copper mass over the leaching efficiency by measuring the concentration of the leaching solution before and after the reaction with ICP-OES. The leaching efficiency is defined by equation S9.

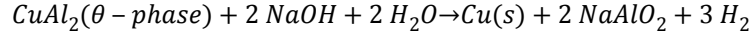
$$\eta_{leaching} = \frac{m_{Al,start} - m_{Al,end}}{m_{Al,start}} = \frac{(c_{Al,end} - c_{Al,start}) \cdot V_{Laughe}}{c_{Al,max} \cdot V_{Laughe}} \tag{S9}$$

The nanoporous copper mass was estimated by equation S10. The starting alloy consist of 50 wt.% of copper balanced with aluminium. Therefore the nanoporous copper mass is calculated under the following assumption, that the dissolved aluminium fraction results in the same fraction of nanoporous copper.

$$m_{np-Cu} = \eta_{leaching} \cdot m_{Cu} \quad (S10)$$

$$P_{CH_3OH}(m_{np-Cu}) = \frac{\dot{m}_{CH_3OH}}{m_{np-Cu}} \quad (S11)$$

The heterogeneity of the alloy is not taken into account in the calculation. The Cu-70Al LMD cylinder consists of 86% Θ -phase and 14% α -phase (see Table S2 and Figure S9). Since the alpha phase is washed out during the caustic solution, the nanoporous copper is only produced from the Θ -phase (CuAl₂).



A consideration of this proportion would result in smaller masses of nanoporous copper, resulting in higher methanol productivities. Since the quantitative determination of the Θ -phase come along with a high uncertainty, the results were evaluated with the simplification according to eq. (3) and (5), keeping in mind that the absolute methanol productivities are underestimated.

It is also possible to calculate the productivity on the mass of active copper (amount of active sites). The active copper surface area is measured by an isothermal nitrous oxide flow experiment (s. Figure S1). Therefore $m_{Cu,act}$ is calculated by equation S12.

$$m_{Cu,act} = \frac{S_{Cu,act} \cdot m_{np-Cu} \cdot N' \cdot M_{Cu}}{N_A} \quad (S12)$$

Recent publications show, that N₂O could react next to the copper surface atoms with partial reduced ZnOx species¹ so the active surface area might be overestimated, when a catalyst containing ZnO is used.

Additional Results

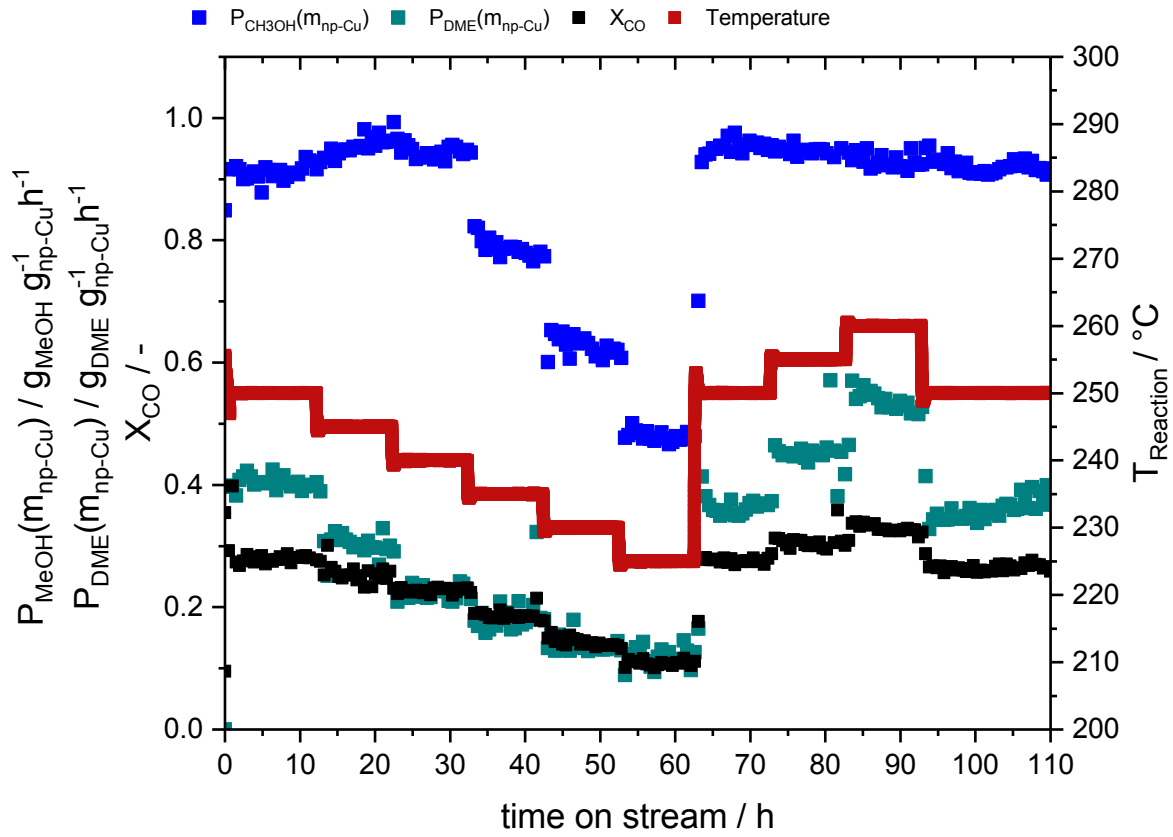


Figure S5: CO hydrogenation experiment with LMD-manufactured Raney-type Cu cylinder structure; $m_{\text{cat}}=3.5 \text{ g}$, $p=75 \text{ bar}$, $T=200\text{-}260^\circ\text{C}$, residence time: 3 s , $V_{\text{ges}}=300 \text{ mlN min}^{-1}$ ($\text{H}_2/\text{CO}=2/1$).

Table S1: mean values of the longterm-experiment of the LMD-manufactured Raney-type Cu cylinder shown in Figure 2; $m_{\text{cat}}=3.5 \text{ g}$, $p=75 \text{ bar}$, $T=200\text{-}260^\circ\text{C}$, residence time: 3 s , $V_{\text{ges}}=300 \text{ mlN min}^{-1}$ ($\text{H}_2/\text{CO}=2/1$).

T_{Reaction}	$P_{\text{CH}_3\text{OH}}(m_{\text{np-Cu}})$	$P_{\text{CH}_3\text{OH}}^{\text{eq}}(m_{\text{np-Cu}})$	$P_{\text{DME}}(m_{\text{np-Cu}})$	X_{CO}	$S_{\text{CH}_3\text{OH}}$
$^\circ\text{C}$	$\backslash \text{g}_{\text{CH}_3\text{OH}} \text{g}_{\text{np-Cu}}^{-1} \text{h}^{-1}$	$\backslash \text{g}_{\text{CH}_3\text{OH}} \text{g}_{\text{np-Cu}}^{-1} \text{h}^{-1}$	$\backslash \text{g}_{\text{DME}} \text{g}_{\text{np-Cu}}^{-1} \text{h}^{-1}$	\backslash	\backslash
250.00	0.92 ± 0.01	3.72	0.39 ± 0.03	0.28 ± 0.01	0.59 ± 0.03
240.00	0.96 ± 0.01	4.01	0.30 ± 0.01	0.25 ± 0.01	0.69 ± 0.04
230.00	0.94 ± 0.01	4.27	0.22 ± 0.01	0.23 ± 0.00	0.73 ± 0.02
220.00	0.79 ± 0.03	4.49	0.19 ± 0.04	0.19 ± 0.01	0.75 ± 0.02
210.00	0.62 ± 0.01	4.69	0.13 ± 0.01	0.14 ± 0.00	0.79 ± 0.01
200.00	0.48 ± 0.01	4.85	0.12 ± 0.02	0.11 ± 0.00	0.78 ± 0.03
250.00	0.96 ± 0.01	3.72	0.36 ± 0.01	0.28 ± 0.01	0.61 ± 0.01

255.00	0.94±0.01	3.57	0.46±0.01	0.30±0.01	0.56±0.02
260.00	0.93±0.01	3.40	0.53±0.01	0.33±0.00	0.50±0.01
250.00	0.92±0.01	3.72	0.38±0.02	0.27±0.01	0.61±0.01

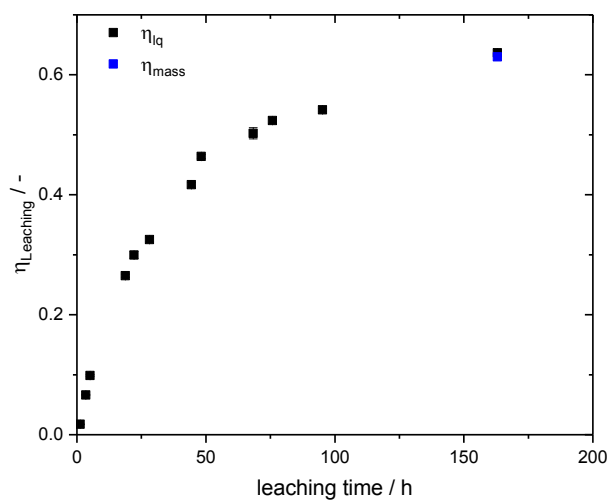


Figure S6: Kinetic of Leaching reaction of CuAl70 LMD cylinder, RT, 4.9M NaOH/0.5 M Na₂Zn(OH)₄, 165 h, min=7.2 g (3 CuAl70 LMD cylinder 9.5mmx6mm).

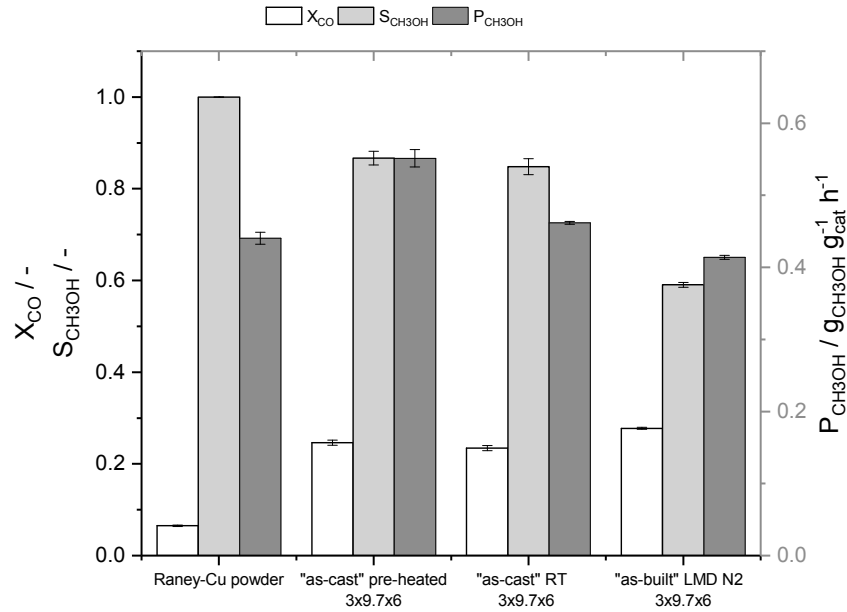


Figure S7: Comparison of different shaped Raney-Cu catalyst, $m_{cat}=3-3.8$ g, $\eta_{Leaching}=0.4-0.7$, $V_{ges}=300$ ml min^{-1} ($H_2/CO=2/1$), $p=75$ bar, $t_{reaction}=10-12$ h, arrangement of 3 smaller cylinder with 9.7 mmx 6mm height on one another, "as-cast" RT: casted cylinder at room temperature, "as-cast" pre-heated: cast cylinder in pre-heated mold, "as-built" LMD: additive manufactured cylinder with LMD method.

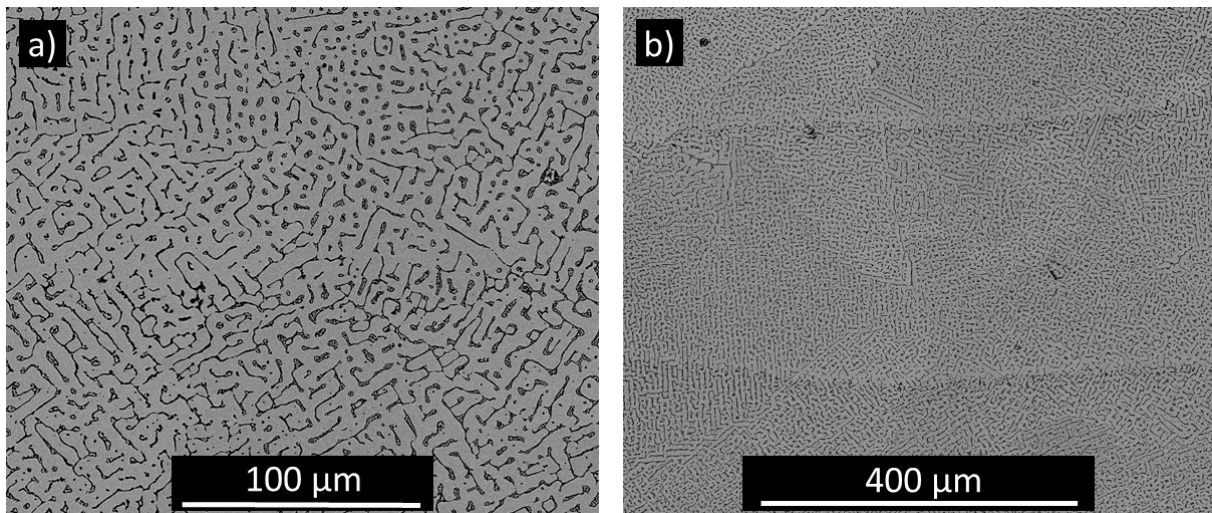


Figure S8: SEM-micrograph of an as built Cu-70Al LMD cylinder showing different phases: grey: Θ -phase dendrites (35 at% Cu) and black eutectic α -Al-, and Θ -lamellae for different magnifications (a) 250 μm and (b) 750 μm .

Table S2: Phase Composition of the as built Cu-70Al cylinder calculated from the SEM micrographs in Figure S9. Black-Pixel correspond to the eutectic α -Al phase and the grey pixel to Θ -phase.

	eutectic α -Al / %	Θ -phase ($CuAl_2$) / %
250 μm	13.46	86.53
750 μm	14.67	85.13
average	14.07	85.83

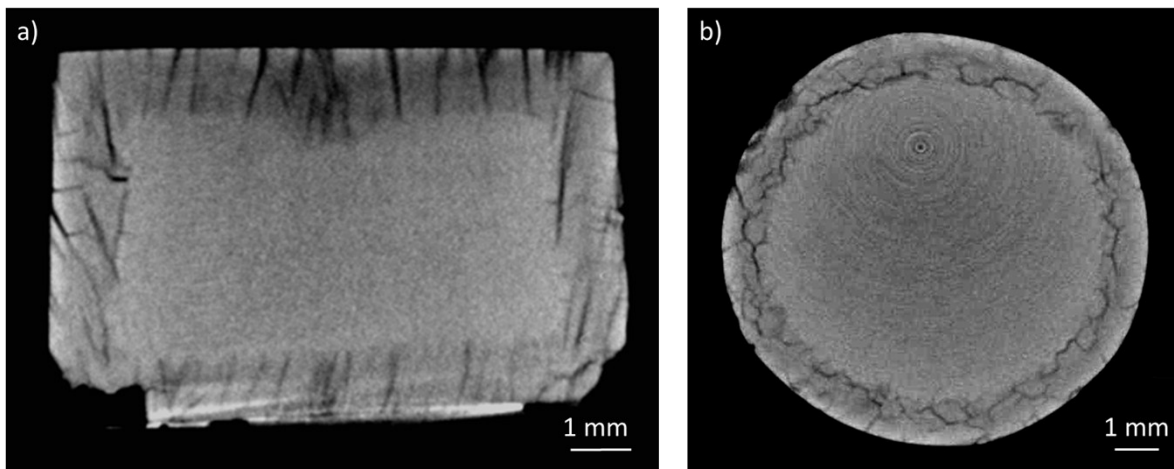


Figure S9: Computed tomography (CT) measurements performed using a Fraunhofer CT-alpha big with a detector resolution of 1024 by 1024 pixels and a voxel size of 19 μm . (a) Longitudinal cross section (b) plan view.

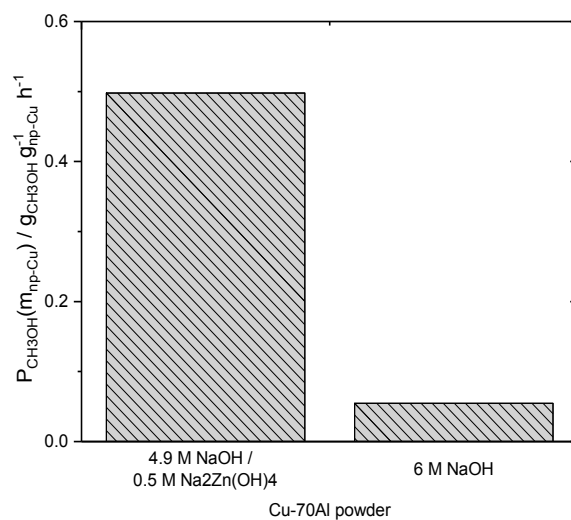


Figure S10: Influence of leaching solution, leaching conditions: Cu-70Al powder, $T=20\text{ }^\circ\text{C}$, 24 h, $\eta_{\text{Leaching}}=0.99$, catalyst composition: 4.9 M NaOH / 0.5 M Na₂Zn(OH)₄ : 89 wt.% Cu, 2 wt.% Al, 9 wt.% Zn; 6 M NaOH: 99.76 wt.% Cu, 0.24 wt.% Al ; reaction conditions: $V_{\text{ges}}=300\text{ mlN min}^{-1}$ ($\text{H}_2/\text{CO}=2/1$), $p=75\text{ bar}$, $T_{\text{Reaction}}=250\text{ }^\circ\text{C}$ treaction=10-12 h.

NH₃-TPD measurements

The NH₃ TPD measurements were performed with an Porotec TPDR 1100. Therefore 200 mg of sample were weight in and heated in 25 mlN min⁻¹ He with 10 °C min⁻¹ to 250 °C. The temperature was hold for 1 hour and the sample was cooled in 25 mlN min⁻¹ He to 100 °C. The ammonium loading was conducted at 100 °C in 25 mlN min⁻¹ NH₃ for 1 hour. Afterwards the sample was flushed in 25 mlN min⁻¹ He again to remove not chemisorbed NH₃. For the NH₃-TPD measurements the sample was heated under 25 mlN min⁻¹ He flow with 10 °C min⁻¹ to 450 °C and hold for 1 hour. A thermal conductivity detector analyse the desorbing NH₃. The measured curves of the NH₃-TPD are shown in Figure S11 and the calculated results are shown in table S3

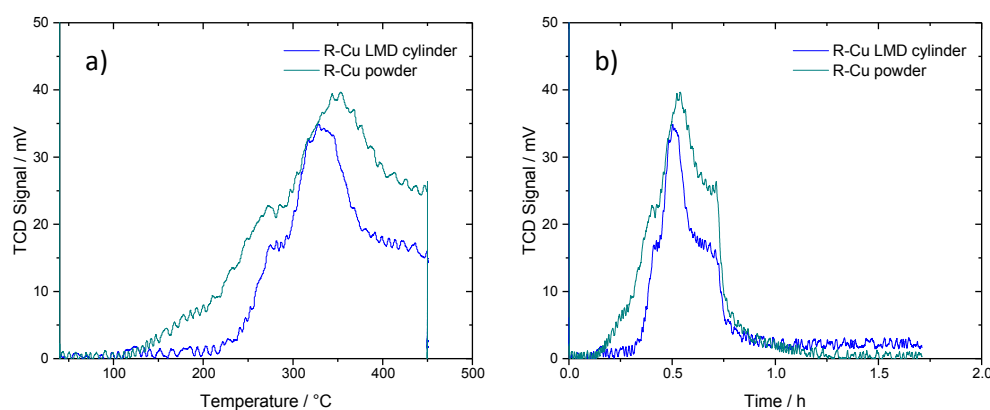


Figure S11: NH₃ TPD profiles for passivated Raney type catalysts: (a) TCD Signal over temperature; (b) TCS Signal over time.

Table S3: Content of acid sites and temperature maximum for NH₃-TPD profiles.

	NH ₃ adsorbed / $\mu\text{mol g}^{-1}$	T _{max} / °C
R-Cu LMD cylinder	219.43	353
R-Cu powder	110.3	339

References

1. M. B. Fichtl, J. Schumann, I. Kasatkin, N. Jacobsen, M. Behrens, R. Schlögl, M. Muhler and O. Hinrichsen, *Angewandte Chemie International Edition*, 2014, **53**, 7043-7047.