Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supporting Information

An efficient and recyclable Cu@UiO-67-BPY catalyst for selective oxidation of alcohols and epoxidation of olefins

Rui Li [a], Xiujuan Li [a], Daniele Ramella [b], Yuzhen Zhao [*c], Yi Luan [*a]

[a] School of Materials Science and Engineering, University of Science and Technology Beijing, 30 Xueyuan Road, Haidian District, Beijing 100083, P. R. China.

[b] Department of chemistry, Temple University-Beury Hall, 1901, N. 13th Street Philadelphia PA 19122, United States.

[c] Xi'an Key Laboratory of Advanced Photo-electronics Materials and Energy Conversion Device, School of Sciences, Xijing University, Xi'an, 710123, China.

* Corresponding author, Yi Luan, E-mail address: yiluan@ustb.edu.cn, Tel.: +86 10 82376882.

Table S1 Various copper catalysts of selective aerobic oxidation of benzyl alcohol.

Entry	Catalyst	Solvent	Catalyst loading	Time (h)	Temp. (℃)	Yield (%)	Oxidant	TON [a]	TOF (h^{-1}) [b]
1	$CuCl_2$-UiO-67-BPY	CH_3CN	1.0 mol%	12	r. t	>99	O_2	99	8.25
2	$Cu(OAc)_2$-UiO-67-BPY	CH_3CN	1.0 mol%	12	r. t	84	O_2	84	7
3	$Cu(NO_3)_2$-UiO-67-BPY	CH_3CN	1.0 mol%	12	r. t	95	O_2	95	7.9
4	UiO-66-Sal-$CuCl_2$[1]	CH_3CN	4.0 mol%	24	60	>99	O_2	24.8	1.03
5	$Cu_3(BTC)_2$[2]	CH_3CN	1.0 mol%	12	60	16	O_2	16	1.33
6	Cu-BDC[3]	CH_3CN	1.0 mol%	12	60	18	O_2	18	1.5
7	Cu-TDPAT[4]	CH_3CN	1.0 mol%	12	60	12	O_2	12	1
8	Cu (II)–$5N_3IP$[5]	CH_3CN	3.0 mol%	20	60	>99	air	33	1.65
9	$Fe_3O_4/Cu_3(btc)_2$[6]	CH_3CN	4.4 mol%	6	75	>99	O_2	22.5	3.75
10	MCM-41-bpy-CuI[7]	EtOH	5.0 mol%	22	50	91	air	18.2	0.83
11	SPS–Cu(II) @$Cu_3(BTC)_2$[8]	CH_3CN	2.0 mol%	8	75	>99	O_2	49.5	6.19
12	Au@Cu(II)-MOF[9]	toluene	3.0 mol%	20	110	98	air	32.7	1.64

[a] Turnover number = mol converted/mol of active sites. [b] Turnover frequency =Turnover number/reaction time.

References

[1] J. Hou, Y. Luan, J. Tang, A. M. Wensley, M. Yang and Y. Lu, *J. Mol. Catal. A: Chem.*, 2015, **407**, 53.

[2] X. W. Zhang, W. J. Dong, Y. Luan, M. Yang, L. Tan, Y. G. Guo, H. Y. Gao, Y. H. Tang, R. Dang, J. Li, G. Wang, *J. Mater, Chem. A*, 2015, **3**, 4266.

[3] C. G. Carson, K. Hardcastle, J. Schwartz, X. T. Liu, C. Hoffmann, R. A. Gerhardt, R. Tannenbaum, *Eur. J. Inorg. Chem.* 2009, **16**, 2338.

[4] H. H. Wu, K. X. Yao, Y. H. Zhu, B. Y. Li, Z. Shi, R. Krishna, J. Li, *J. Phys. Chem. C*, 2012, **116**, 16609.

[5] N. Ahmad, H. A. Younus, A. H. Chughtai, K. Van Hecke, Z. A. K. Khattak, Z. Gaoke, M. Danishh, F. Verpoort, *Catal. Sci. Technol.*, 2018, **8**, 4010.

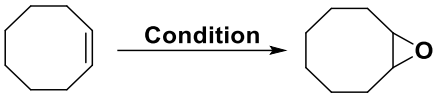
[6] J. Li, H. Gao, L. Tan, Y. Luan, M. Yang, *Eur. J. Inorg. Chem.* 2016, **30**, 4906.

[7] H. Zhao, Q. Chen, L.Wei, Y. Jiang, M. Cai, *Tetrahedron*, 2015, **71**, 8725.

[8] X. Zhang, W. Dong, Y. Luan, M. Yang, L. Tan, Y. Guo, H. Gao, Y. Tang, R. Dang, J. Li, G. Wang, *J. Mater. Chem. A*, 2015, **3**, 4266.

[9] J. Wang, F. Jin, H. Ma, X. Li, M. Liu, J. Kan, G. Chen, Y. Dong, *Inorg. Chem.*, 2016, **55**, 6685.

Table S2 Various catalysts for the Epoxidation of Cyclooctene.



Entry	Catalyst	Solvent	Catalyst loading	Time (h)	Temp. (℃)	Yield (%)	Conv. (%)	Sel. (%)	Oxidant	TON [a]	TOF (h^{-1}) [b]
1	$CuCl_2$-UiO-67-BPY	CH_3CN	1.0 mol%	4	40	99	>99	>99	O_2	99	24.75
2	$Cu(OAc)_2$-UiO-67-BPY	CH_3CN	1.0 mol%	4	40	93	93	>99	O_2	93	23.25
3	$Cu(NO_3)_2$-UiO-67-BPY	CH_3CN	1.0 mol%	4	40	92	92	>99	O_2	92	23
4	Mo@UiO-67[10]	-	1.0 mol%	4	50	99	>99	>99	TBHP	99	24.75
5	UiO-67-MoO_2Cl_2(bpydc)[11]	TFT	1.0 mol%	24	75	97	97	>99	TBHP	97	4.04
6	Fe_3O_4@P4VP@ZIF-8[12]	CH_3CN	1.0 mol%	12	60	99	>99	>99	O_2	99	8.35
7	Cu-Br-MOF[13]	toluene	1.0 mol%	8	80	99	>99	>99	TBHP	99	12.38
8	CoPMA@UiO-bpy[14]	CH_3CN	0.7 mol%	6	70	91	91	>99	H_2O_2	130	21.67
9	Zr-MOF-bpy-$CuBr_2$[15]	toluene	5.0 mol%	12	90	84.3	88.5	95.3	TBHP	17	1.42

[a] Turnover number = mol converted/mol of active sites. [b] Turnover frequency =Turnover number/reaction time.

References

[10] M. Kaposi, M. Cokoja, C. H. Hutterer, S. A. Hauser, T Kaposi, F. Klappenberger, A. Pöthig, J. V. Barth, W. A. Herrmann, F. E. Kühn, *Dalton Trans.*, 2015, **44**, 15976.

[11] P. Neves, A. C. Gomes, T. R. Amarante, F. A. Almeida Paz, M. Pillinger, I. S. Gonçalves, A. A. Valente, *Microporous Mesoporous Mater.*, 2015, **202**, 106.

[12] J. Hou, Y. Luan, J. Yu, Y. Qi, G.Wang, Y. Lu, *New J. Chem.*, 2016, **40**, 10127.

[13] S. Parshamoni, J. Telangae, S. Sanda, S. Konar, *Chem. Asian J.*, 2016, **11**, *540.*

[14] X. Song, D. Hu, X. Yang, H. Zhang, W. Zhang, J. Li, M. Jia, J. Yu, *ACS Sustainable Chem. Eng.*, 2019, **73**, 3624.

[15] T. Toyao, K. Miyahara, M. Fujiwaki, T. H. Kim, S. Dohshi, Y. Horiuchi and M. Matsuoka, *J. Phys. Chem. C*, 2015, **119**, 8131.

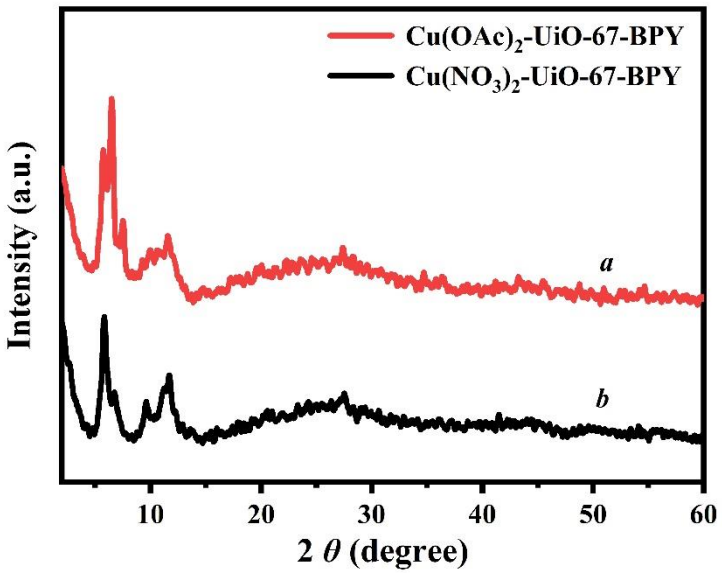


Fig. S1 PXRD pattern of (a) $Cu(OAc)_2$-UiO-67-BPY catalyst and (b) $Cu(NO_3)_2$-UiO-67-BPY catalyst.

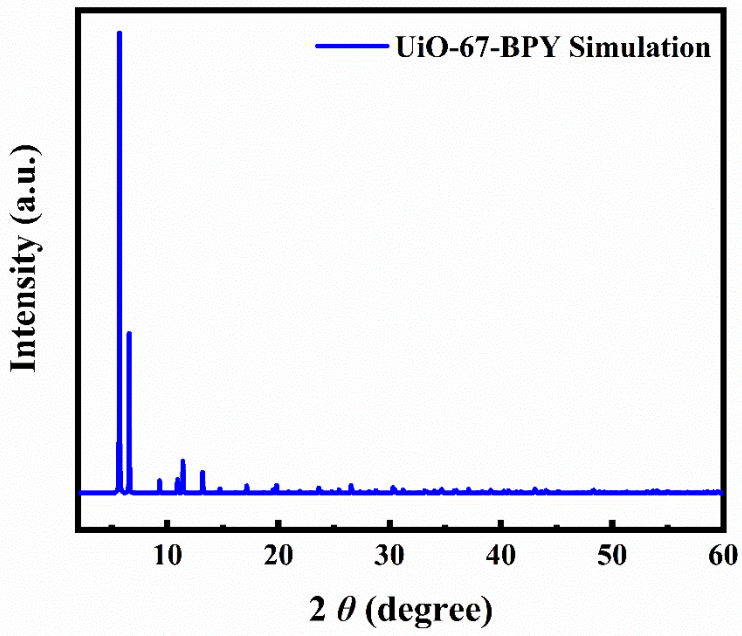


Fig. S2 PXRD pattern of UiO-67-BPY simulation.

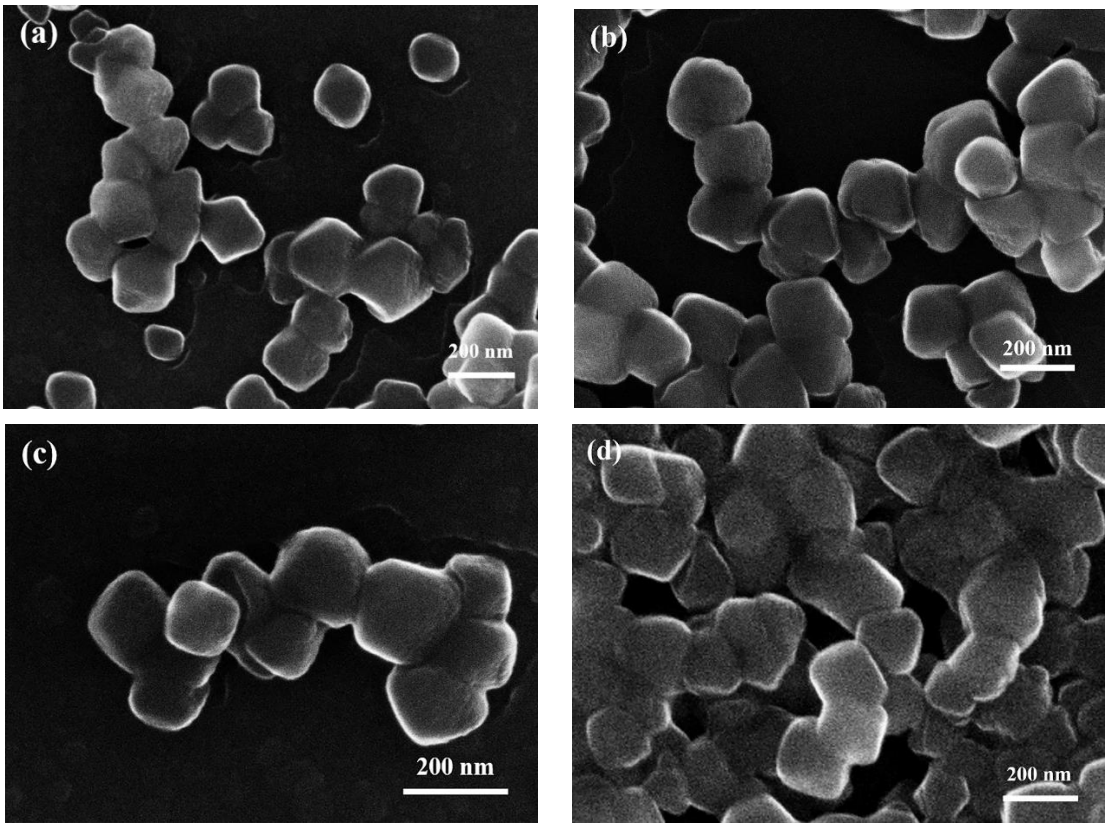


Fig. S3 SEM images of (a) UiO-67-BPY, (b) $CuCl_2$-UiO-67-BPY, (c) $Cu(NO_3)_2$-UiO-67-BPY and (d) $Cu(OAc)_2$-UiO-67-BPY.

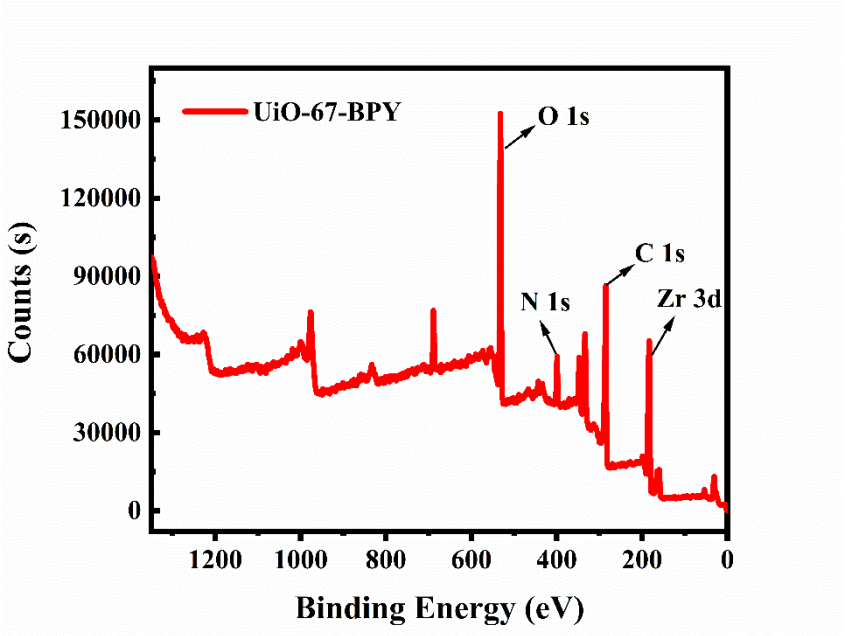


Fig. S4 XPS spectra of UiO-67-BPY.

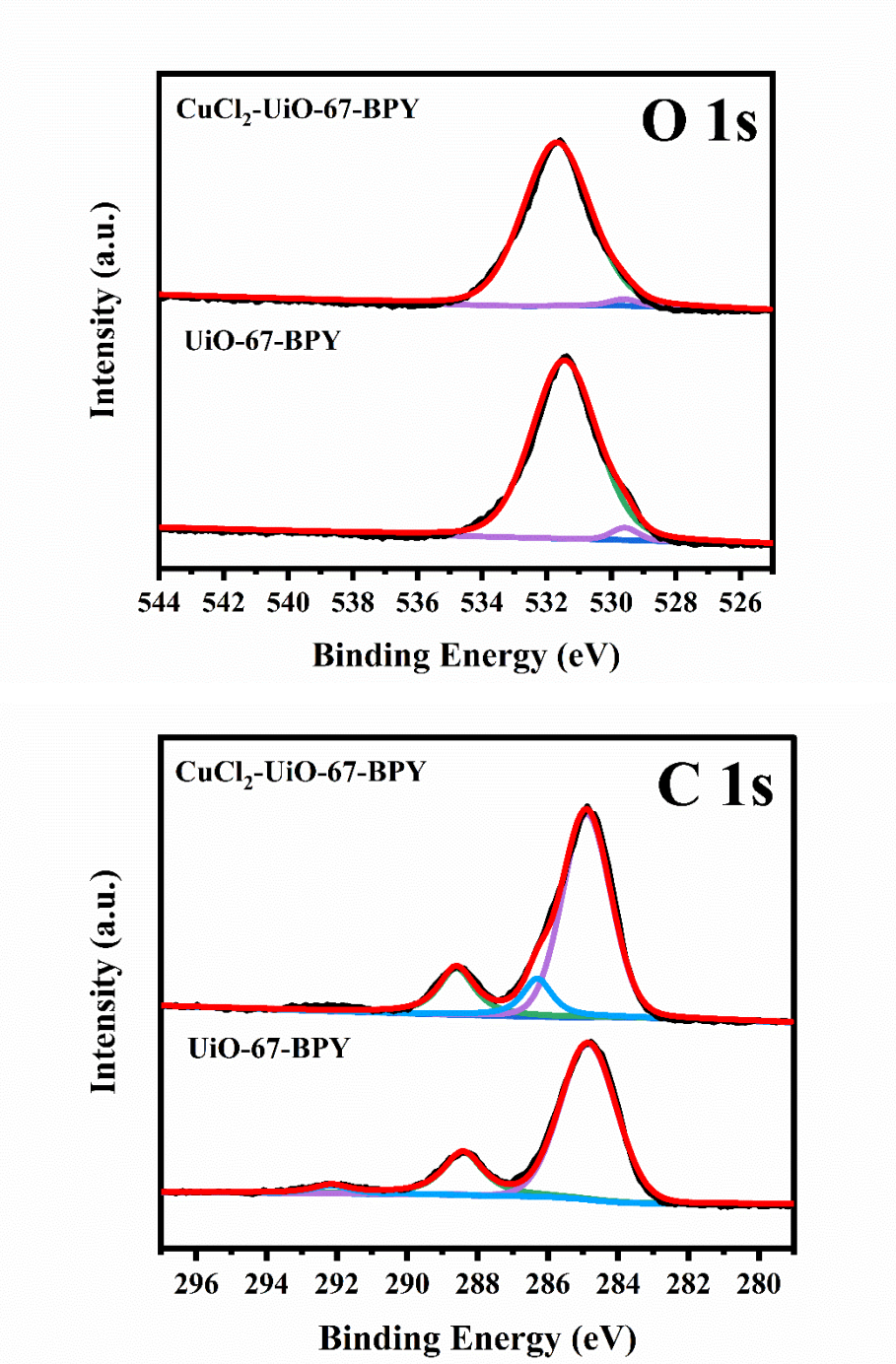


Fig. S5 Comparison of XPS spectra of UiO-67-BPY and $CuCl_2$-UiO-67-BPY.