catalysts

Supplementary Information: Mechanism Analysis and Kinetic Modelling of Cu NPs Catalysed Glycerol Conversion into Lactic Acid

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1. Composition of the Gas Phase

Table S1. Composition of the gas phase in the course of glycerol conversion.

Gas	%Vol
N_2	4.152
O_2	0.462
H_2	95.112
CH_4	0.009
CO	0.032
CO_2	0.004
Total	99.771

2. Effect of Stirring Speed

2.1. Homogeneous Catalysis

Table S2. Effect of stirring speed on glycerol conversion in the presence of NaOH.

rpm	Conversion of glycerol (%)
0	7.3
400	9.1
800	12.0
1000	12.1

Reaction conditions: NaOH as a catalyst, initial glycerol concentration of 0.92 mol·L^{-1}, NaOH/glycerol molar ratio of 1.1:1, reaction temperature of 503 K.

2.2. Tandem Catalysis

Table S3. Effect of stirring speed on glycerol conversion in the presence of Cu NPs and NaOH.

rpm	Conversion of glycerol (%)
0	43.7
400	49.5
800	88.6
1000	89.0

Reaction conditions: Cu NPs–NaOH as a catalyst, initial glycerol concentration of 0.92 mol·L^{-1}, glycerol/Cu molar ratio of 25.4:1, NaOH/glycerol molar ratio of 1.1:1, reaction temperature of 513 K.

3. Evaluation of external and internal mass transfer

3.1. The Weisz-Prater Criterion

The Weisz-Prater criterion (C_{WP}) is used to check whether the reaction is internal diffusion limited. The Weisz-Prater parameter was calculated by using the following equation:

$$C_{WP} = \frac{-r'_{GLY} \cdot \rho_s \cdot R^2}{D_e \cdot C_{AS}}. \quad (1)$$

The internal diffusion is negligible when C_{WP} is << 1. Effective diffusivity of glycerol into water:

$$D_e = \frac{D_{AB} \cdot \varphi \cdot \sigma}{\tau}. \quad (2)$$

The parameters used in the above equation are given in Table S4:

Table S4. Parameters for calculating the Weisz–Prater criterion.

Parameter	Description	Value
$-r'_{GLY}$	observed reaction rate	$3.89 \cdot 10^{-4}$ mol·g_{cat}^{-1}·s^{-1}
ρ_s	solid catalyst density	8.96 g·cm^{-3}
R	average catalyst particle radius	$1.17 \cdot 10^{-5}$ cm
C_{AS}	concentration of glycerol at catalyst surface	$1.1 \cdot 10^{-3}$ mol·cm^{-3}
D_e	effective diffusivity of glycerol into water at 523K	$2.11 \cdot 10^{-5}$ cm^2·s^{-1}
ϕ	catalyst porosity	0.4 [1]
σ	constriction factor	0.8 [1]
τ	tortuosity	3.0 [1]

[1] Typical value of porosity, constriction factor and tortuosity, respectively.

The average catalyst particle radius is $1.17 \cdot 10^{-5}$ cm, but for further calculations we will stick to the worst scenario and take the value of $5 \cdot 10^{-5}$ cm.

D_{AB} is the diffusion coefficient of glycerol into water at 513 K (diffusivity of solute A into solvent B at 513 K).

The diffusion coefficient was calculated using the Wilke–Chang equation:

$$D_{AB} = \frac{1.173 \cdot 10^{-16} \cdot (\phi \cdot M_B)^{1/2} \cdot T}{\mu_B \cdot V_A^{0.6}}, \quad (3)$$

where φ is the association parameter of water (2.26), M_B is the molecular weight of water (18 kg·$kmol^{-1}$), T is the absolute temperature (513 K), μ_B is the solution viscosity ($1.11 \cdot 10^{-4}$ kg·s^{-1}·m^{-1}), V_A is the molar volume at the normal boiling point (0.0756 m^3·$kmol^{-1}$).

$$D_{AB} = \frac{1.173 \cdot 10^{-16} \cdot (2.26 \cdot 18)^{1/2} \cdot 513}{1.11 \cdot 10^{-4} \cdot 0.0756^{0.6}} = 1.63 \cdot 10^{-8}\ \text{m}^2\text{穢}^{-1} = 1.63 \cdot 10^{-4}\ \text{cm}^2\text{穢}^{-1}. \quad (4)$$

Effective diffusivity of glycerol into water at 513 K:

$$D_e = \frac{D_{AB} \cdot \varphi \cdot \sigma}{\tau} = \frac{1.63 \cdot 10^{-4} \cdot 0.4 \cdot 0.8}{3.0} = 1.74 \cdot 10^{-5}\ \text{cm}^2\text{穢}^{-1}. \quad (5)$$

$$C_{WP} = \frac{-r'_{GLY} \cdot \rho_s \cdot R^2}{D_e \cdot C_{AS}} = \frac{3.89 \cdot 10^{-4} \cdot 8.96 \cdot (5 \cdot 10^{-6})^2}{1.74 \cdot 10^{-5} \cdot 1.1 \cdot 10^{-3}} = 4.55 \cdot 10^{-4}. \quad (6)$$

The C_{WP} value of glycerol into water is equal to $4.55 \cdot 10^{-4}$ << 1 on substitution of the above values and from this we can infer that internal diffusion is negligible in the above reaction.

3.2. The Mears Criterion

Mears criterion is used to check whether the reaction is limited by external diffusion:

$$C_{mears} = \frac{-r'_{GLY} \cdot \rho_b \cdot R \cdot n}{k_c \cdot C_{AS}} < 0.15, \quad (7)$$

where $-r'_{GLY}$ is the observed reaction rate ($3.89 \cdot 10^{-4}$ mol·g_{cat}^{-1}·s^{-1}), n is the reaction order (2), R is the average catalyst particle radius ($1.17 \cdot 10^{-5}$ cm, the worst scenario for calculations – $5 \cdot 10^{-5}$ cm), ρ_b is the bulk density (0.35 g·cm^{-3}), C_{AS} is the concentration of glycerol in solution ($1.1 \cdot 10^{-3}$ mol·cm^{-3}), k_c is the mass transfer coefficient for glycerol–water, m·s^{-1}.

The mass transfer coefficient for glycerol–water is calculated as:

$$k_c = \frac{Sh \cdot D_{AB}}{d_p}, \quad (8)$$

where D_{AB} is the diffusion coefficient of glycerol into water at 513 K ($1.63 \cdot 10^{-4}$ cm^2·s^{-1}), d_p is the catalyst particle diameter, Sh is the Sherwood number, which is calculated as:

$$Sh = 2 + 0.6 \cdot \mathrm{Re}^{0.5} \cdot Sc^{1/3}, \quad (9)$$

where Sc is the Schmidt number, Re is the Reynolds number.

The Schmidt number is found as follows:

$$Sc = \frac{V}{D_{AB}}, \quad (10)$$

where V is the kinetic viscosity of water at 513K ($1.36 \cdot 10^{-3}$ cm^2·s^{-1}).

$$Sc = \frac{1.36 \cdot 10^{-3}}{1.63 \cdot 10^{-4}} = 8.34. \quad (11)$$

The impeller Reynolds number is calculated as:

$$\mathrm{Re} = \frac{N \cdot D^2 \cdot \rho}{\mu}, \quad (12)$$

where N is the rotational speed of the impeller (1000/60 = 16.67 s^{-1}), D is the impeller diameter ($3.5 \cdot 10^{-3}$ m), ρ is the density of water at 513 K (813 kg·m^{-3}), μ is the dynamic viscosity of water at 513 K ($1.11 \cdot 10^{-4}$ kg·s^{-1}·m^{-1}).

$$\mathrm{Re} = \frac{N \cdot D^2 \cdot \rho}{\mu} = \frac{16.67 \cdot (3.5 \cdot 10^{-3})^2 \cdot 813}{1.11 \cdot 10^{-4}} = 1509. \quad (13)$$

$$Sh = 2 + 0.6 \cdot \mathrm{Re}^{0.5} \cdot Sc^{1/3} = 2 + 0.6 \cdot 1509^{0.5} \cdot (8.34)^{1/3} = 49.27 \quad (14)$$

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$$k_c = \frac{Sh \cdot D_{AB}}{d_p} = \frac{49.27 \cdot 1.63 \cdot 10^{-4}}{10^{-4}} = 80.2 \quad (15)$$

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$$C_{mears} = \frac{-r'_{gly} \cdot \rho_b \cdot R \cdot n}{k_c \cdot C_{AS}} = \frac{3.89 \cdot 10^{-4} \cdot 0.35 \cdot 1.5 \cdot 10^{-5} \cdot 2}{80.2 \cdot 1.1 \cdot 10^{-3}} = 4.63 \cdot 10^{-8} << 0.15 \quad (16)$$

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The C_{mears} value of glycerol to water is equal to $4.63 \cdot 10^{-8}$ << 0.15 on substitution of the above values and from this we can infer that external diffusion is negligible in the above reaction.

4. Error Analysis

4.1. Experimental Error

Experiments in tandem catalysis glycerol conversion were repeated, and values of substrate/product concentration were calculated (Tables S5 and S6), the error of which was taken into account when parameter estimation was carried out.

Table S5. Results of repeated experiments with NaOH.

T (K)	Time (min)	C_{GLY}	C_{DG}	C_{LA}	C_{PG}	C_{AA}	C_{HO^-}
513	60	1.189	0.012	0.046	0.003	0.001	0.964
513	60	1.228	0.008	0.033	0.002	0.000	0.986
513	120	1.143	0.013	0.058	0.004	0.003	0.949
513	120	1.192	0.011	0.043	0.005	0.002	0.966
513	180	1.098	0.017	0.070	0.006	0.003	0.937
513	180	1.154	0.014	0.058	0.007	0.003	0.950
513	240	1.045	0.018	0.082	0.008	0.006	0.922
513	240	1.126	0.018	0.070	0.009	0.004	0.936
513	300	0.998	0.023	0.114	0.009	0.008	0.887
513	300	1.098	0.019	0.087	0.010	0.006	0.917
513	360	0.962	0.026	0.115	0.013	0.010	0.884
513	360	1.080	0.022	0.096	0.012	0.008	0.906
513	420	0.934	0.027	0.136	0.014	0.013	0.860
513	420	1.063	0.025	0.111	0.014	0.011	0.885

Table S6. Results of repeated experiments with Cu NPs catalyst in the base media.

T, K	Time (min)	C_{GLY}	C_{DG}	C_{LA}	C_{PG}	C_{AA}	C_{HO^-}
513	20	0.632	0.025	0.039	0.048	0.011	0.612
513	20	0.691	0.016	0.340	0.049	0.015	0.654
513	40	0.513	0.026	0.478	0.056	0.014	0.518
513	40	0.532	0.015	0.453	0.059	0.023	0.534
513	60	0.416	0.029	0.549	0.062	0.017	0.443
513	60	0.472	0.017	0.571	0.064	0.013	0.426
513	120	0.303	0.032	0.615	0.065	0.022	0.373
513	120	0.348	0.021	0.620	0.067	0.034	0.356
513	180	0.232	0.035	0.672	0.067	0.026	0.313
513	180	0.246	0.023	0.649	0.081	0.053	0.308
513	240	0.171	0.035	0.698	0.065	0.035	0.281
513	240	0.183	0.024	0.660	0.084	0.072	0.278
513	300	0.145	0.036	0.712	0.063	0.032	0.266
513	300	0.156	0.025	0.673	0.091	0.056	0.243
513	360	0.118	0.037	0.717	0.062	0.042	0.259
513	360	0.119	0.026	0.698	0.081	0.054	0.189
513	420	0.096	0.034	0.721	0.060	0.065	0.256
513	420	0.106	0.025	0.711	0.091	0.074	0.188

4.2. Measuring Error

The maximum error for HPLC analysis (repeated injection of one sample) is less than 0.1 %, which is much lower compared with experimental error (approximately 2–15%).

4.3 Error Analysis of Reaction Parameters-Weighted Least Squares

The goal of suing weighted least squares is to ensure that each data point has an appropriate level of influence on the final parameter estimation. However, it is difficult to evaluate the appropriate level of each component (*e.g.*, GLY, LA, *etc.*), therefore the weight factor for each species and replicates (repeated experimental results) were considered is 1.0 during estimation of reaction parameters.

5. Analysis of Cu NPs Catalyst

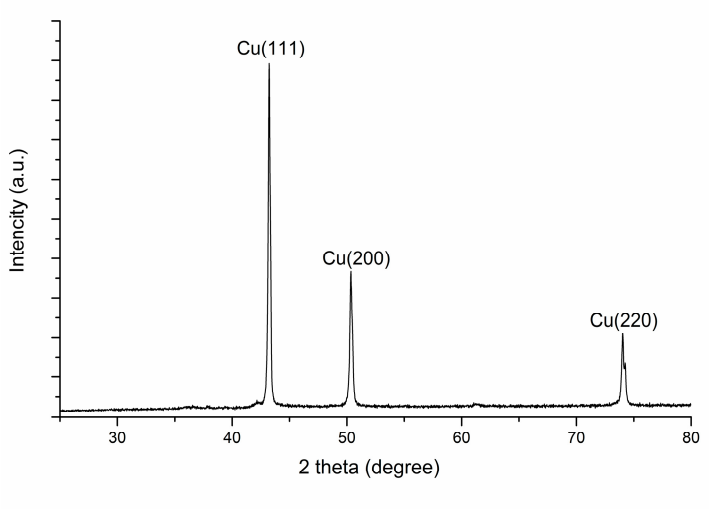

Figure S1. XRD patterns of Cu NPs catalyst.

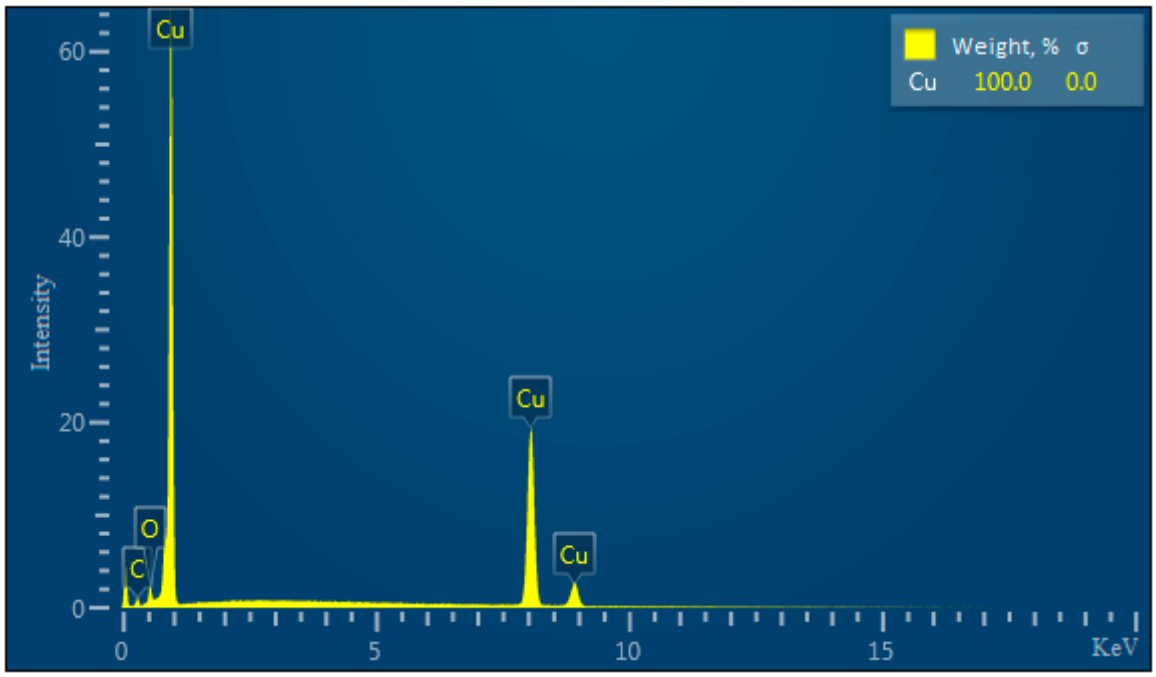

Figure S2. EDS of Cu NPs catalyst.

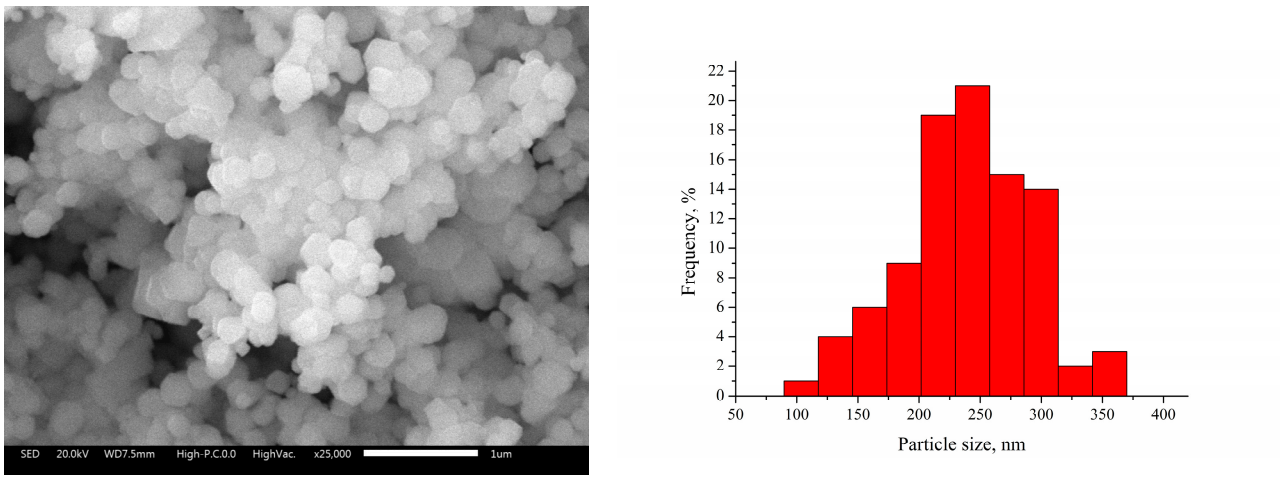

Figure S3. SEM image and particle size distribution of Cu NPs catalyst.