Supporting information for

Cu(II)/Cu(0)@UiO-66-NH_2: base metal@MOFs as heterogeneous catalysts for olefin oxidation and reduction

Jian-Cheng Wang, Yu-Hong Hu, Gong-Jun Chen, and Yu-Bin Dong*

College of Chemistry, Chemical Engineering and Materials Science, Collaborative Innovation Center of Functionalized Probes for Chemical Imaging in Universities of Shandong, Key Laboratory of Molecular and Nano Probes, Ministry of Education, Shandong Normal University, Jinan 250014, P. R. China. E-mail: yubindong@sdnu.edu.cn.

Content

1. Materials and measurements

All the chemicals were obtained from commercial sources and used without further purification. UiO-66-NH_2 was synthesized according to literature method.[1] Infrared (IR) samples were prepared as KBr pellets, and spectra were obtained in the 400-4000 cm^{-1} range using a Perkin-Elmer 1600 FTIR spectrometer. ^1H NMR data were collected using an AM-300 spectrometer. Chemical shifts are reported in δ relative to TMS. The scanning electron microscopy (SEM) micrographs were recorded on a Gemini Zeiss Supra TM scanning electron microscope. The X-ray diffraction (XRD) experiments were obtained on a D8 ADVANCE X-ray powder diffract to meter with CuKα radiation (λ = 1.5405 Å). Thermo gravimetric analyses were carried out on a TA Instrument Q5 simultaneous TGA under flowing nitrogen at a heating rate of 10°C/min. ICP-LC was performed on an IRIS InterpidII XSP and NU Atto M. HRTEM (High resolution transmission electron microscopy) analysis was performed on a JEOL 2100 Electron Microscope at an operating voltage of 200 kV. GC analysis was performed on a 7890B gas chromatograph (Agilent Technologies, CA, USA) equipped with a flame ionization detector (FID) and a split/splitless injector. The GC capillary column (DB-WAX, 30 m length × 0.53 mm; HP-5, 30 m length × 0.32 mm) was purchased from the Agilent Technologies. XPS spectra were obtained from THI5300 (PE). ICP measurement was performed on an IRIS Interpid (II) XSP and NU AttoM.

2. Synthesis and characterization of 1 and 2

Synthesis of 1. UiO-66-NH_2 (0.50 mmol, 10.0 g) was dispersed into a EtOH solution (2 mL) of $Cu(OAc)_2$ (0.02 mol/L) at room temperature for 1 h. The resulting solids were collected by centrifugation, washed with EtOH (3 times) and dried at 80°C to generate **1** as a light green crystalline solid. IR (KBr pellet cm^{-1}): 3346(s), 1569(vs), 1425(s), 1259(vw), 1027(vw), 769(ms), 653(s), 481(w). Elemental Analysis (%): calcd for $C_{52.8}H_{47.2}Zr_6Cu_{1.2}N_6O_{36.8}$: C 32.06, H 2.41, N 4.25; found: C 31.89, H 2.26, N 4.36.

Table S1. ICP result for **1**

element	Zr 339.198	Zr 343.823	Zr 257.139	Zr 272.262	Cu 324.754	Cu 327.396	Cu 224.700
unit	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
average value	**81.4381**	**80.2119**	**78.5334**	**79.8095**	**11.5515**	**12.19780**	**10.0829**
sd	1.17903	0.76806	1.19402	0.73362	0.15422	0.22592	0.08217
rsd	1.448	0.958	1.52	0.919	1.335	1.852	0.815
min	0.00057	0.00003	0.00923	0.00757	0.00015	0.00036	0.0024
max	120	120	120	120	12	12	12

Based on above analysis, the Zr/Cu ratio in **1** is 1 : 0.2, so the formula of **1** can be described as 1.2 $Cu(OAc)_2$@UiO-66-NH_2.

Synthesis of 2.[2,3] An aqueous solution of $NaBH_4$ (2 mL, 7.5 mg/mL) was added dropwise to a suspended solution of **1** (150 mg) in EtOH (10 mL)/CH_2Cl_2 (50 mL) at 0°C in N_2 atmosphere. The reaction system was stirred for additional half an hour at room temperature. The resulting solids were collected by centrifugation to generate **2** as a dark cyan crystalline solid. IR (KBr pellet cm^{-1}): 3371(s), 2109(vw), 1571(ms), 1345(vs), 1258(vw), 1007 (ms), 769 (vw), 628(ms). Elemental Analysis (%): calcd for $C_{48}H_{40}Zr_6CuN_6O_{32}$: C 31.61, H 2.21, N 4.61; found: C 31.51, H 2.07, N 4.74.

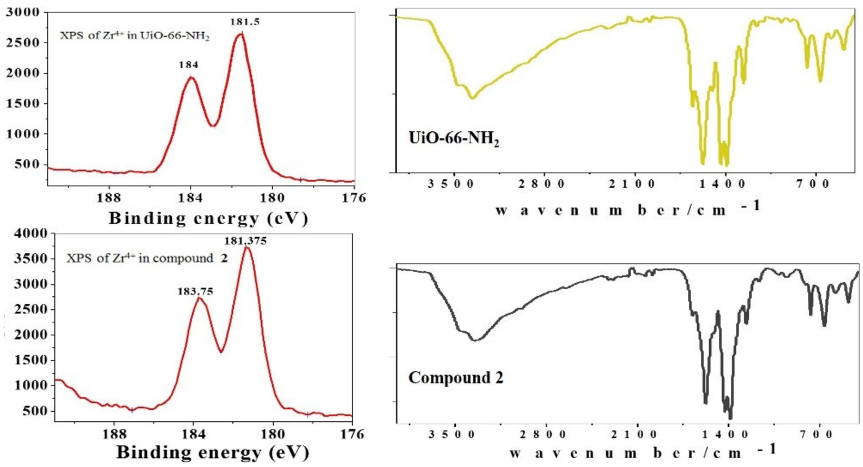


Fig. S1 Left: XPS spectra of UiO-66-NH_2 and **2**. As shown in the figure, the peaks at 184.0 and 181.5 eV in UiO-66-NH_2 and the peaks at 183.75 and 181.375 eV in compound **2** for $3d^{3/2}$and $3d^{5/2}$ are well consistent with those values for Zr(IV) in ZrO_2.[3b] Right: IR spectra of UiO-66-NH_2 and **2**. These spectra indicated that the UiO-66 framework is stable after copper loading and reduction.

Table S2. ICP result for **2**

element	Zr 339.198	Zr 343.823	Zr 257.139	Zr 272.262	Cu 324.754	Cu 327.396	Cu 224.700
unit	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
average value	**107.353**	**107.721**	**106.35**	**107.173**	**13.26450**	**13.97790**	**11.6479**
sd	0.32739	0.43628	0.30476	0.04525	0.11929	0.00728	0.0664
rsd	0.305	0.405	0.287	0.042	0.899	0.052	0.57
min	0.00057	0.00003	0.00923	0.00757	0.00015	0.00036	0.0024
max	120	120	120	120	12	12	12

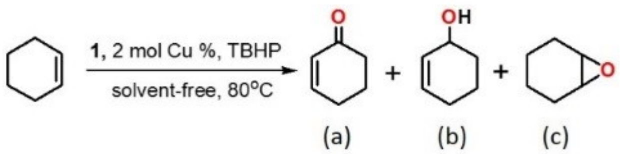
Based on above analysis, the Zr/Cu ratio in **2** is 1 : 0.17, so the formula of **2** can be described as 1.0 Cu(0) @UiO-66-NH_2.

Table S3. ICP result for Cu loading based on UiO-66

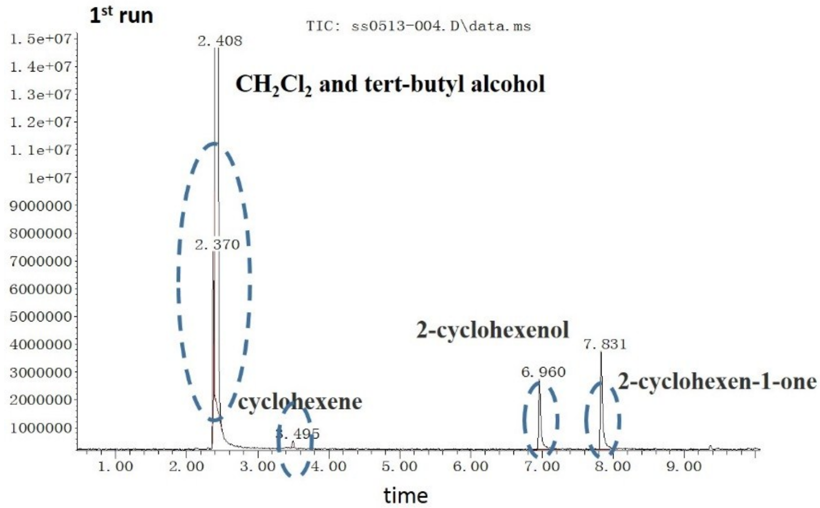
element	Zr 339.198	Zr 343.823	Zr 257.139	Zr 272.262	Cu 324.754	Cu 327.396	Cu 224.700
unit	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
average value	**107.443**	**107.521**	**106.95**	**107.543**	**4.57570**	**4.96867**	**4.15632**
sd	0.35739	0.42528	0.30476	0.04455	0.10819	0.00808	0.0644
rsd	0.396	0.315	0.299	0.040	0.900	0.050	0.55
min	0.00066	0.00002	0.00843	0.00747	0.00013	0.00034	0.0021
max	120	120	120	120	12	12	12

Based on above analysis, the Zr/Cu ratio in UiO-66 is 1 : 0.06, so the formula can be described as 0.36Cu(II)@ UiO-66.

3. Catalytic properties of 1



1 (0.02 mmol, 34.2mg) was added to a solution of cyclohexene (1.0 mmol, 102.0 μL), TBHP (2.0 mmol, 201.2 μL). After stirred at room temperature for 5 min., the system was heated at 80°C for 12 h (monitored by GC). After addition of methylene chloride (5 mL), **1** was recovered by centrifugation and directly reused for next catalytic cycle. The product yield was determined by GC-MS.



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2-cyclohexenol
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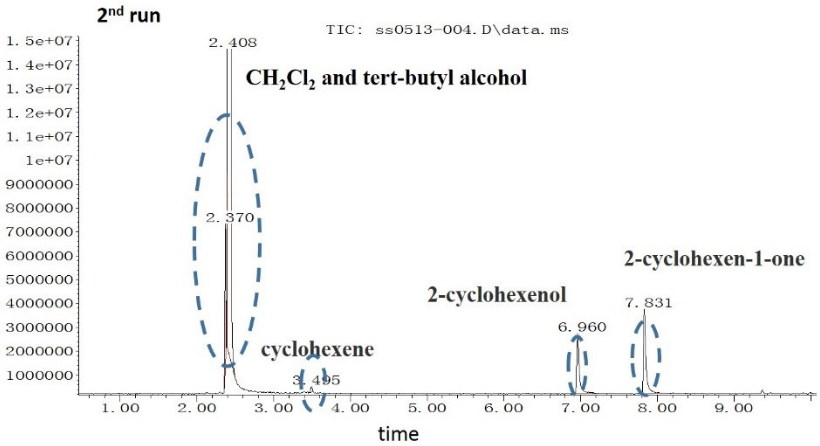
6.960
2-cyclohexen-1-one
cyclohexene
3.495
time



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CH2Cl2 and tert-butyl alcohol
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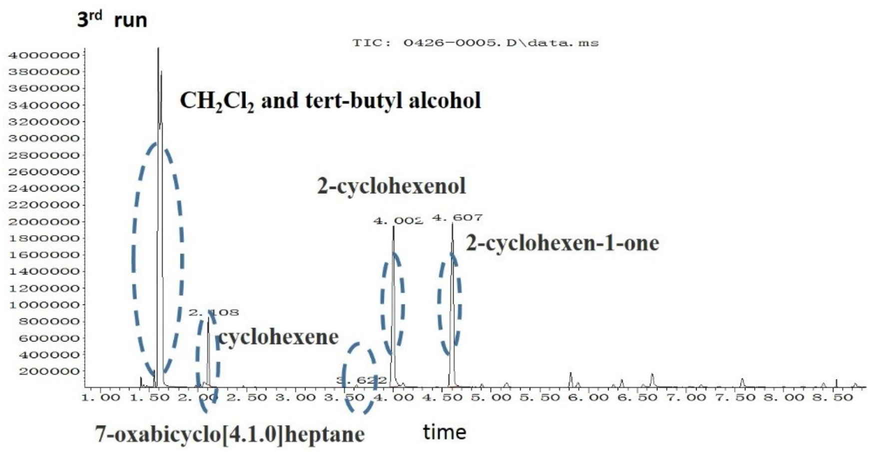
2-cyclohexen-1-one
2-cyclohexenol
7.831
6.960
cyclohexene
3.495
time



3rd run
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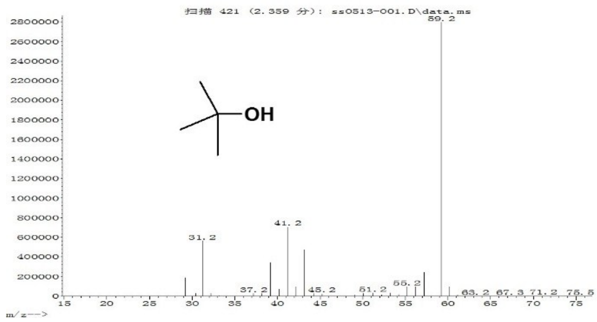
time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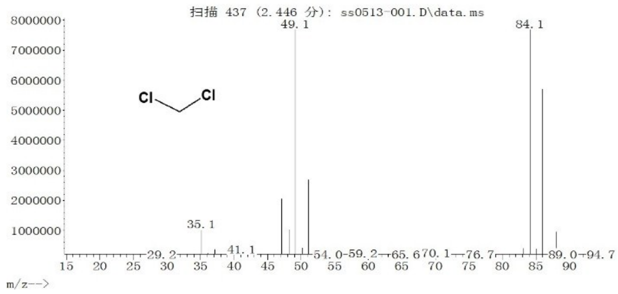
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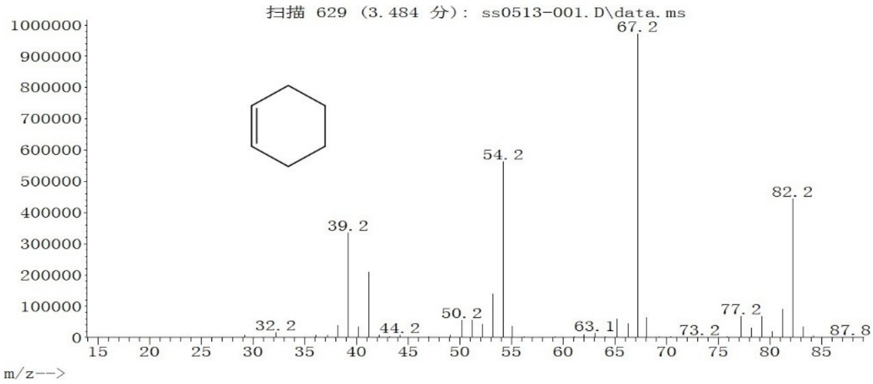
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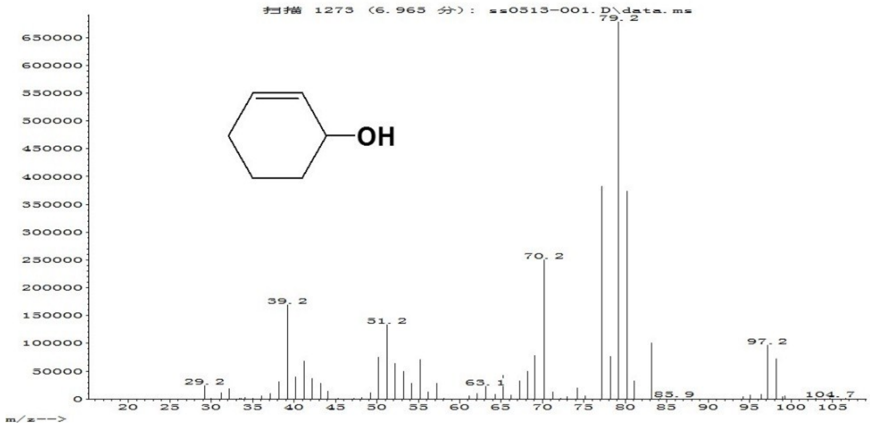
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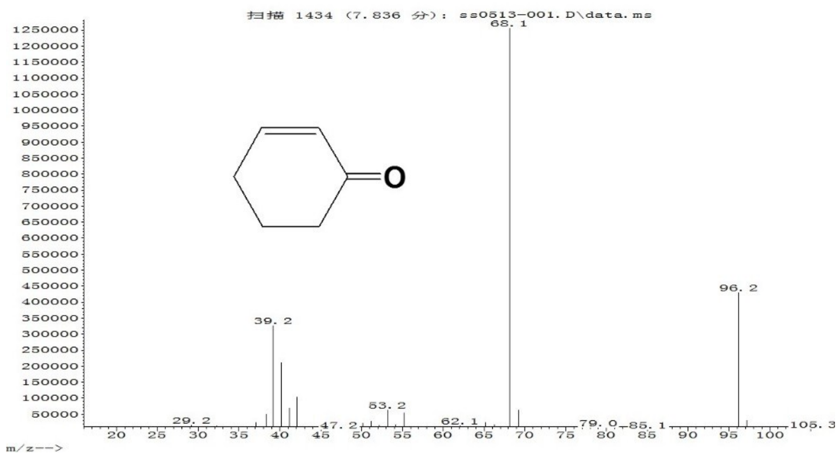
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m/z-->

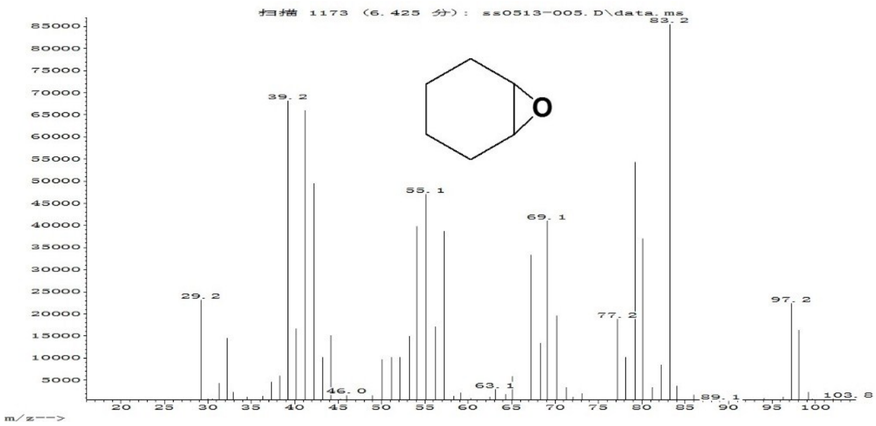


Fig. S2 GC-MS spectra for three catalytic runs.

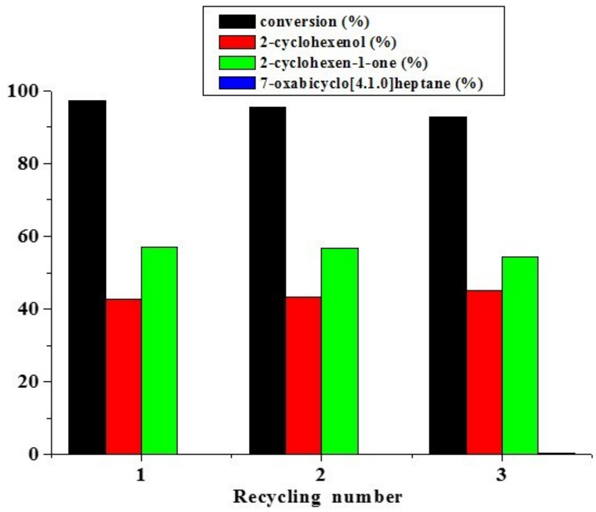


Fig. S3 Recycling catalytic test.

Table S4. Summary of the cyclohexene oxidation catalyzed by MOF-type heterogeneous catalysts

Ref.	Catalyst	Solvent	Cyclohexene	Condition	Oxidant	Conversion	Product type
4	Ti-POM/MIL-101	acetonitrile	0.2 mol	70℃/6 h	H_2O_2	39%	3
5	$[Co^{II}(BPB)]\cdot3DMF$	1,2-dichloroethane	1 mmol	80℃/12 h	TBHP [a]	62%	3
6	$[Cu(H_2btec)(bipy)]_\infty$	1,2-dichloroethane	40 mmol	75℃/24 h	TBHP	64.5%	3
7	MFU-1	Cyclohexene	Neat	70℃/24 h	TBHP	27.5%	3
8	MFU-2	Cyclohexene	Neat	70℃/24 h	TBHP	16%	3
	NHPI@MFU-1	Cyclohexene	Neat	35℃/9 h	oxygen	～20%	3
9	$NH_4[Cu_3-(\mu_3-OH)(\mu_3-4-carboxy\ pyrazolato)_3]$	Cyclohexene	Neat	70℃/24 h	TBHP	20%	3
10	MIL-47	chloroform	0.1 mmol	50℃/7 h	TBHP	60%	4
11	COMOC-3	chloroform	2.75 mmol	50℃/7 h	TBHP	38%	4

12	$[Cu(H_2btec)(bipy)]_\infty$	1,2-dichloroethane	40 mmol	75℃/24 h	TBHP	68.4%	3
13	Ni-MOF	Cyclohexene	Neat	80℃/20 h	O2 balloon	13.2%	4
	Co-MOF	Cyclohexene	Neat	80℃/10 h	O2 balloon	8.1%	4
	Cu-MOF	Cyclohexene	Neat	80℃/10 h	O2 balloon	11.7%	4
14	CZJ-1	acetonitrile	0.1 mmol	r.t./6 h	PhIO [b]	99%	1
15	$[Co(H_2\text{-DHBDA})(bpe)]_n$	acetonitrile	10 mmol	40℃/24 h	H_2O_2	82%	2
16	Cu^{2+}@COMOC-4	chloroform	61.3 mmol	40℃/7 h	O2（1atm）	49%	4
17	$[Mn(LH)(H_2O)]_n$	Acetone/ Methanol	1 mmol	0-26℃/24 h	H_2O_2	47%	2
18	Cu-MOF-74	acetonitrile	1 mmol	70℃/24 h	TBHP	90%	5
	Co-MOF-74	acetonitrile	1 mmol	70℃/24 h	TBHP	71.5%	5
	Mn-MOF-74	acetonitrile	1 mmol	70℃/24 h	TBHP	68.2%	5
	Ni-MOF-74	acetonitrile	1 mmol	70℃/24 h	TBHP	40%	5
	Zn-MOF-74	acetonitrile	1 mmol	70℃/24 h	TBHP	5%	5
19	$[Co(L\text{-}RR)(H_2O)\cdot H_2O]_\infty$	Cyclohexene	Neat	70℃/24 h	TBHP	18.6%	1
20	$[Cu_2(bipy)_2(btec)]_\infty$	n-decane	1 mmol	75℃/6 h	TBHP	55%	3
21	UiO-66-sal-MoD	acetonitrile	0.5 mmol	80℃/24 h	TBHP	70.3%	2
22	Mo-Sal-Amp-CuBTC	chloroform	8 mmol	61℃/1 h	TBHP	87%	1
23	Ti-UiO-66	acetonitrile	2 mmol	50-70℃/24 h	H_2O_2	26.8%	4
24	$Co_3(OH)_2(tpta)$	Cyclohexene	Neat	70℃/7 h	TBHP	73.6%	3
25	Ni-MOF-74	Cyclohexene	Neat	80℃/20 h	O2 balloon	37.2%	4
	Co/Ni-MOF-74-1	Cyclohexene	Neat	80℃/20 h	O2 balloon	39.2%	4
	Co/Ni-MOF-74-4	Cyclohexene	Neat	80℃/20 h	O2 balloon	54.7%	4
26	PW-MOF	acetonitrile	1 mmol	50℃/6 h	H_2O_2	80%	2
27	$[Co_3(pimdc)_2(H_2O)_6]\cdot 5H_2O$	Cyclohexene	Neat	70℃/20 h	TBHP	70.6%	3
28	CuLa-MOF	Cyclohexene	Neat	120℃/24 h	O2（5atm）	77%	3
29	$[Cu_2(PDA)_2(Ald)_2(H_2O)_2]\cdot 8H_2O$	1,2-dichloroethane	0.2 mmol	55℃/3 h	TBHP	65%	1
30	Mn-TPP@ZIF-8	acetonitrile	250 mmol	80℃/24 h	TBHP	96%	2
31	ZrP⊂HKUST-1	Cyclohexene	Neat	80℃/20 h	O2 balloon	59.5%	4
This work	**1**	Cyclohexene	Neat	80℃/12 h	TBHP	97.4%	2

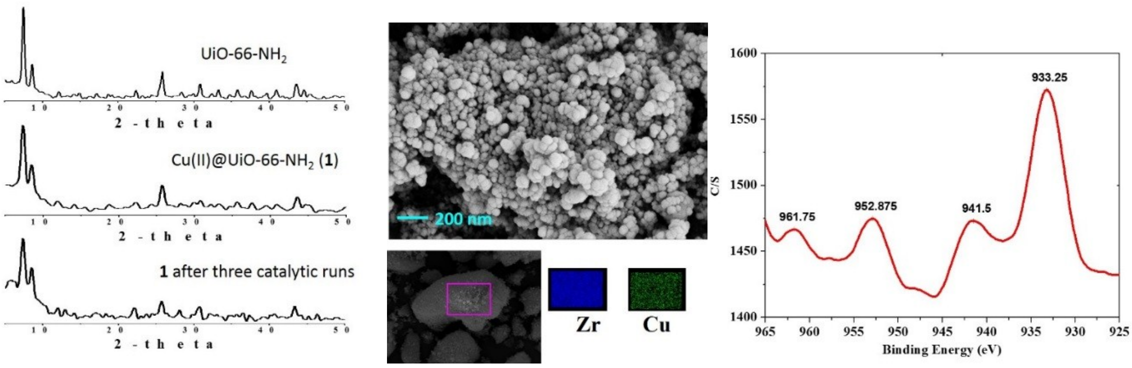


Fig. S4 Left: XRPD patterns of UiO-66-NH_2, **1** and **1** after three catalytic runs. Middle: SEM-EDS spectra of **1** after three catalytic runs. Right: XPS spectrum of **1** after three catalytic runs.

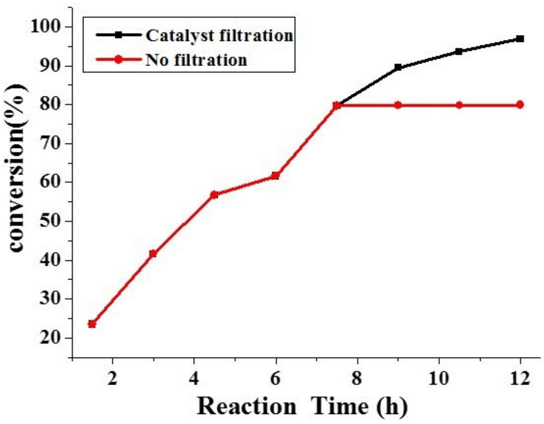
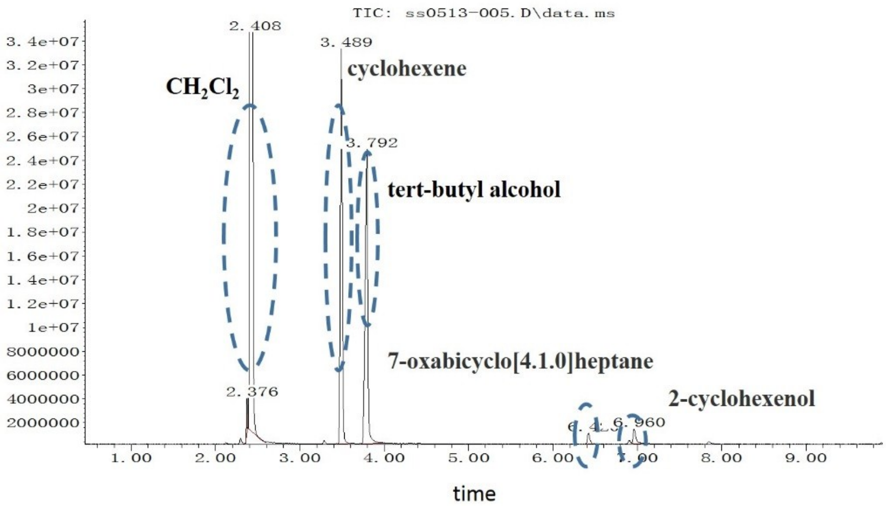


Fig. S5 Reaction time examination (black line) and leaching test (red line) for olefin oxidation catalyzed by **1**. The result demonstrated that **1** is responsible for the catalytic activity.

Table S5. ICP result for **1** after three catalytic runs

element	Zr 339.198	Zr 343.823	Zr 257.139	Zr 272.262	Cu 324.754	Cu 327.396	Cu 224.700
unit	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
average value	**81.8441**	**79.8368**	**78.1417**	**79.4977**	**10.83129**	**12.06824**	**9.85398**
sd	0.25922	0.08839	0.09539	0.18533	0.0632	0.07649	0.02176
rsd	0.317	0.111	0.122	0.233	0.772	0.914	0.302
min	0.00057	0.00003	0.00923	0.00757	0.00015	0.00036	0.0024
max	120	120	120	120	12	12	12

Based on above analysis, the leaching amount of copper in **1** after three catalytic runs is only 3.0 %.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3. 489
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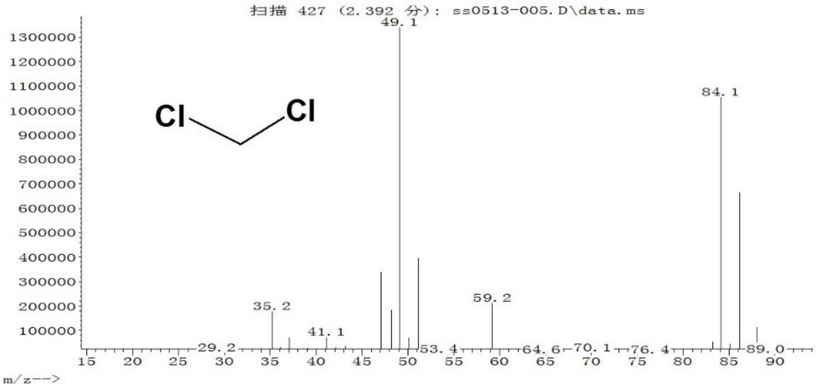
2. 376
2-cyclohexenol
6. 960
time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Cl
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59. 2
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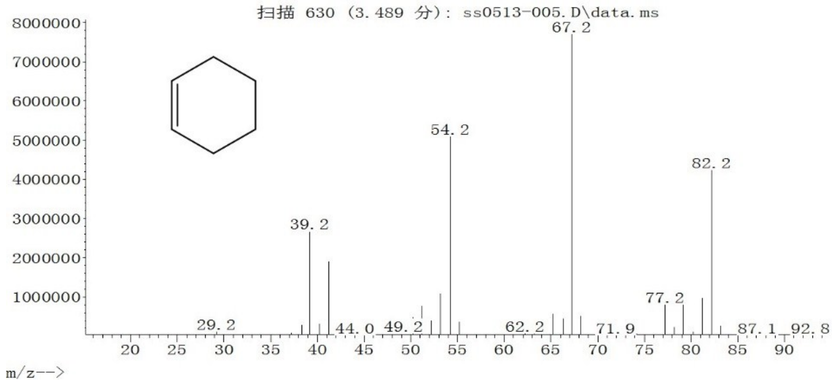
64. 6
70. 1
76. 4
89. 0
m/z-->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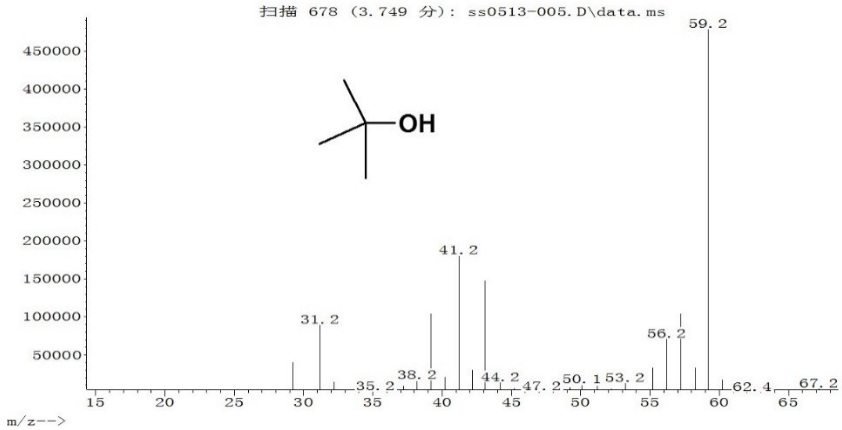
92. 8
m/z-->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62. 4
67. 2
m/z-->

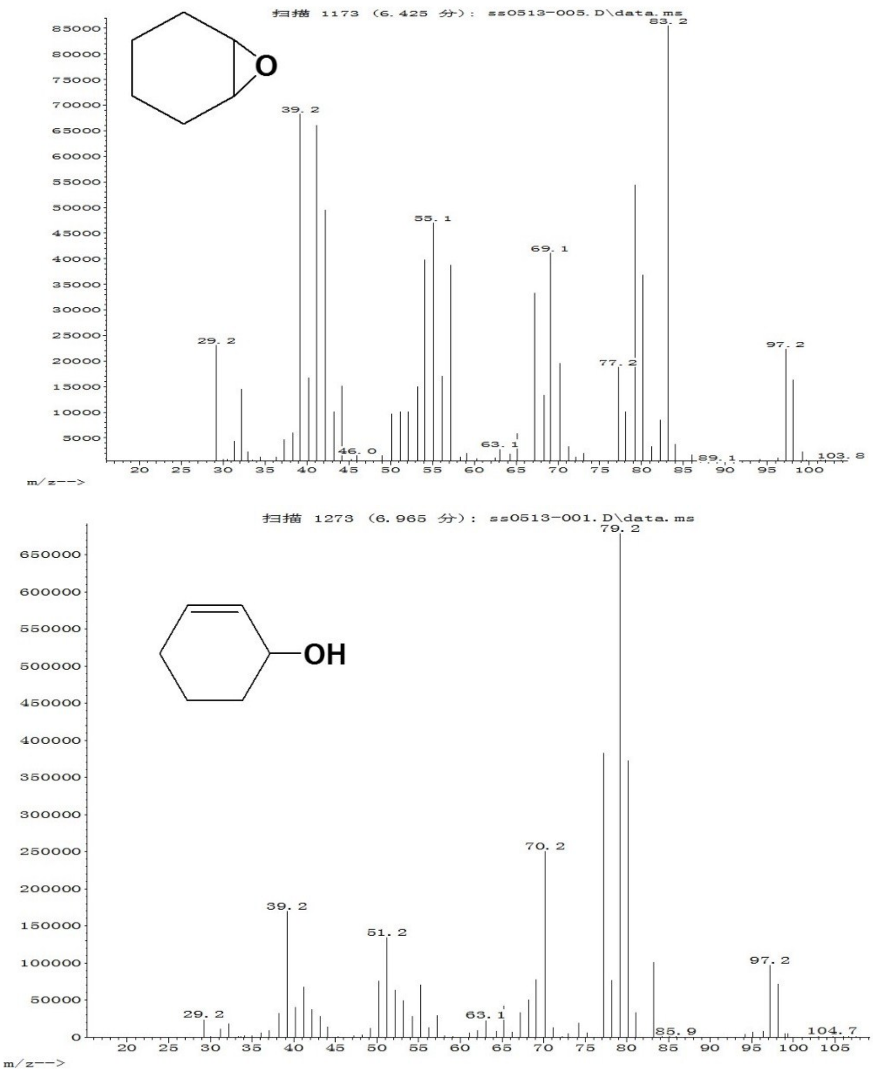
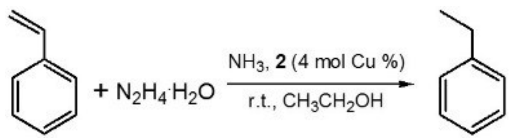


Fig. S6 GC-MS spectra of the cyclohexene oxidation catalyzed by UiO-66-NH_2, indicating that the encapsulated Cu(II) species is responsible for the catalytic activity.

4. Catalytic properties of 2



2 (10 mg, 4 % mmol) was added to a solution of styrene (0.14 mmol, 16 μL), $N_2H_4{\cdot}H_2O$ (80 wt %, 20 μL), $NH_3{\cdot}H_2O$ (18 wt %, 10 μL) was stirred at room temperature for 15 min (monitored by GC). After reaction, **2** was recovered by centrifugation and directly reused in next catalytic run.

Table S6. Styrene hydrogenation catalyzed by **2**.

entry	T (h)	conv. (%)[a]	select. (%)[a]	TOF [h^{-1}][b]
1	0.25	> 99	100	100
2	0.25	> 99	100	100
3	0.25	> 99	100	100
4	0.25	> 99	100	100
5	0.25	> 99	100	100

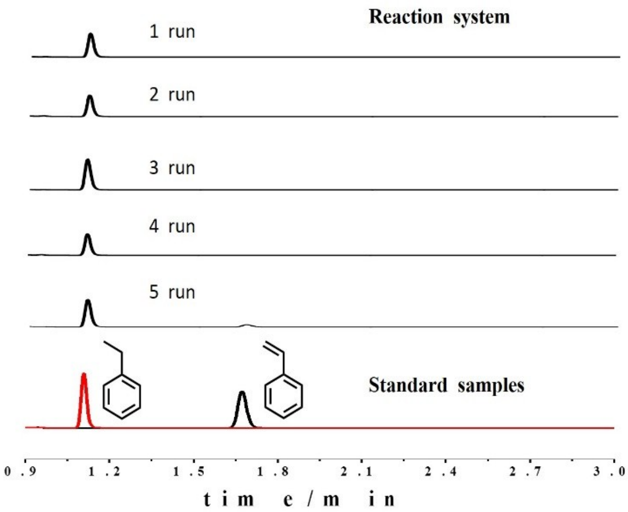


Fig. S7 GC spectra of the standard samples and reaction system (five catalytic runs).

Table S7. ICP result for **2** after five catalytic cycles

element	Zr 339.198	Zr 343.823	Zr 257.139	Zr 272.262	Cu 324.754	Cu 327.396	Cu 224.700
unit	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
average value	**56.0534**	**59.2143**	**53.1726**	**54.3494**	**6.24995**	**6.41018**	**5.45333**
sd	0.88636	0.9903	1.38961	1.23447	0.10667	0.07888	0.10408
rsd	1.581	1.672	2.613	2.271	1.707	1.231	1.909
min	0.00057	0.00003	0.00923	0.00757	0.00015	0.00036	0.0024
max	120	120	120	120	12	12	12

Based on above analysis, the leaching amount of copper in **2** after three catalytic runs is only 5.8 %.

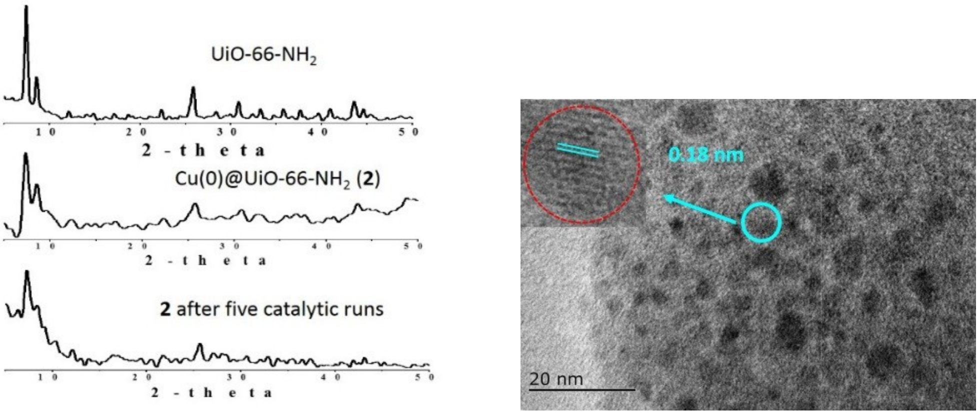


Fig. S8 Left: XRPD patterns of UiO-66-NH_2, **2** and **2** after five catalytic runs. Right: HR-TEM image of **2** after five catalytic runs.

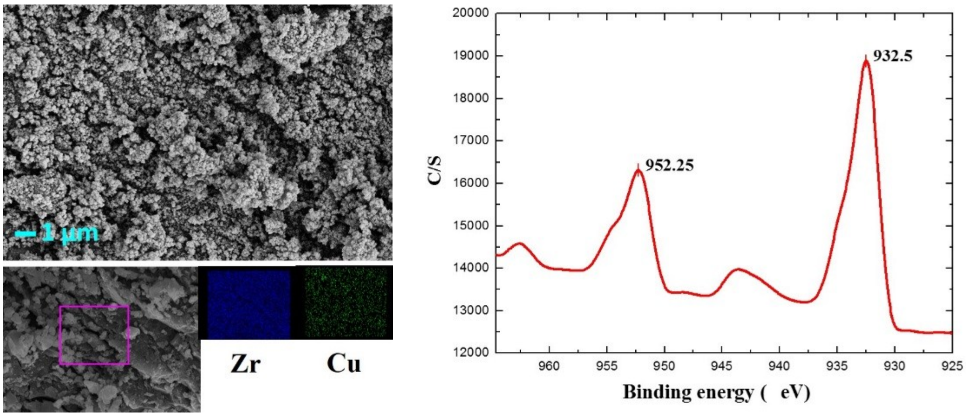


Fig. S9 Left: SEM-EDS spectra of **2** after five catalytic runs. Right: XPS spectrum of **2** after five catalytic runs.

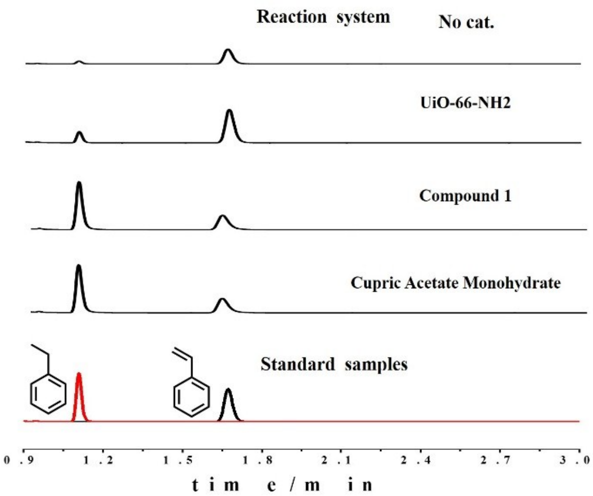


Fig. S10 GC spectra of styrene reduction catalysed by $Cu(OAc)_2$, UiO-66-NH_2 and **1** or without any catalyst under the same reaction conditions.

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