Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Supporting Information for:

Highly active copper catalyst obtained through rapid MOF decomposition

Anh H. T. Nguyen-Sorenson,[a] Clifton M. Anderson,[a] Santosh K. Balijepalli,[a] Kyle A. McDonald,[b] Adam J. Matzger,[b] and Kara J. Stowers[a]*

Corresponding Author

*Address correspondence to kstowers@chem.byu.edu

Department of Chemistry and Biochemistry, Brigham Young University, C100 Benson Building, Provo, Utah, USA 84602

Department of Chemistry, University of Michigan, 930 N. University, Ann Arbor MI, USA 48109-1055

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Supplementary Figures and Tables

Supplementary information

Energy dispersive X-ray (EDX) analysis indicates the presence of carbon and copper components in the Cu@C nanocomposite (Fig. S1).

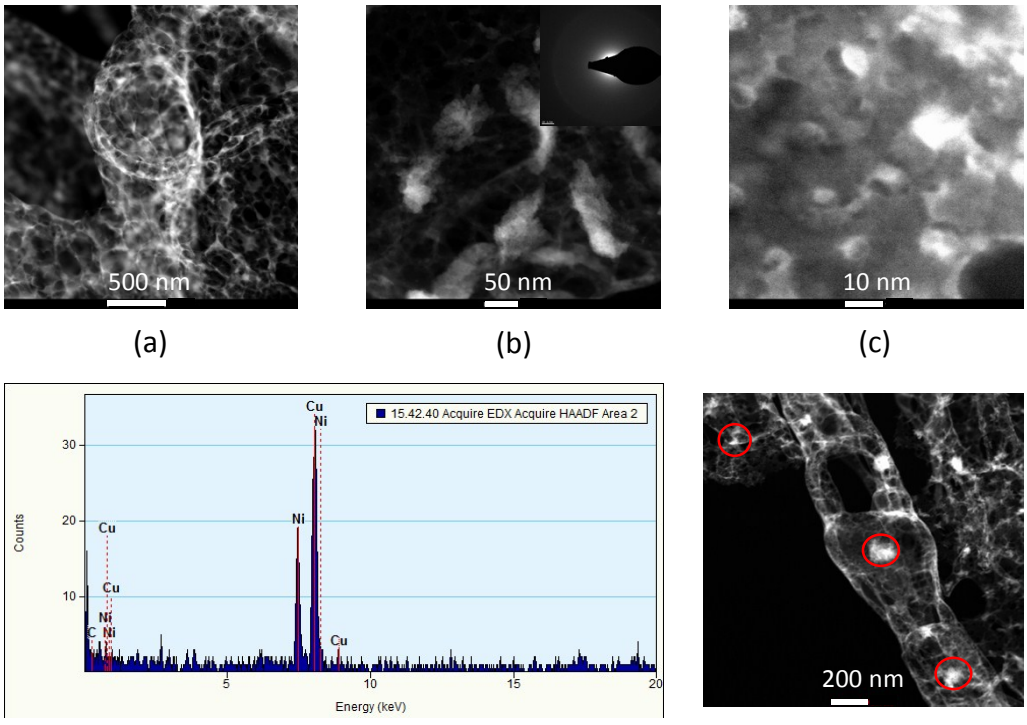
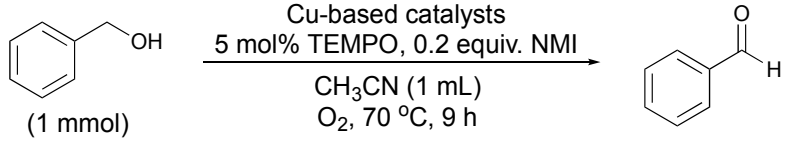


Figure S1. TEM images of **a-Cu@C**; a) wide view of Cu features in anisotropic carbon matrix, b) magnification of **a-Cu@C** with inset STEM derived diffuse diffraction pattern, c) magnification of **a-Cu@C** d) TEM-EDX images of **a-Cu@C** (Ni peaks are from TEM sample holder).

The catalytic activity for aerobic oxidation with TEMPO and molecular oxygen is compared between different Cu-based catalysts.

Table S1. Cu-catalyzed aerobic oxidation of benzyl alcohol



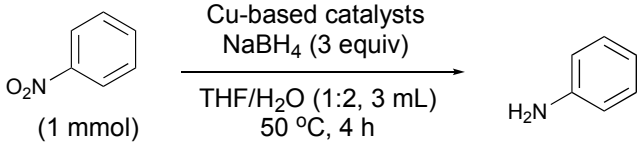
(1 mmol)

Entry	Catalyst (mol%)	Yield[b] (%)	TON[c]	Reference
1	None	n.a.	n.a.	This work
2	Cu-C (5.0)	94	18.8	1
3	Cu(I/II)-Amp-CPG (5.0)	97	19.4	2
4	CuI + $^{t}Bu_2$-bipy (5.0)	96	19.2	3
5	CuAAC-3a (5.0)	100	20	4

[a] Reaction conditions: benzyl alcohol (1 mmol), TEMPO (5 mol% to benzyl alcohol), NMI (0.2 equiv.), catalyst (0.5 – 5.0 mol% to benzyl alcohol), and CH_3CN (1 mL) under O_2 balloon, 70 °C, 9 h. [b] Determined by GC-MS using biphenyl as internal standard. [c] Turnover number (TON) = [moles of converted substrate (benzyl alcohol)] × (moles of Cu)$^{-1}$.

The catalytic activity for reduction of nitroaromatic molecules is compared between different catalysts.

Table S2. Cu-catalyzed reduction of nitrobenzene with $NaBH_4$

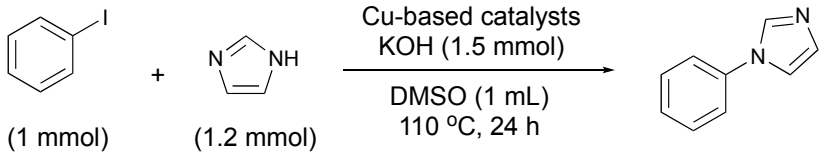


Entry	Catalyst (mol%)	Time (h)	Yield (%)	TON	Reference
1	**a-Cu@C** (10.0)	2	87	8.7	This work
2	Cu-C (50.0)	< 1 min	100	2	5
3	CuO (10.0)	2	79	7.9	6
4	Cu NPs (10.0)	2	98	9.8	6
5	CuNP/WS-1 (~2.12)	3	93	44	7

[a] Reaction conditions: nitrobenzene (1 mmol), $NaBH_4$ (3 equiv. to nitrobenzene), catalyst (5.0 – 50.0 mol% to nitrobenzene), and THF/H_2O (1:2, 3 mL), 50 °C, 2-4 h. [b] Determined by GC-MS using biphenyl as internal standard. [c] Turnover number (TON) = [moles of converted substrate (nitrobenzene)] × (moles of Cu)$^{-1}$.

The catalytic activity for N-arylation is compared between different Cu-based catalysts.

Table S3. Cu-catalyzed N-arylation of imidazole using iodobenzene*



Entry	Catalyst (mol%)	Conv. (%)	Yield[b] (%)	TON	Reference
1	None	n.a.	n.a.	n.a.	This work
6	HKUST-1 (10.0)	85	85	8.5	8
7	Cu(II)-Fe_3O_4@SiO_2 (0.5)	81	81	162	9
8	Cu NPs-MCN (2.5)	98	98	39.2	10
9	Fe_3O_4@SiO_2/Salen-Cu(II) (0.4)	82	82	205	11

*See reference 15. [a] Reaction conditions: iodobenzene (1 mmol), imidazole (1.2 mmol), catalyst (0.5 – 10.0 mol% to iodobenzene), KOH (1.5 mmol), DMSO (1 mL), 110 °C, 24 h. [b] Determined by GC-MS using biphenyl as internal standard. [c] Turnover number (TON) = [moles of converted substrate (iodobenzene)] × (moles of Cu)$^{-1}$.

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