Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supporting Information

Selective Glycerol Oxidation over Ordered Mesoporous Copper Aluminum Oxide Catalysts

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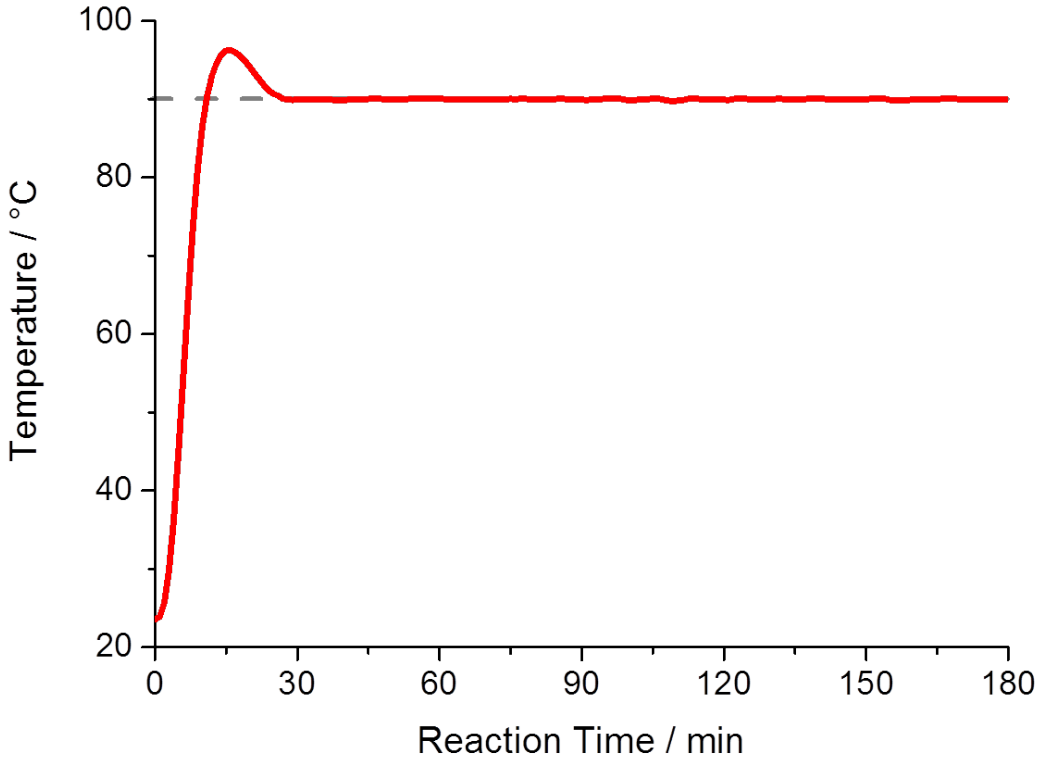

Figure S1: Temperature profiles of the reaction medium during catalytic glycerol oxidation.

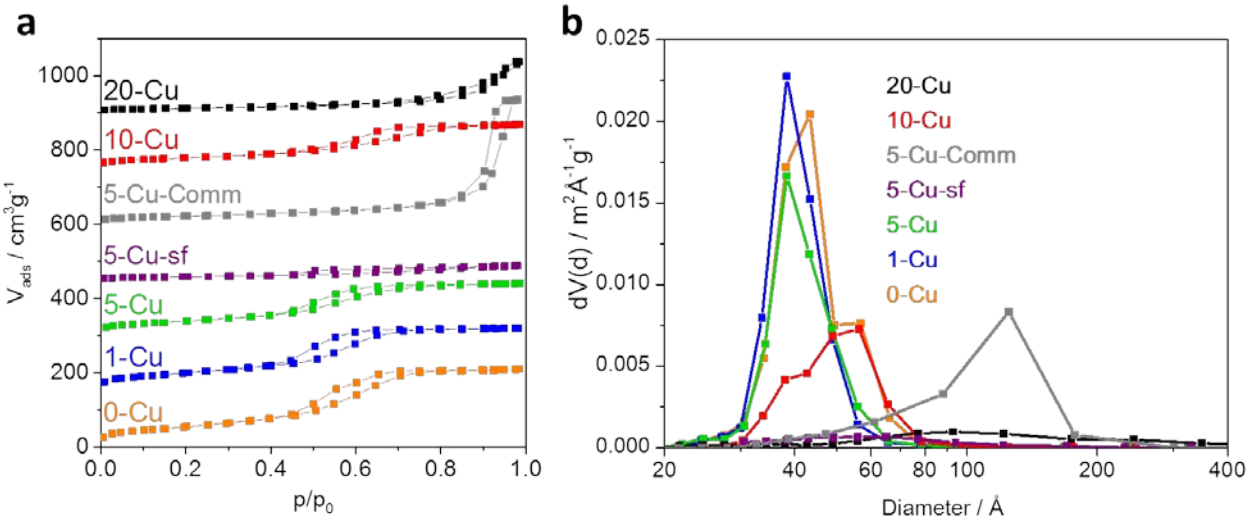

Figure S2: (a) Nitrogen physisorption isotherms (offset by 150 cm^3g^{-1} for clarity) and (b) pore size distributions of Cu-Al_2O_3 catalysts.

Table S1: BET surface areas, pore volumes, and pore diameters from nitrogen physisorption. Cu concentration in mass % determined via EDX.

Sample	A_{BET} [a] / m^2g^{-1}	V_p [a] / cm^3g^{-1}	d_p [a] / nm	m_{Cu} [b] / %
0-Cu	195	0.33	4.4	0
1-Cu	180	0.26	3.8	1.2
5-Cu	145	0.22	3.8	5.2
5-Cu-sf	30	0.06	--	6.9
5-Cu-Comm	80	0.52	--	6.8
10-Cu	105	0.18	--	11.8
20-Cu	45	0.21	--	20.6

[a] BET-surface area ($\mathbf{A_{BET}}$) , pore volume ($\mathbf{V_p}$), and pore diameter ($\mathbf{d_p}$) determined from nitrogen physisorption.

[b] Concentration of Cu in mass % of the samples determined by EDX.

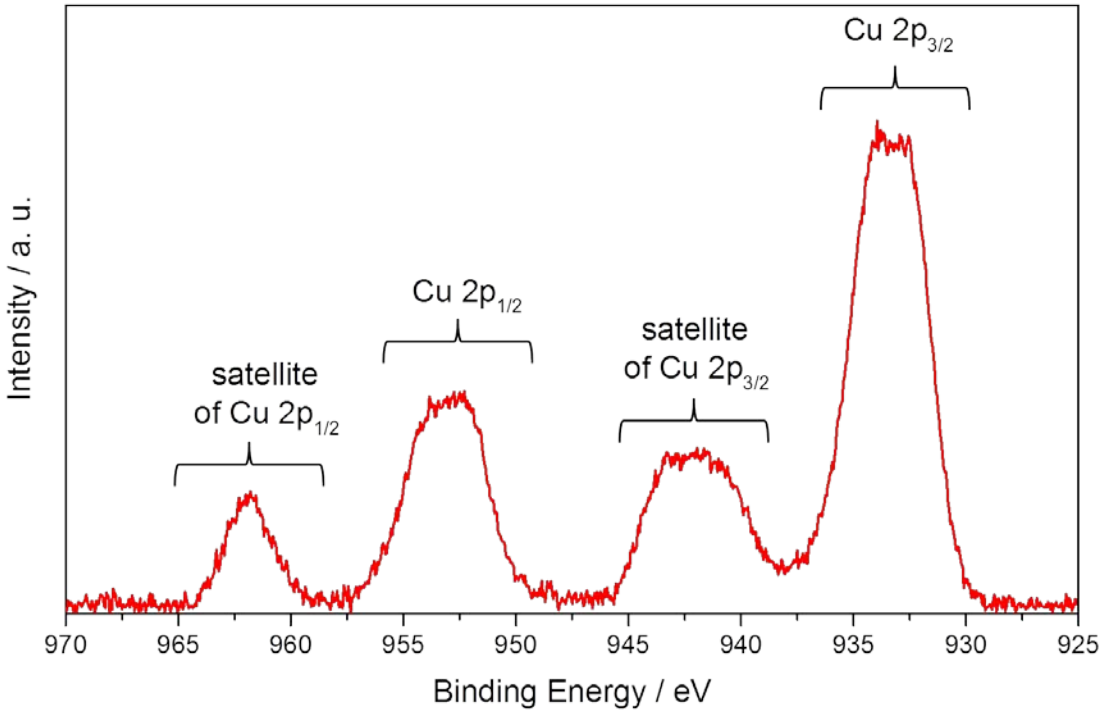

Figure S3: Cu 2p XPS spectrum of 5-Cu.

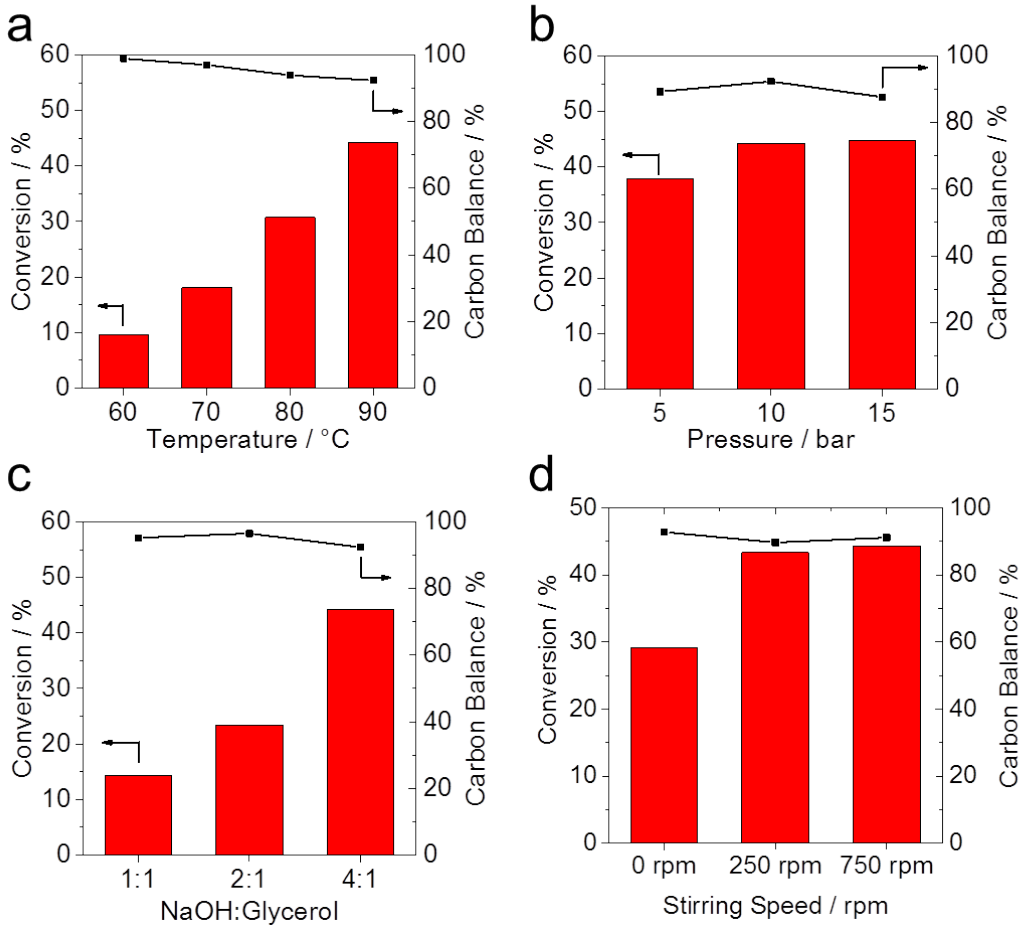

Figure S4: (a) Glycerol conversions and carbon balances of 5-Cu at different temperatures. Reaction conditions: 30 mg catalyst, 15 mL aq. 0.05 M glycerol solution, 4:1 NaOH:glycerol, 10 bar oxygen, 3 h, 750 rpm. (b) Glycerol conversions and carbon balances of 5-Cu at different oxygen pressures. Reaction conditions: 30 mg catalyst, 15 mL aq. 0.05 M glycerol solution, 4:1 NaOH:glycerol, 90 °C, 3 h, 750 rpm. (c) Glycerol conversions and carbon balances of 5-Cu at different oxygen pressures. Reaction conditions: 30 mg catalyst, 15 mL aq. 0.05 M glycerol solution, 10 bar oxygen, 90 °C, 3 h, 750 rpm. (d) Glycerol conversion and carbon mass balance of 5-Cu at different stirring speeds. Reaction conditions: 30 mg catalyst, 15 mL aq. 0.05 M glycerol solution, 4:1 NaOH:glycerol, 10 bar oxygen, 90 °C, 3 h.

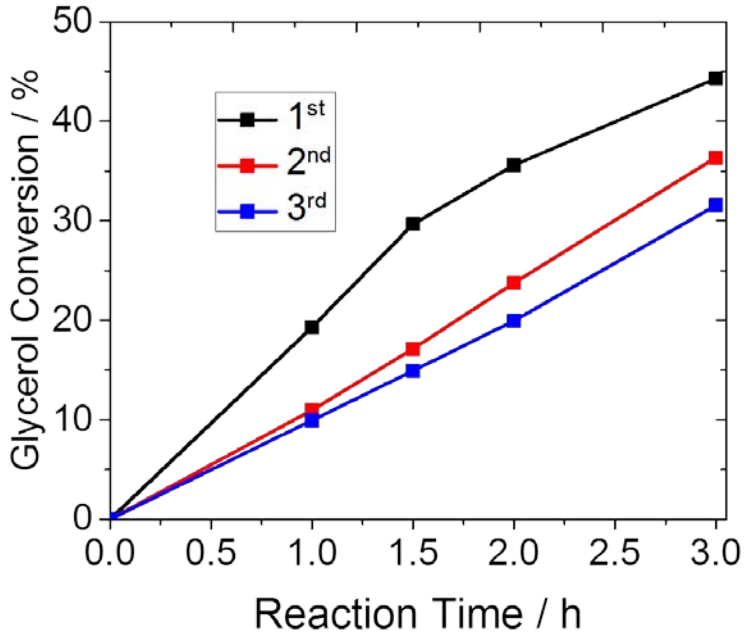

Figure S5: Recycling experiments with 5-Cu. Reaction conditions: 30 mg catalyst, 15 mL aq. 0.05 M glycerol solution, 4:1 NaOH:glycerol, 90 °C, 10 bar oxygen, 750 rpm. The catalyst was recovered by centrifugation and washed with water between the catalytic reactions.

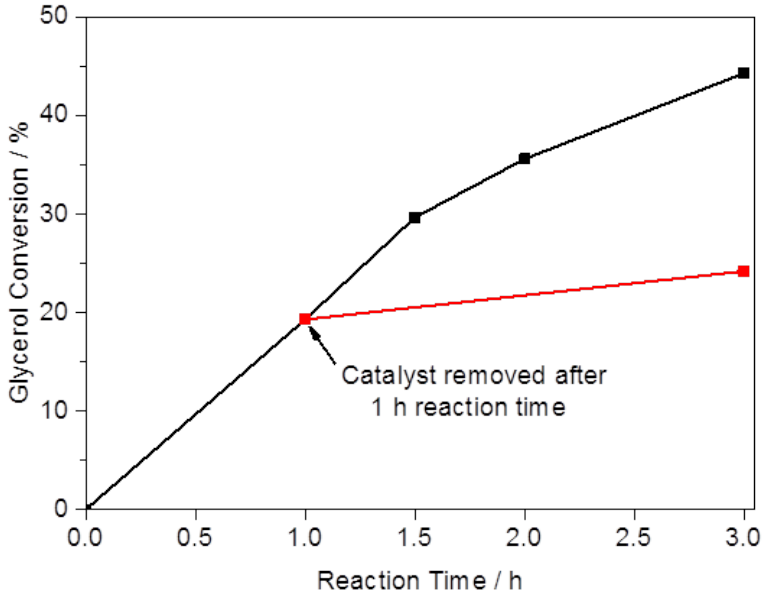

Figure S6: Glycerol conversion of 5-Cu (black) and glycerol conversion after removing the solid catalyst after a reaction time of one hour and subsequently preceding the reaction for further two hours (red). Reaction Conditions: Reaction conditions: 30 mg catalyst, 15 mL aq. 0.05 M glycerol solution, 4:1 NaOH:glycerol, 90 °C, 10 bar oxygen, 750 rpm.

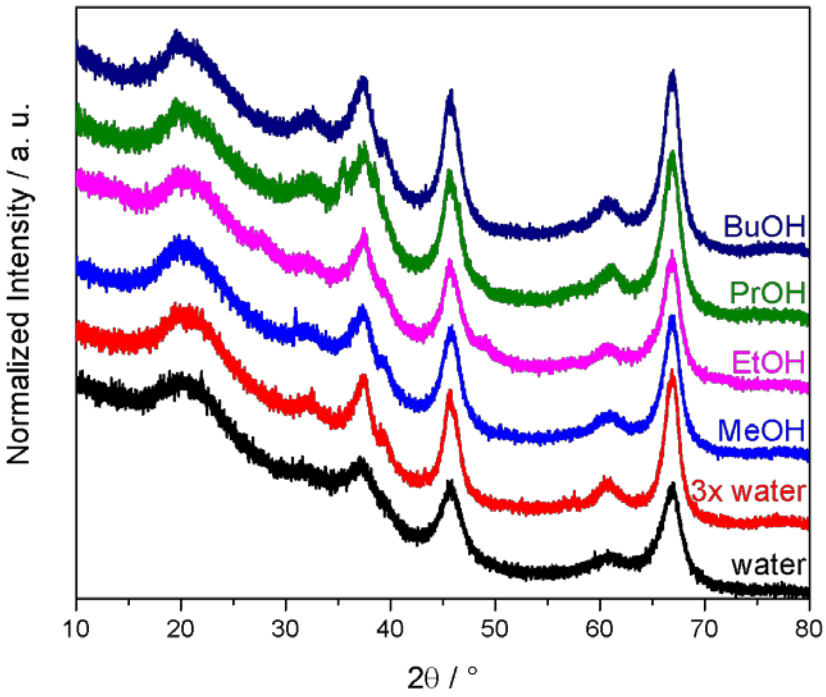

Figure S7: Transmission XRD patterns of 5-Cu after catalytic reaction in water (afer a single 3h experiment and after 3x3h) and different water/co-solvent mixtures (50 vol%) as indicated in the figure. Reaction conditions: 30 mg catalyst, 15 mL aq. 0.05 M glycerol solution, 4:1 NaOH:glycerol, 90 °C, 10 bar oxygen, 750 rpm stirring speed.

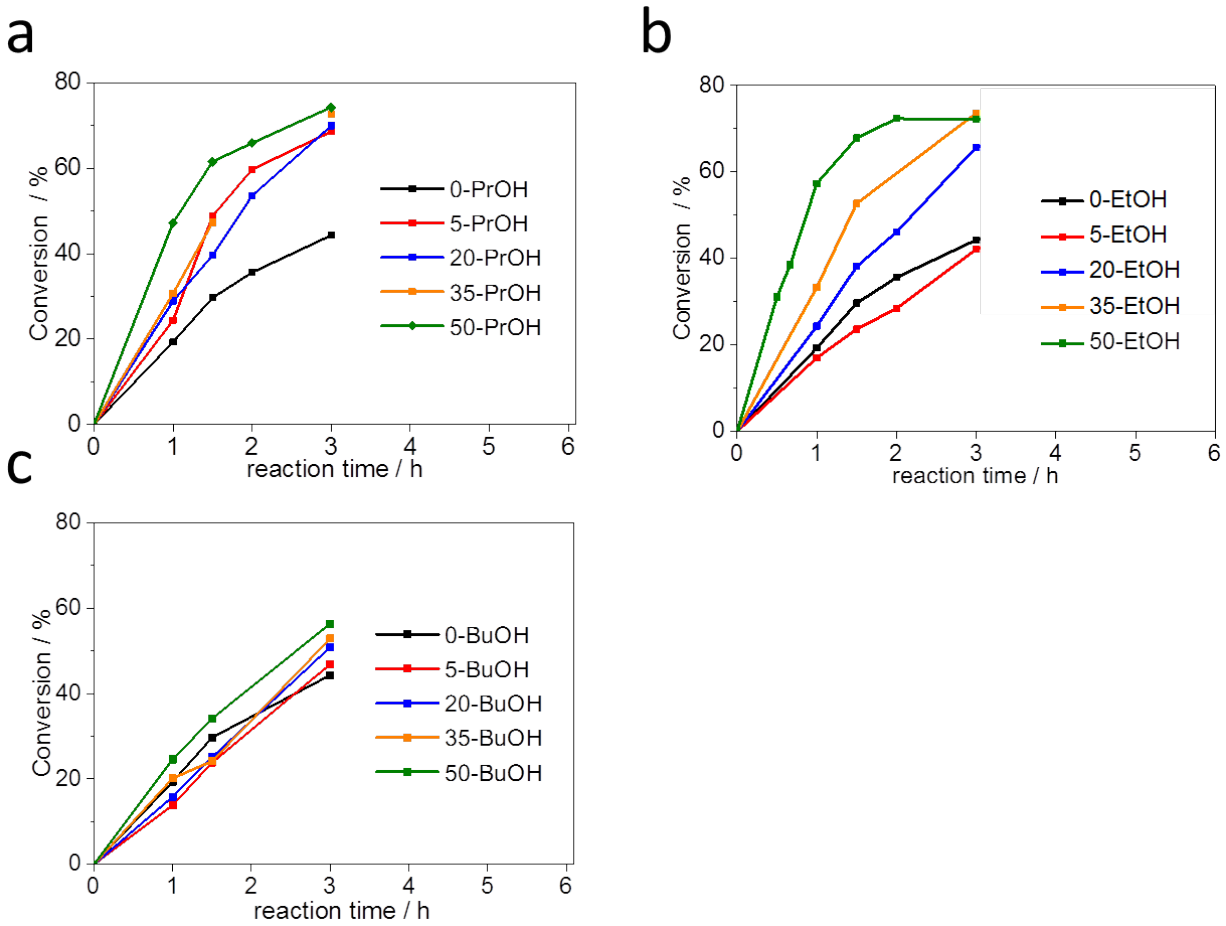

Figure S8: Glycerol conversion profiles in water / 1-propanol (a), ethanol (b), and *tert.*-butanol (c) mixtures with different volume ratios. Reaction conditions: 30 mg catalyst, 15 mL aq. 0.05 M glycerol solution, 4:1 NaOH:glycerol, 90 °C, 10 bar oxygen, 750 rpm stirring speed.

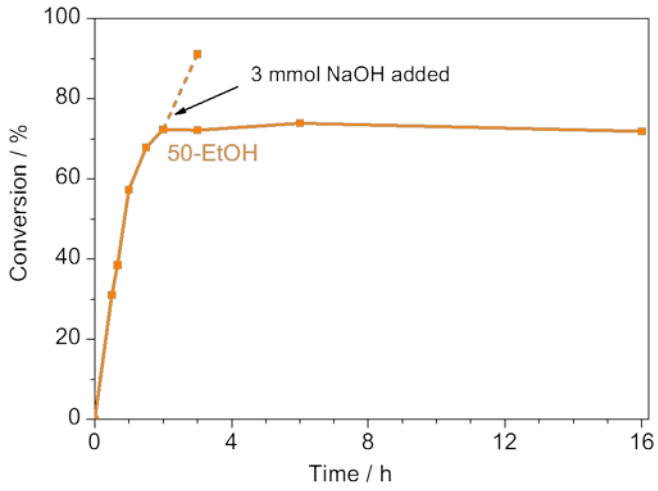

Figure S9: Glycerol conversion of 5-Cu (solid line). After 2 h 3 mmol NaOH were added to the reaction mixture and the reaction was continued for another hour (dashed line). Reaction conditions: 30 mg catalyst, 15 mL aq. 0.05 M glycerol solution, 4:1 NaOH:glycerol, 90 °C, 10 bar oxygen, 750 rpm stirring speed.

Table S2: Selectivities and carbon mass balances of the selective glycerol oxidation in water/ethanol mixtures at a conversion of approximately 36 %.

EtOH / Vol%	X / %	Time / h	Selectivity / %					Carbon balance / %
			glycolic	glyceric	formic	tartronic	oxalic	
0	36	2	38	21	18	1	0	92
5	42	3	34	23	15	2	4	91
20	38	1.5	35	20	27	2	4	92
35	33	1	38	16	21	0	0	93
50	36	0.67	33	7	23	0	0	88

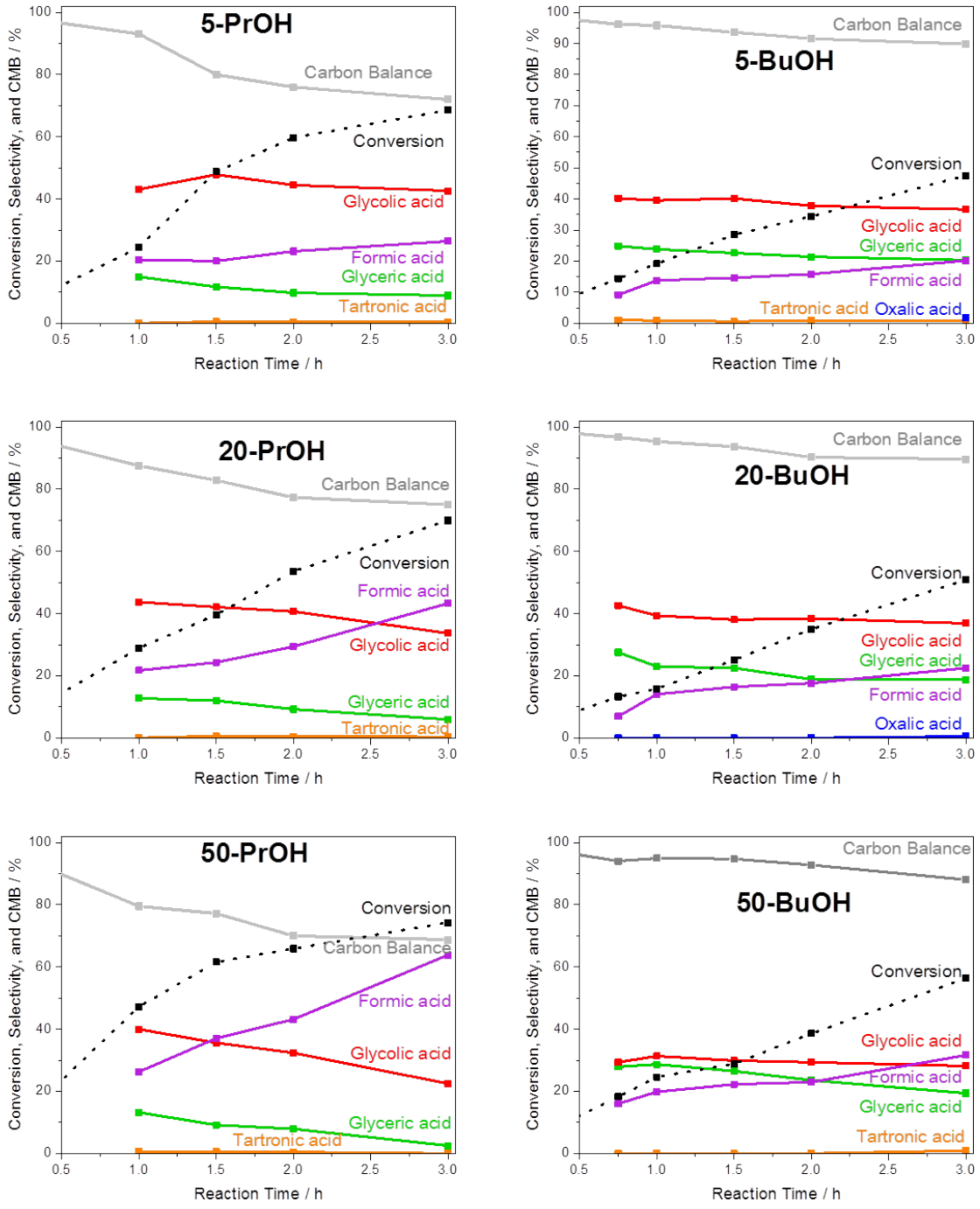

Figure S10: Selectivity, conversion, and carbon mass balance over time in different water/co-solvent mixtures as indicated in the figures. Reaction conditions: 30 mg 5-Cu, 15 mL aq. 0.05 M glycerol solution, 4:1 NaOH:glycerol, 90 °C, 10 bar oxygen, 750 rpm stirring speed.

Calculation of Conversion, Selectivity, Carbon Mass Balance, and Initial Reaction Rate

Conversions were calculated according to Equation 1.

$$X_{gly}(t) = \frac{C^0_{gly} \cdot V_i - C_{gly}(t) \cdot V(t)}{C^0_{gly} \cdot V_i} \cdot 100 \qquad \text{Eq. 1}$$

The selectivities to the products were calculated based on the number of carbon atoms according to Equation 2:

$$S_i(t) = \frac{n_i \cdot C_i(t) \cdot V_i}{3 \cdot (C^0_{gly} \cdot V_i - C_{gly}(t) \cdot V(t))} \cdot 100 \qquad \text{Eq. 2}$$

The carbon mass balance is calculated according to Equation 3:

$$CB(t) = \frac{3 \cdot C_{gly}(t) \cdot V_i + \sum[n_i \cdot C_i(t) \cdot V(t)]}{3 \cdot C^0_{gly} \cdot V_i} \cdot 100 \qquad \text{Eq. 3}$$

The initial reaction rate was calculated according to Equation 4 from the glycerol conversion after 1 h. Until this time the rate of glycerol conversion was constant in each case:

$$r_0 = \frac{C^0_{gly} \cdot V_i - C_{gly}(t) \cdot V(t)}{m_{cat} \cdot t \cdot V_i} \qquad \text{Eq. 4}$$

with:

C^0_{gly} – initial molar concentration of glycerol in mol/L

V_i - initial reaction volume

$C_{gly}(t)$ – molar concentration of glycerol at time t

$V(t)$ - reaction volume at time t

n_i – number of carbon atoms in oxidation product i

$C_i(t)$ – molar concentration of oxidation product i at time

r_0 – initial reaction rate

t – reaction time

V – reaction volume