Supplementary information

Copper/TEMPO-Catalyzed Continuous Aerobic Alcohol Oxidation in a Micro-Packed Bed Reactor

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Contents

1. General experimental information

Color changes were observed during the solution preparation and aerobic oxidation of benzyl alcohol. During the solution preparation, the colorless acetonitrile solution of NMI (69 mg, 10 mol%) and Bpy (65 mg,5 mol%) changed to red-brown with addition of solid $Cu(MeCN)_4(OTf)$ (153 mg, 5 mol%) and became deeper upon the addition of

TEMPO (52 mg, 4 mol%). Then benzyl alcohol (0.9 g, 0.4 mol/L) and internal standard Toluene (1.04 ml, 0.01 mol) were added to the solution (acetonitrile, 19.64 g), which should be protected by nitrogen and used promptly.

As shown in Fig. S1, during the aerobic oxidation of benzyl alcohol, the color was transformed first to green, which means a benzyl alcohol conversion close to 95%. And then it gradually changed to blue, because the copper species presented in solution predominantly in the form of Cu(II).

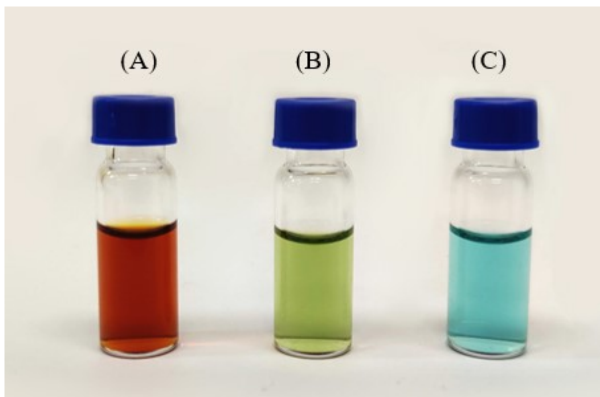

Fig. S1. Color changes during the aerobic oxidation of benzyl alcohol with the Cu(I) /TEMPO catalyst system. (A) Red-brown: starting material solution. (B) Green: near-quantitative production. (C) Blue: the product stands still in the air.

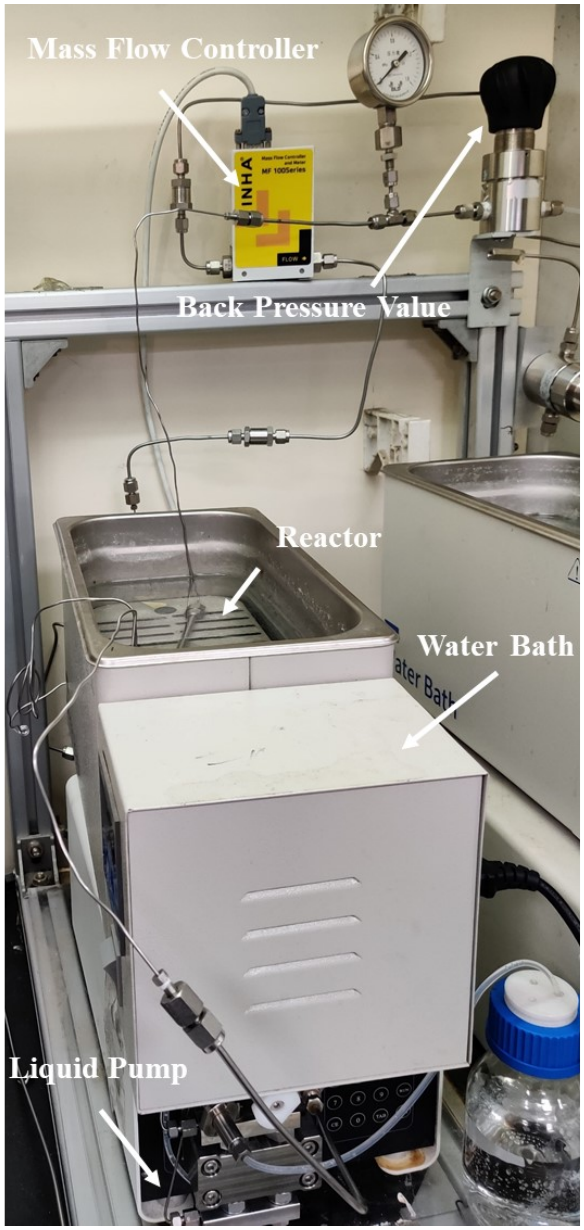

Fig. S2. Real experimental setup of microreactor system for aerobic oxidation.

2. GC analyzing conditions

The liquids from the outlet of cooling system were collected when the system reached a steady state, and then the samples were diluted with acetonitrile to the mass fraction of substrates below 5wt% and analyzed by GC. GC analyses were performed using a Hp-5 column (30m × 320μm × 0.25μm) installed in the Agilent 8860 GC system equipped with a FID detector. The column flow rate 1.5ml/min of N_2 with a split ratio of 20:1. The column temperature started at 70 °C, ramped at 20 °C/min to 280 °C (10.5 min), maintained 200 °C for 5 min, and the detector was held at 300 °C. 2 mol% toluene was used as internal standard. Residence times for substances screening as follows: Toluene (2.31 min), Benzyl alcohol (3.60 min)/ Benzaldehyde (3.17 min), 1-Octanol (3.76 min)/ Octanal (3.37 min), 2-Octanol (3.37 min)/2-Octanal (3.28 min), 3-Methyl-2-buten-1-ol (2.30 min)/ 3-Methyl-2-butena (2.36 min), Cyclohexanemethanol (4.88 min)/ Cyclohexanecarboxaldehyde (4.45 min), 3-Phenyl-1-propanol (4.86 min)/ Phenylpropyl aldehyde (4.44 min).

3. Standard curves of benzyl alcohol and benzaldehyde

Under the analyzing conditions, the standard curves of benzyl alcohol and benzaldehyde are shown in Fig. S2.

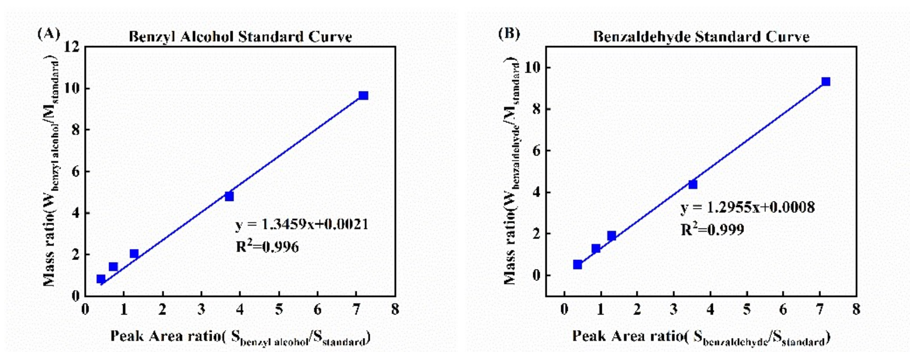

Fig. S3. GC internal standard curves of benzyl alcohol (A) and benzaldehyde (B)

4.Effect of liquid flow rate on the aerobic oxidation performance at 35 bar

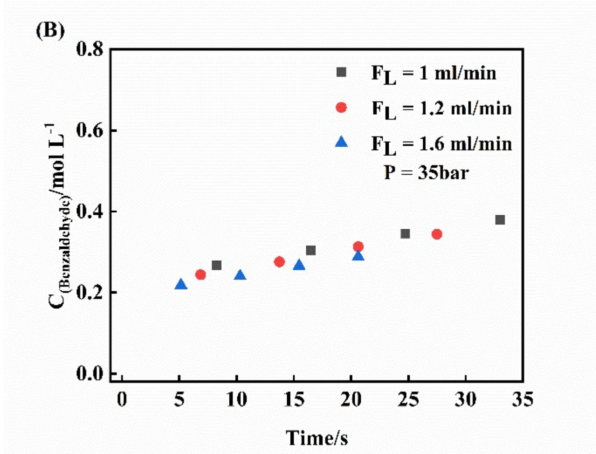

Fig. S4. Effects of gas and liquid flow rates on the aerobic oxidation performance. Experimental conditions: 40 °C, 35bar, 0.4mol/L of benzyl alcohol.

5. Plot of f(x) versus time for reaction rate constant

Fig. S4 shows the plot of $f(x)$ versus time at various temperatures, where the slope of the fitting line contains the reaction rate. The calculation results indicate the values of k increase since reaction temperatures vary from 20 °C to 45 °C and show good conformance with the experimental data (Fig. 3).

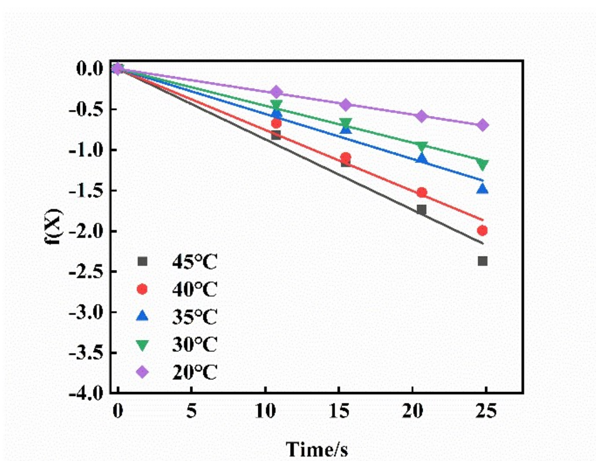

Fig. S5. Plot of f (x) versus time for reaction rate constant at the temperature range of 20-45 °C.

6. Calculation of k value

The k values were obtained from the slope of curves in Fig. S4 and the equation was as follows:

$$k = -\frac{slope}{\left(C_{Cu,0}^{2.25} \cdot P_{O_2,0}\right)} \quad (1)$$

Table S1. The correlation coefficients R^2 of fitting the experimental data and $\ln(k)$ value at corresponding temperatures

Temperature/ °C	**slope**	**R^2**	$\ln(k)$
45	-0.0869 ± 0.004	0.990	8.454
40	-0.0753 ± 0.002	0.994	8.306
35	-0.0562 ± 0.002	0.996	8.014
30	-0.0453 ± 0.001	0.995	7.795
20	-0.0274 ± 0.001	0.991	7.284