The synthesis of a bifunctional copper metal organic framework and its application in the aerobic oxidation/Knoevenagel condensation sequential reaction

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Supporting Information

General Information. The structure and phase of the samples were evaluated by X-ray powder diffraction (XRD, Rigaku DMAX-RB 12 KW) with Cu Kα radiation (λ=0.15406 nm). The morphology of the as-obtained product was characterized by scanning electron microscopy (SEM, ZEISS SUPRA55). Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) were conducted on a TEI Tecnai F20. The samples for the SEM, TEM and HRTEM measurements were dispersed in ethanol and sonicated for a few minutes and supported onto the silicon slice and the holey carbon film on a Cu grid, respectively. Infrared spectra were recorded on a NICOLET 6700 infrared spectrophotometer. Analytical thin layer chromatography was performed using EMD 0.25 mm silica gel 60-F plates. Flash column chromatography was performed on Sorbent Technologies 60 Å silica gel. Adsorption-desorption isotherms of N_2 were measured at 77 K by an N_2 adsorption system after each sample was evacuated at 493 K for 12 h. The specific surface areas were obtained through the Brunauer–Emmett–Teller (BET) method using Micromeritics ASAP 2420 adsorption analyzer. The specific surface areas were calculated by the Brunauer–Emmett–Teller (BET) method. The pore size distributions were derived from the adsorption branches of isotherms by using the Barrett–Joyner–Halenda (BJH) model. By directly measuring the amount of liquid N_2 adsorbed in the pores or desorbed from the pores of the porous material versus pressure, the BET surface area and BJH pore size distribution can be obtained.

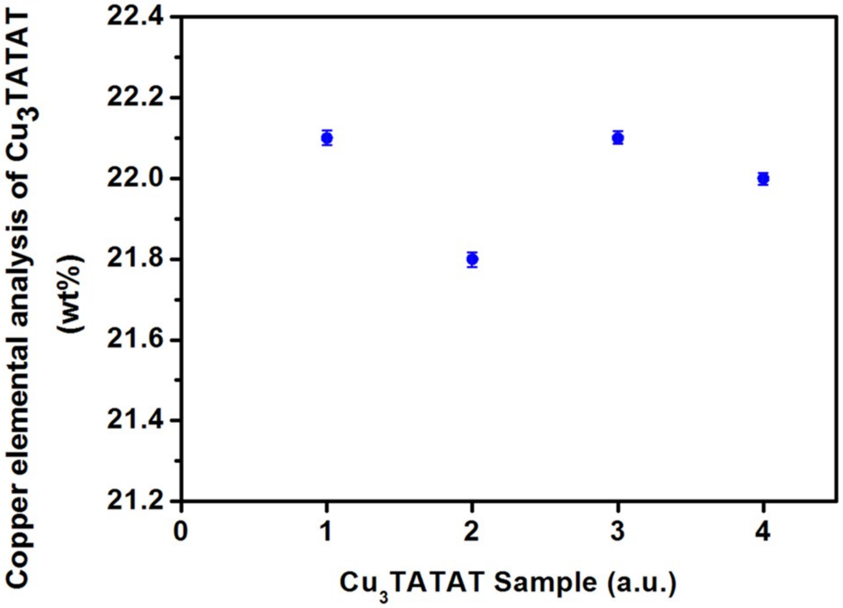
Table S1 One-pot multicomponent reaction using series of Cu_3TATAT.

Sample	Conversion (%)	Selectivity (%)
Cu_3TATAT-1	87	99
Cu_3TATAT-2	91	99
Cu_3TATAT-3	95	99
Cu_3TATAT-4	74	99

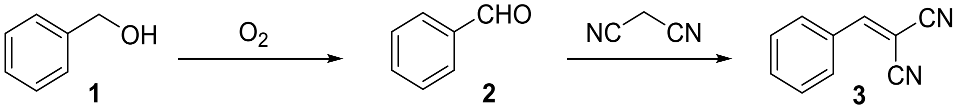
Reaction condition: Cu_3TATAT catalyst (8 mol% based on copper), alcohol (1.0 mmol), malononitrile (1.5 mmol), TEMPO (0.5 equiv.), in CH_3CN (5 mL) was stirred at 75 ^oC using 1 atm O_2 ballon for 12 h.

Table S2. Elemental analysis of copper derived Cu_3TATAT material

Sample	Cu(wt%)	C(wt%)	N(wt%)	H(wt%)
Cu_3TATAT-1	22.1	40.3	10.0	6.1
Cu_3TATAT-2	21.8	41.1	10.8	5.8
Cu_3TATAT-3	22.1	40.4	10.4	6.1
Cu_3TATAT-4	22.0	41.5	10.1	6.3
Cu_3TATAT in theory $Cu_3(TDPAT)(H_2O)_3$ ($C_{27}H_{18}N_6O_{15}Cu_3$)	22.2	40.44	9.98	6.02



One-pot Aerobic alcohol oxidation/Knoevenagel condensation reaction condition for Fig. 5



In a typical process, a mixture of benzyl alcohol (1.0 mmol), malononitrile (1.5 mmol), copper source and base, TEMPO (0.5 equiv.), were stirred in 5 mL CH_3CN at 75 ^{o}C. The reaction was placed into a 25 mL round bottom flask affixed with a reflux condenser with 1 atm O_2 balloon for 12 h. After a certain reaction time, the filtered liquid samples were analyzed by GC-MS using nitrobenzene as an internal standard.

As for Fig. 5, while 8 mol% of Cu_3TATAT-3 (based on copper) was used as the catalyst, the amount of N group was calculated to be 16 mol% (0.16 mmol).

0.027 mmol of B1 (16 mol% based on the nitrogen) were used for entry B1.

0.053 mmol of B2 (8 mol% based on the nitrogen, however, the same amount of triazine group as B1) were used for entry B2.

0.08 mmol of B3 (8 mol% of aniline amine group with same the same aniline amine group as B1) were used for entry B3.

0.08 mmol of B4 (8 mol% of aniline amine group with same the same aniline amine group as B1) were used for entry B4.

0.027 mmol of B5 were used for entry B5.

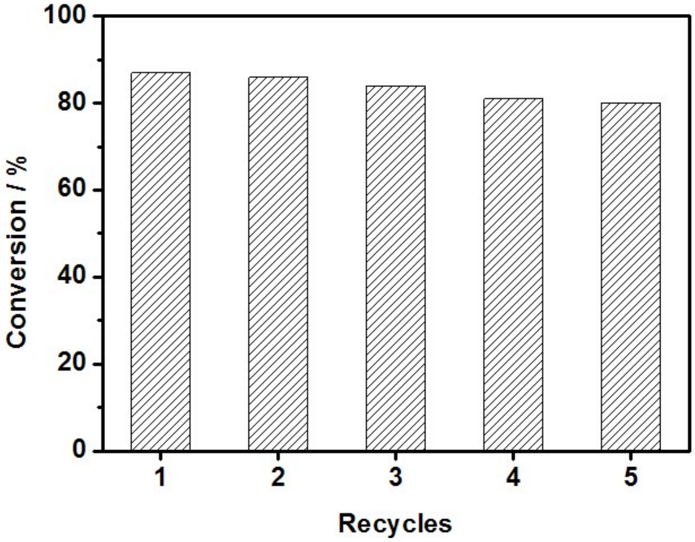


Fig. S1 Recycle test of Cu_3TATAT-1 in one-pot reaction of benzyl alcohol and malononitrile.

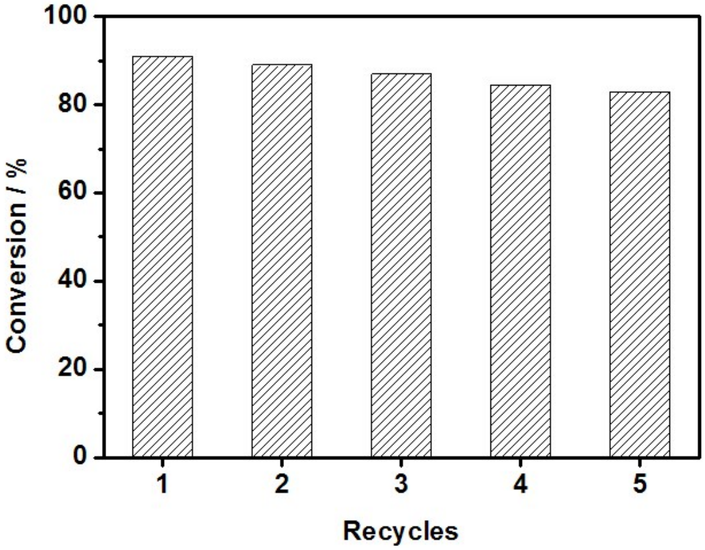


Fig. S2 Recycle test of Cu_3TATAT-2 in one-pot reaction of benzyl alcohol and malononitrile.

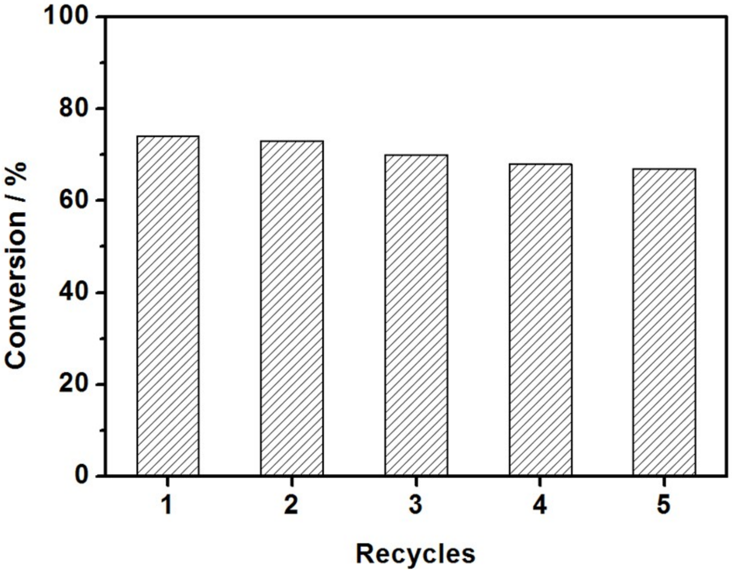


Fig. S3 Recycle test of Cu_3TATAT-4 in one-pot reaction of benzyl alcohol and malononitrile.

Table S3 Solvent and temperature effect in the one-pot reaction[a]

Entry	Solvent	Yield	Selectivity
1	Toluene	56%	99%
2	EtOH	12%	79%
3	Chlorobenzene	3%	99%
4	Acetonitrile	95%	99%
5	1,2-Dichloroethane	16%	83%
6	THF	5%	99%

[a] Reaction conditions: catalyst (8 mol% based on copper), benzyl alcohol (1.0 mmol), malononitrile (1.5 mmol), TEMPO (0.5 equiv.) in 5 mL solvent at 75 °C using 1 atm O_2 balloon for 12 h

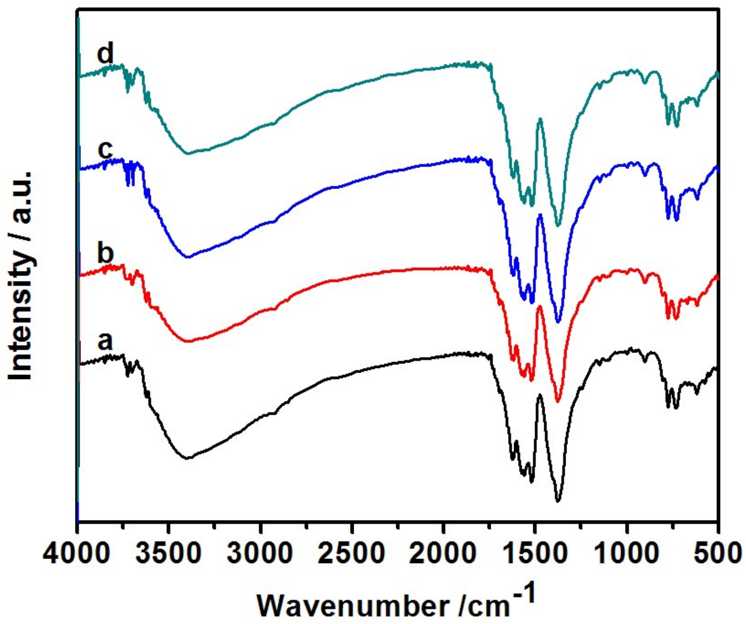


Fig. S4 3 FT-IR spectra of (a) Cu_3TATAT-1, (b) Cu_3TATAT-2, (c) Cu_3TATAT-4 and (d) Cu_3TATAT-3 after 5 catalytic recycles.

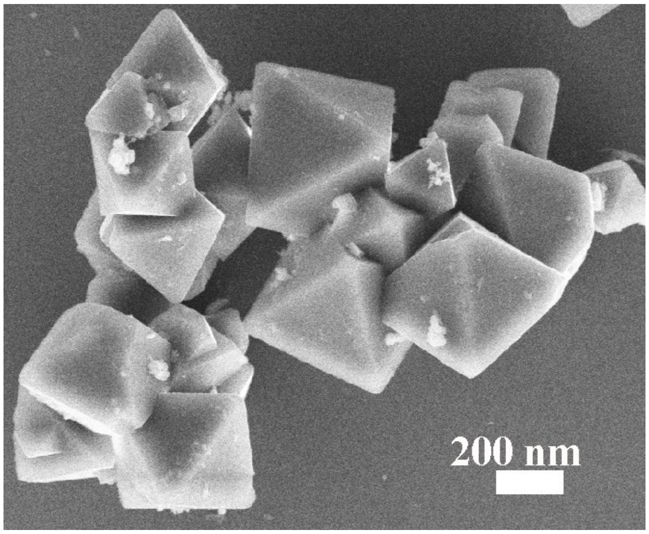


Fig. S5 SEM image of recycled Cu_3TATAT-3 catalyst.

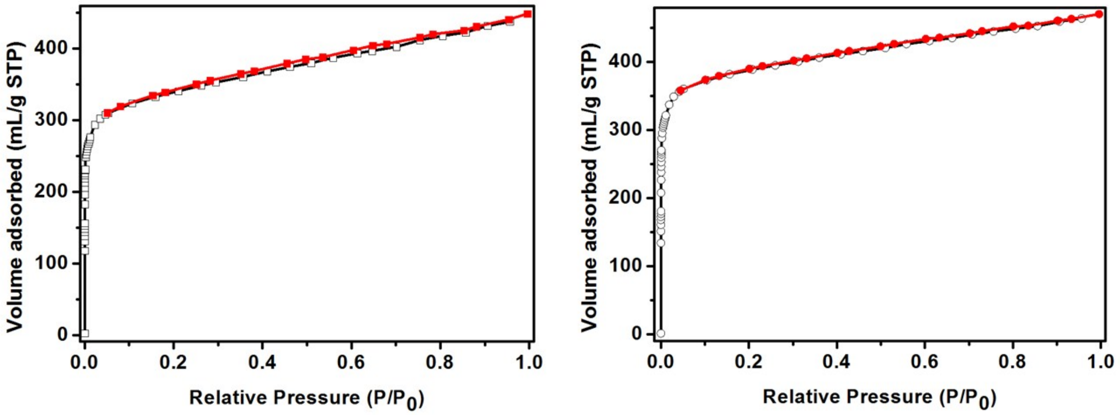


Fig. S6 N_2 adsorption/desorption isotherms of Cu_3TATAT-1 and Cu_3TATAT-2.

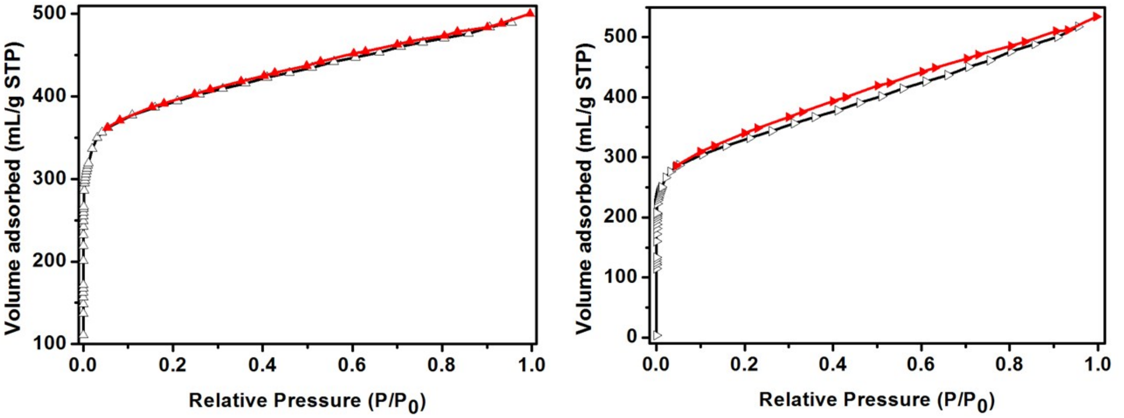


Fig. S7 N_2 adsorption/desorption isotherms of Cu_3TATAT-3 and Cu_3TATAT-4.

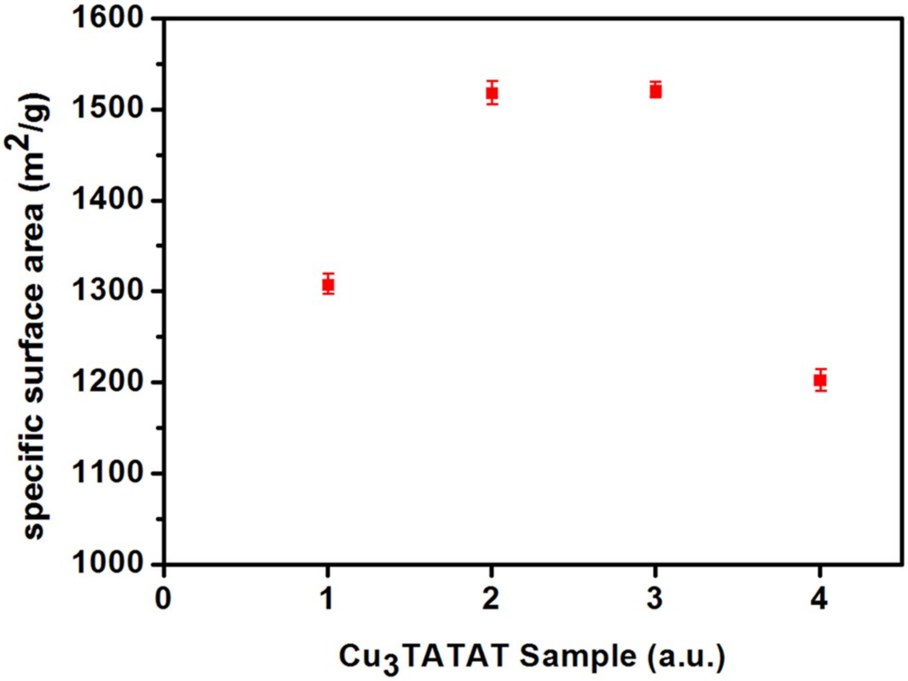


Fig. S8 BET surface area of Cu_3TATAT samples with error bars.

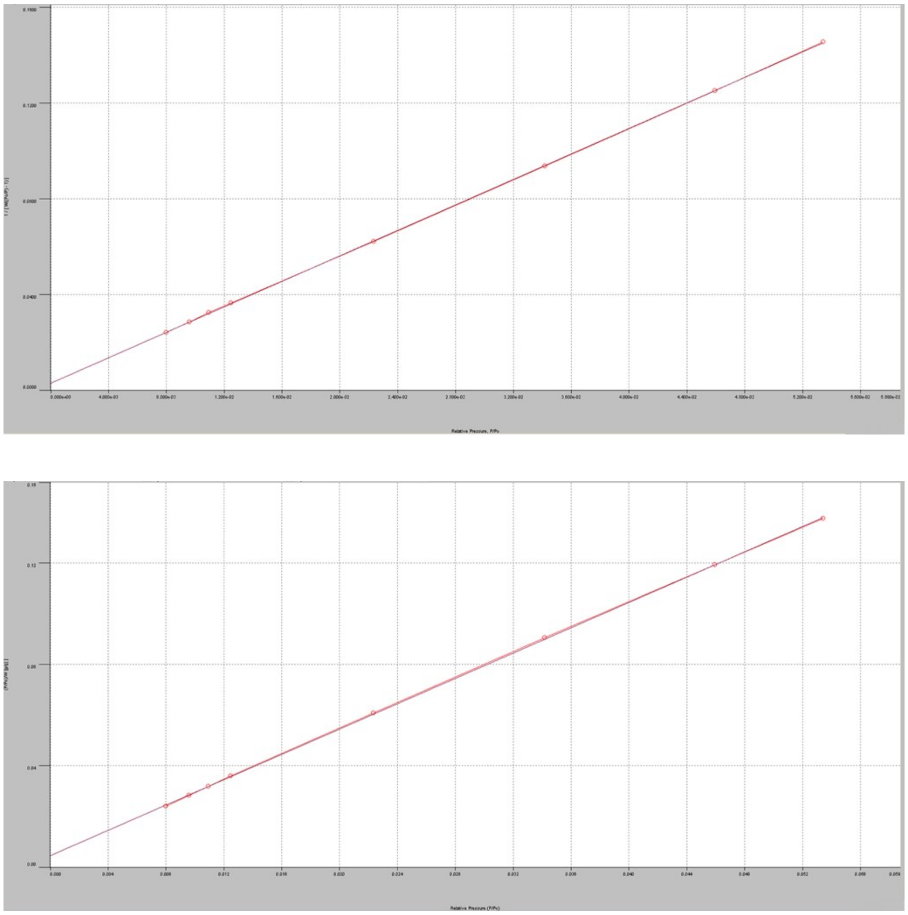


Fig S9 BET and Langmuir plot for Cu_3TATAT-1 sample.

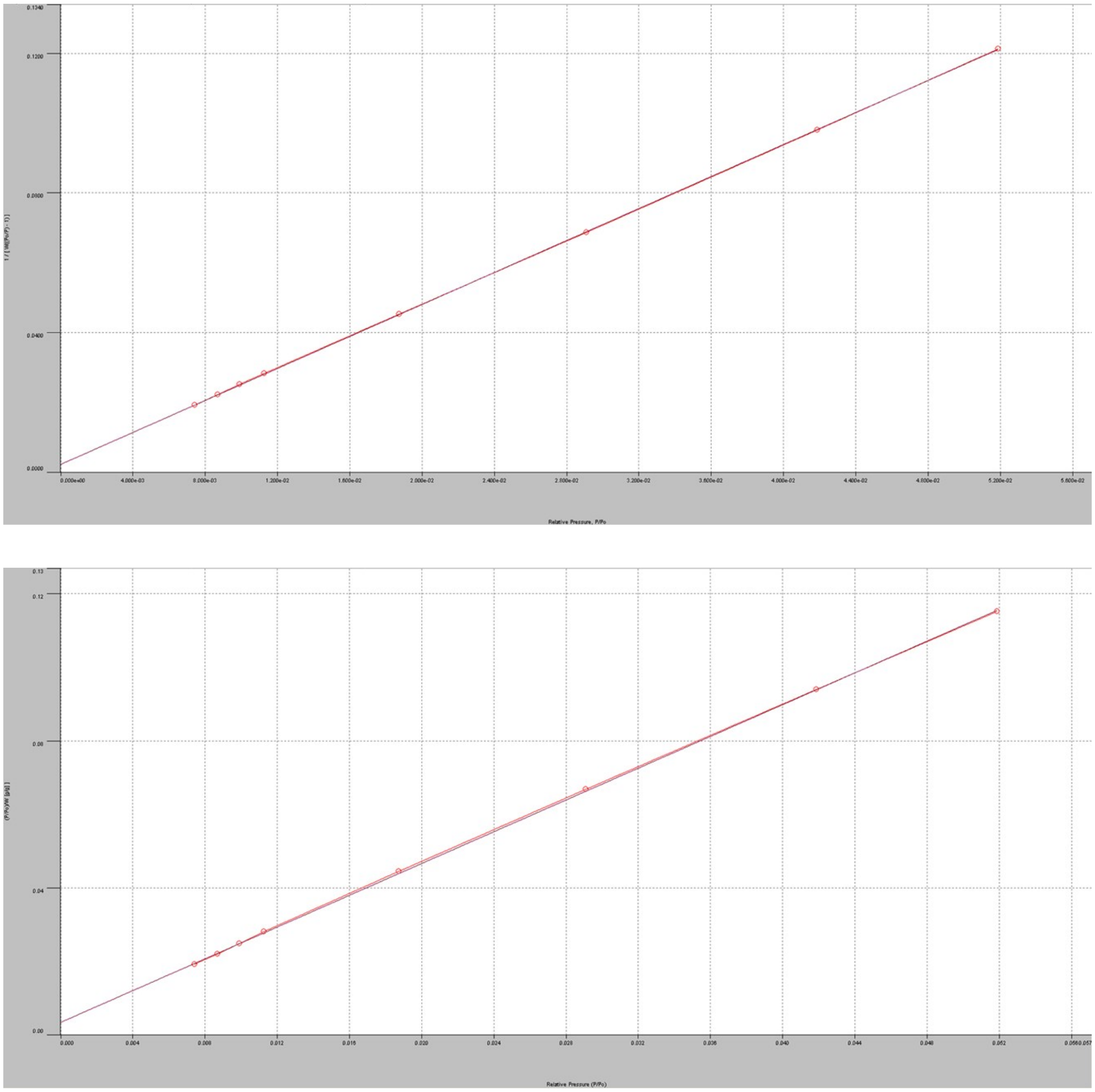


Fig S10 BET and Langmuir plot for Cu_3TATAT-2 sample.

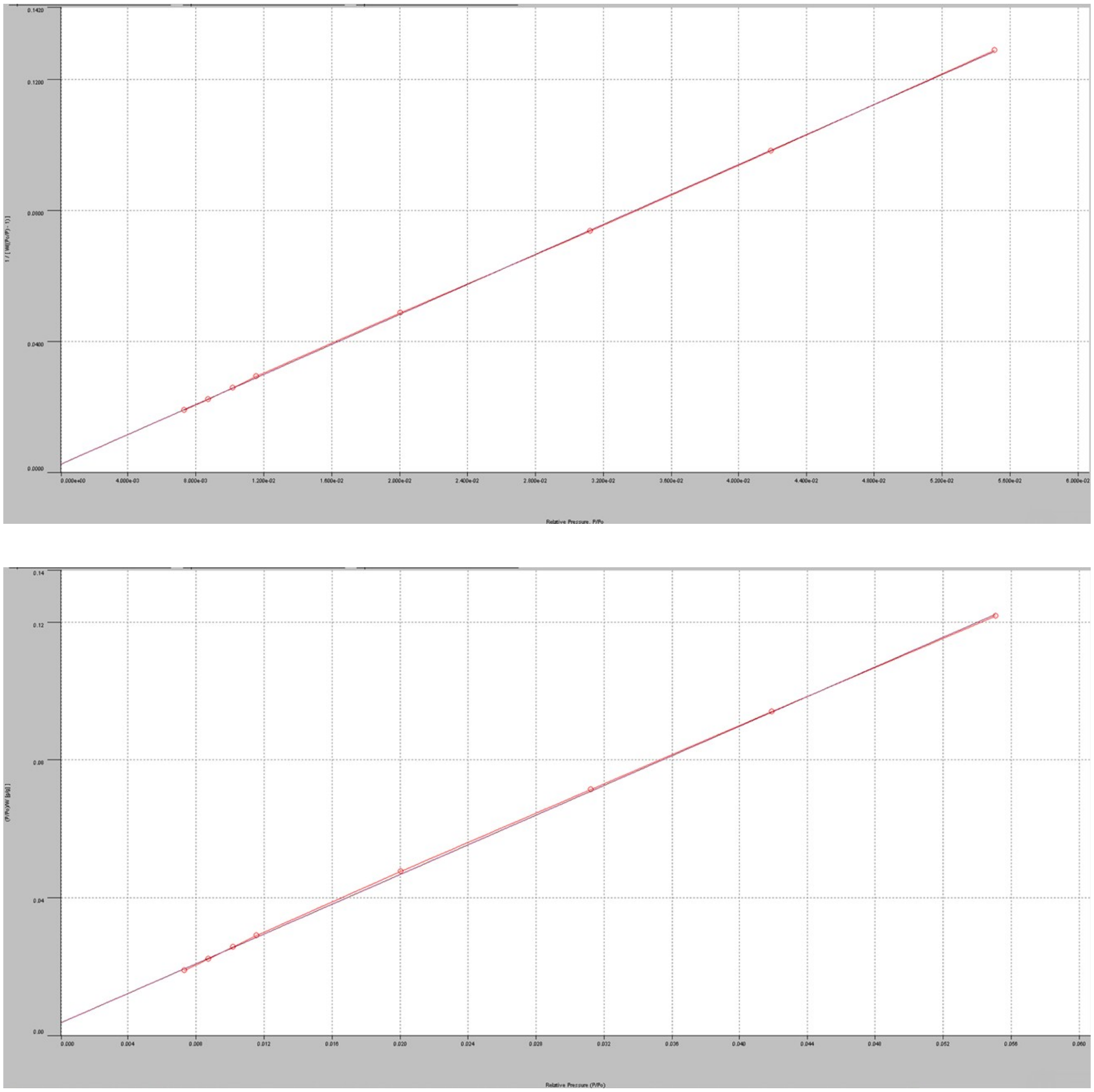


Fig S11 BET and Langmuir plot for Cu_3TATAT-3 sample.

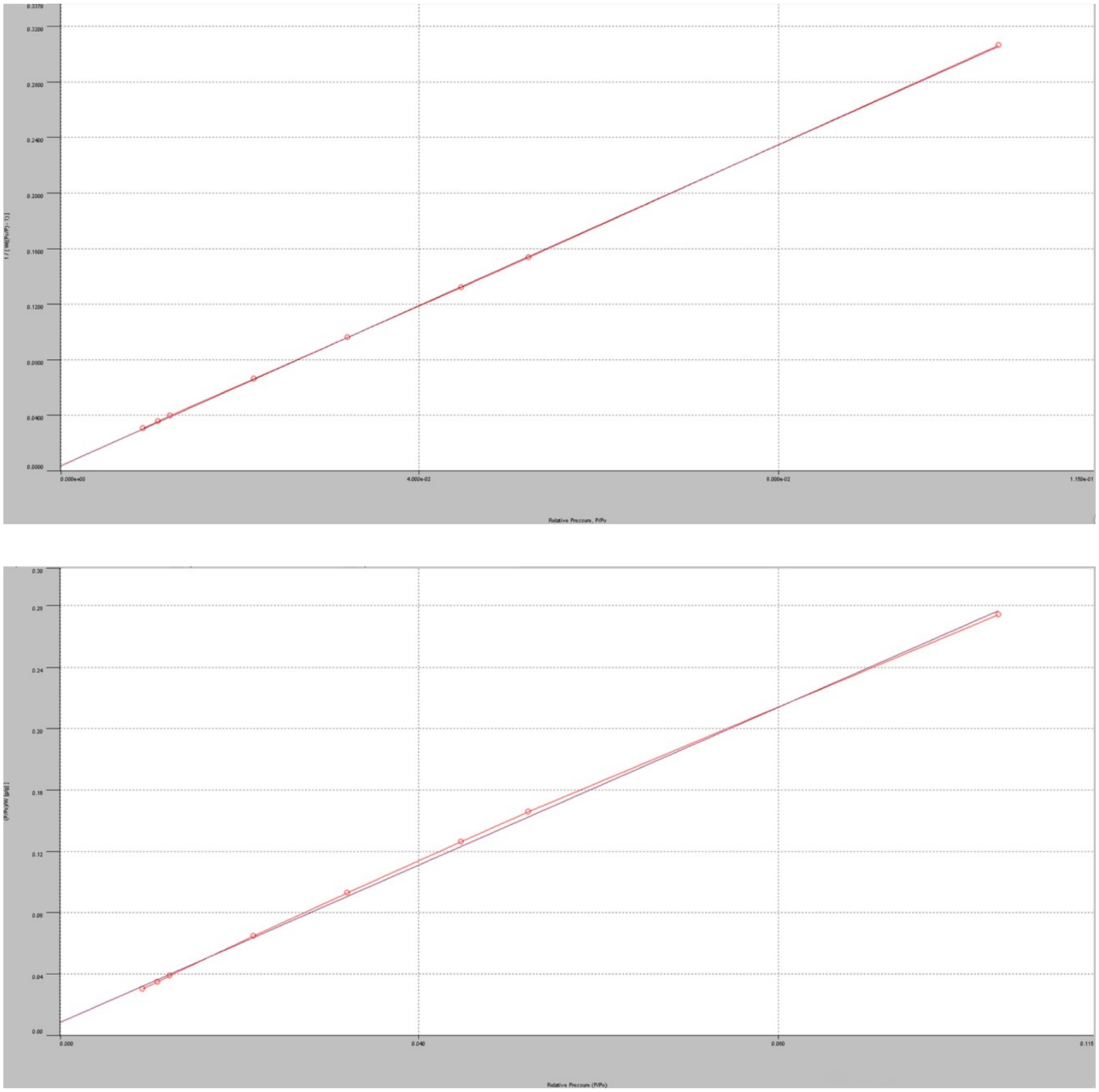
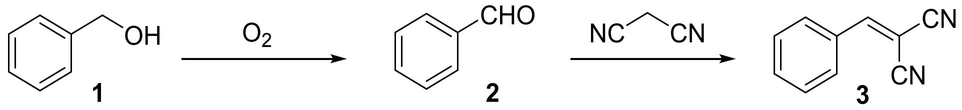


Fig S12 BET and Langmuir plot for Cu_3TATAT-4 sample.

Table S4. Literature comparison for secondary alcohol oxidation.



Catalyst	Loading	Reaction time	T (ºC)	Solvent	Yield	Reference
Pd_1–Au_1/LDH	100 mg/1 mmol	1.5 h	80	H_2O	74%	1
Zr-MOF-NH_2	56 mol%	48 h	25	*p*-xylene	91%	2
NH_2-MIL-101(Fe)	13 mol%	40 h	25	trifluorotoluene/ acetonitrile 10:1		3
Cu3TATAT-3	8 mol%	12 h	75	CH_3CN	99%	This work

1. Chen Chen, Hanmin Yang, Jizhong Chen, Ran Zhang, Li Guo, Huimei Gan, Baoning Song, enwen Zhu, Li Hua, Zhenshan Hou, One-pot tandem catalytic synthesis of α, β-unsaturated nitriles from alcohol with nitriles in aqueous phase, Catal. Comm., 2014, 47, 49–53.
2. Takashi Toyao, Masakazu Saito, Yu Horiuchi, Masaya Matsuoka, Development of a novel one-pot reaction system utilizing a bifunctional Zr-based metal–organic framework, Catal. Sci. Technol., 2014, 4, 625-628.
3. Dengke Wang and Zhaohui Li, Bi-functional NH_2-MIL-101(Fe) for one-pot tandem photo-oxidation/Knoevenagel condensation between aromatic alcohols and active methylene compounds, Catal. Sci. Technol., 2015, 5, 1623-1628.