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Cu(I)-based Metal-organic Frameworks as Efficient and Recyclable Heterogeneous Catalysts for Aqueous-medium C-H Oxidation

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ABSTRACT: The enantioselective transformation of ubiquitous C−H bonds into valuable C=O bonds offers an efficient synthetic approach to construct carbonyl functionalized molecules. However, the grand obstacles in the reaction are the selectivity issues and side reactions under the harsh reaction conditions. In order to overcome the limits, two Cu(I)-based MOFs $\{(NEt_4)_{0.5}[Cu_3(TTPB)_{0.75}(CN)_{0.5}(H_2O)]•H_2O\}_n$ (**1**) and $\{[Cu_2(TTPB)_{0.5}]•DMF•2H_2O\}_n$ (**2**) were synthesized (H_4TTPB =5,5'-(4',5'-bis(4-(1*H*-tetrazol-5-yl)phenyl)-[1,1':2',1''-terphenyl]-4,4''-diyl) bis(1*H*-tetrazole)) under hydrothermal condition with (triethylamine (TEA) and ethyldiisopropylamine (DIPEA) as structure-directing agents, respectively. Of these, **1** shows an anionic three-dimensional (3D) framework composed of two kinds of cage-like micropores with 7 × 17 Å and 10 × 17 Å, respectively. In comparison, **2** exhibits 3D framework with open channels (14 × 8 Å). The stability studies showed that the crystallinity of **1** and **2** could remain in a series of organic solvents (ethanol, N,N-dimethylformamide, chloroform, dioxane, toluene), acid and alkali aqueous solutions (pH=1-13) at room temperature for 48 h. **1** and **2** with coordinatively unsaturated Cu(I) sites were applied as heterogeneous catalysts for the oxidation of arylacycloalkanes in aqueous medium and exhibited excellent catalytic activities, selectivities and recyclabilities. Moreover, free-radical reaction mechanism and reversible valence-tautomeric conversions of central copper were confirmed during the process by control experiment.

Introduction

Metal-organic frameworks (MOFs), a class of crystalline materials, which demonstrate ample structure types, tunable pores and intriguing functionalities, have attracted great research interests in numerous fields including catalysis, gas storage and separation, luminescence, chemical sensors, drug delivery[1-10]. In recent years, particular interesting has been paid to the application of MOFs as heterogeneous molecular catalysts and catalyst supports. Especially, due to their highly tunable platforms to construct molecule catalysts for plentiful chemical transformation, MOFs have been given much promise as single site catalysts to modulate size-, shape-, chem- and enantioselective reactions.[11,12] Compared with homogeneous catalysts, MOFs materials are easy to separate and recycle from the reaction mixture, offering particular environmental and sustainable advantages for the chemical transformation.[13,14] Besides, MOFs possess uniform pore sizes/environments and unparalleled surface areas in contrast to traditional heterogeneous catalysts, including zeolite, SiO_2, and activated carbon. More importantly, MOFs possess uniformly distributed catalytically active centers with identical microenvironments throughout the solid, which can achieve superior selectivity and reactivity to other catalytic systems.[15,16] In recently, our group has reported that some Cu(I) coordination polymers can be as green heterogeneous catalysts for direction C-H bond activation of arylalkanes to ketones and perform the reaction with high regioselectivity due to the unique spatial confinement effect.[17]

On the other hand, the oxidation of benzylic methylene groups usually aim to obtain products, such as cyclic ketones, esters and amides, which have been widely used to build blocks of dyes and other fine chemicals[18-20]. In the traditional methods, strong oxidizing agents (e.g., $KMnO_4$) usually require massive oxidants and multivalent transition metals (e.g., Cu, Fe, V, Ru) are irreversible conversions of central metal valence, resulting in a large amount of waste.[21-23] Therefore, to ameliorate these defects, catalytically active metal-organic frameworks (MOFs) may represent a feasible platform to as single-site heterogeneous catalysts, achieving excellent activity of arylacycloalkanes oxidation with satisfied selectivity to ketone.

In this work, two Cu(I)-based MOFs $\{(NEt_4)_{0.5}[Cu_3(TTPB)_{0.75}(CN)_{0.5}(H_2O)]\cdot H_2O\}_n$ (**1**) and $\{[Cu_2(TTPB)_{0.5}]\cdot DMF\cdot 2H_2O\}_n$ (**2**) (H_4TTPB=5,5'-(4',5'-bis(4-(1*H*-tetrazol-5-yl) phenyl) -[1,1':2',1"-terphenyl]-4,4"-diyl)bis(1*H*-tetrazole)) were successfully synthesized with different structure-directing agents (TEA and DIPEA). The stability experiments showed that the frameworks of **1** and **2** could remain in a series of organic solvents, acidic and basic solution. We also demonstrated that **1** and **2** can serve as promising heterogeneous catalysts toward C=O bond formation in the oxidation of arylacycloalkanes in aqueous medium.

Experimental section

Materials and Physical Measurements. All reagents and solvents were purchased from J&K Chemicals and used without any purification. NMR spectroscopy was recorded on 400 MHz Bruker Avance-400 spectrometer and the chemical shift was reported relative to the signals of an internal standard of TMS (0.0 ppm). Powder X-ray diffraction (PXRD) data was recorded on a Bruker D8 Advance X-ray diffractometer using Cu Kα (λ = 1.5418 Å) radiation. The thermal decomposition characteristic of the samples was analyzed by TGA ranging from 30 to 800 °C by using Netzsch STA 449C thermal analyzer. An Elementar Vario MICRO Elemental analyzer was performed to the elemental analyses (C, H, N). X-ray photoelectron spectroscopy was conducted on an AXIS Supra Quantera microprobe. FT-IR spectroscopy was recorded on a Bruker Vector 22 spectrophotometer with KBr pellets.

Synthesis of 5,5'-(4',5'-bis(4-(1*H*-tetrazol-5-yl)phenyl)-[1,1':2',1''-terphenyl]-4,4''-diyl)bis (1*H*-tetrazole) (H_4TTPB)[24,25]. A mixture of sodium azide (1.56 g, 23 mmol), 1,2,4,5-tetrakis(4-cyanophenyl)benzene (0.39 g, 0.8 mmol) and triethylamine hydrochloride (4.80 g, 19.6 mmol) in 10 mL of toluene/methanol (ratio 2/1) was stirred under reflux at 110 °C for three days. After cooling to room temperature, 1 M NaOH aqueous solution (15 mL) was added into the mixture. The mixture (colorless clear solution) was stirred for 0.5 h at room temperature. 15 mL 1 M HCl aqueous solution was added into the mixture till the pH value was about 1. Then white precipitate was collected by filtration and washed with water and ethanol, dried at room temperature. Yield: 0.5 g (95%). ^{1}H NMR (400 MHz, DMSO), δ [ppm]: 8.06 (d, J = 8 Hz, 8H), 7.69 (s, 2H), 7.56 (d, J = 8 Hz, 8H). ^{13}C NMR (400 MHz, DMSO), δ [ppm]: 155.38, 143.09, 139.18, 132.62, 131.14, 127.41, 123.32.

Synthesis of $\{(NEt_4)_{0.5}[Cu_3(TTPB)_{0.75}(CN)_{0.5}(H_2O)]\bullet H_2O\}_n$ (1). A mixture of CuCN (0.018 g, 0.2 mmol) and H_4TTPB (0.027 g, 0.05 mmol) was dissolved in 8 mL of DMF/EtOH/$NH_3\bullet H_2O$/TEA (ratio 1/1/1/1) and then placed in a 25 mL Teflon-lined stainless steel container. The container was sealed and heated at 165°C for 3 days and then cooled to ambient temperature at a rate of 5 °C / h. The colorless crystals of **1** were isolated with a yield of 53% (based on CuCN). Elemental analysis calcd (%) for $C_{60}H_{55}Cu_6N_{26}O_4$: C, 46.07; H, 3.39; N, 23.29. Found: C, 46.02; H, 3.45; N, 23.17. IR (KBr, cm^{-1}): 3364.03 (m), 2099.47 (s), 1443.75 (m), 1007.54 (s), 842.91 (s), 708.49 (s).

Synthesis of $\{[Cu_2(TTPB)_{0.5}]\bullet DMF\bullet 2H_2O\}_n$ (2). A mixture of CuCN (0.018 g, 0.2 mmol) and H_4TTPB (0.027 g, 0.05 mmol) was dissolved in 8 mL of DMF/EtOH/$NH_3\bullet H_2O$/DIPEA (ratio 1/1/1/1) and then placed in a 25 mL Teflon-lined stainless steel container. The container was sealed and heated at 165 °C for 3 days and then cooled to ambient temperature at a rate of 5 °C / h. The colorless crystals of **2** were isolated with a yield of 43% (based on CuCN). Elemental analysis calcd (%) for $C_{17}H_9Cu_2N_8$: C, 42.87; H, 3.57; N, 22.51. Found: C, 42.77; H, 3.49; N, 22.68. IR (KBr, cm^{-1}): 3441.56 (m), 1440.03 (s), 1443.75 (m), 1005.97 (s), 837.98 (s), 759.77 (s).

Typical Procedure for C-H bond activation of arylacycloalkane to ketones. A mixture of arylacycloalkane (1 mmol), tert-butyl hydroperoxide (TBHP) (1.5 mmol) and catalyst (0.05 mmol) in H_2O (2 mL) was ultrasound at room temperature for 4 or 6 h in the air. After reaction finished, catalyst was recycled by centrifugation. The residue was extracted with ethyl acetate and H_2O. The organic phases were combined, dried by anhydrous Na_2SO_4 and concentrated in vacuo. The crude product was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (5/1, v/v) as eluent to afford product. The ^{1}H NMR data of pure products were consistent with previous literature report (see Figure S4).[26,27]

Crystal Data Collection and Refinement. The data of **1** and **2** were collected on a Bruker APEX-III CCD diffractometer at room temperature using Mo Kα radiation (λ = 0.71073 Å). The two structures were resolved and refined using the SHELX-97 software[28,29]. All non-H atoms were refined with anisotropic thermal parameters and the H atoms of carbon or nitrogen molecules were located in geometrically constrained positions and refined by riding. While those that from coordinated water molecules and lattice water molecules could not be determined. Crystal data were listed in Table S1 and in Table S2. Crystallographic data were deposited in the Cambridge Structural Date Centre (CCDC), and can be obtained free of charge at http://www.ccdc.cam.ac.uk/ by using reference numbers 1858008 and 1858009.

Results and discussion

Crystal structure of $\{(NEt_4)_{0.5}[Cu_3(TTPB)_{0.75}(CN)_{0.5}(H_2O)]\bullet H_2O\}_n$ (1). Single-crystal diffraction data indicates that **1** is in orthorhombic space group *Cmca* and an anionic, porous 3D framework with free $[NEt_4]^+$ ions encapsulated inside the cavity (Figure. S1a). The asymmetric unit contains three crystallographically independent Cu(I) cations, three quarters $TTPB^{4-}$, half cyanide and half tetraethylammonium cation. Cu1 is coordinated by three N atoms from three TTPB4- ligands forming triangle geometry. Cu2 is surrounded by three tetrazole N atoms and one N(C) atom from cyanide, presenting slightly distorted tetrahedron geometries. Cu3 lies in distorted triangle geometry with two tetrazole N atoms from different $TTPB^{4-}$ ligands and one oxygen atom from water molecule.

A particular feature of **1** is that the framework is constructed by octahedral cages (see Figure 1a). The central benzene ring and the nods reside at each vertex of the octahedron. Two distorted quadrangular windows of cage are estimated as 7 × 17 Å and 10 × 17Å, respectively. Each ($Cu_6(CN)(H_2O)_2$) nods can link seven $TTPB^{4-}$ ligands and the orientation of adjacent nods in the same chain or interlink chain are packed in an ABAB arrangement (see Figure S1c). Such multiple copper chains and quadrangular organic ligands can expand to generate a fascinating 3D network (see Figure 1b). The XPS analysis showed that the binding energy (BE) was corrected for surface charging by setting the Cu $2p_{3/2}$ peaks to 929 eV, which could verify the purity monovalence of central copper in the samples (see Figure 1d).[30-32] Overall, the framework of **1** is anionic and is filled with $[NEt_4]^+$ ions. Given the charge-balance consideration, there should be a half $[NEt_4]^+$ ion per formula unit. The quaternary ammonium type cation is formed by tertiary amine and alcohol in alkaline conditions. [33,]

(**Figure 1** here)

Crystal structure of $\{[Cu_2(TTPB)_{0.5}]\cdot DMF\cdot 2H_2O\}_n$ (2). According to the single crystal data analysis, **2** crystallizes in triclinic space group *P-1*, contains two types of one-dimensional channels. An asymmetric unit contains two Cu(I) ions and a half $TTPB^{4-}$ (see Figure S1b). The two Cu (Cu1 and Cu2) ions are all coordinated by three tetrazole N atoms and site in the center of triangle geometry. The Cu-N bond lengths are 1.96-2.10 Å, which are matched well with other Cu(I) complexes.[34,35]

In **2**, the ligand H_4TTPB molecule is completely deprotonated and the dihedral angle of the central benzene ring with adjacent benzene rings are 75.243° and 51.364°. All the tetrazole rings adopt the same coordination mode to bridge three Cu(I) ions, forming a tetrazole-Cu-tetrazole-Cu chain (see Figure 2a). Furthermore, such chains can be expanded to construct a 3D pore space framework (see Figure 2b) with the channels 14 × 8 Å (see Figure 2c). Similarly, the monovalence of central copper of **2** was demonstrated by XPS patterns[30-32] (see Figure 2d).

(Figure 2 here**)**

Analysis of stability of 1 and 2. The thermal stabilities of **1** and **2** were performed by thermogravimetric analysis (TGA). The TG curve (Figure S2) showed that an initial weight loss for **1** could correspond to loss of coordinated water molecules, lattice solvents ranging from room temperature to 300 °C (found, 12.81%; cald, 12.74%); from 300 to 450 °C, the following step weight loss was ascribed to the decomposition of the framework. Thermogravimetry(TG) data (Figure S2) for **2** indicated that an initial weight loss could correspond to loss of lattice water molecule and DMF molecule ranging from room temperature to 320 °C (found, 24.34%; cald, 24.11 %), above 320 °C, an sharp weight loss appeared, which was attributed to the collapse of 3D framework.

The acid-base and organic solvent resistance of **1** and **2** were carefully tested by suspending samples in different solvents (ethanol, N,N-dimethylformamide, chloroform, dioxane, toluene) and various gradient pH aqueous solution (pH = 1-13) at room temperature for 48 h. The structural integrities were characterized by PXRD (Figure 3).[36,37] The results indicated the most characteristic peaks of **1** and **2** maintained nearly the same positions when soaked in a sequence of solvents, and a wide pH range of 1 to 13. It suggested that **1** and **2** were chemically stable with the acid-base and solvent resistance. The acid-base and solvent resistance properties of them can be attributed to rigidity of the linker and stronger metal-linker bond. The rigid $TTPB^{4-}$ linker containing multiple metal-binding sites would form coordination bonds with copper ions, resulting in stable architectures. In addition, electron-rich nitrogen with orbital-contained metal can form multiple bond, coordination bond and d-p π-back bond, which could enhance interactions between coppers and tetrazole.[38] Besides, $TTPB^{4-}$ linker (soft base) and Cu(I) (soft acid) are in line with soft/hard acid/base concept, which could construct more stable metal-organic framework with strong metal-ligand bonds.[39]

(Figure 3 here**)**

Cu-MOFs (1 and 2) catalyzed oxidation of arylacycloalkane. Although oxidation of arylacycloalkane has been studied for many years, it remains an enormous challenge on how to design stable catalysts that can sustain in the harsh reaction conditions (e.g. TBHP, H_2O_2) and resolve selectivity issues.

To acquire optimization of the reaction conditions for **1** and **2** as heterogeneous catalysts in the arylacycloalkane oxidation reaction, we discussed the effects of reaction atmosphere. As shown in Table 1, in presence of **1** and **2**, the desired products was obtained with over 90 % yield under the atmosphere O_2 or air, while only 10 % yield within the atmosphere of N_2 was acquired at the same reaction conditions. These results illustrated that O_2 or air was one of the main factors affecting the process. In addition, there were no significantly improvements when the amount of catalysts was over 5 %.

(**Table 1** here)

To expand the scope of catalysts **1** and **2** for C-H bond oxidation, six substrates (cyclanes and heterocyclic alkanes) were transformed to ketone under the optimized conditions (Table 2). It is obvious that **1** and **2** displayed excellent catalytic performance for different substrates. The performance of **1** and **2** are similar, **1** as representative was discussed. When tetrahydronaphthalene was replaced by isochroman and o-xylylene oxide, the yield of the target products were all over 90% and the ring size of cyclanes/heterocyclic alkanes can′t affect the occurrence of oxidation reaction (Table 2, entry 1, 3, 4). Due to highly reactivity, the transformation of isochroman could finish in 4 h with 93 % yield. While tetrahydronaphthalene and o-xylylene oxide were employed as the substrates, the corresponding ketones were obtained with 78 % and 80 % yields, respectively in 4 h and the conversion could attain over 90 % after 6h (Table 2, entry 3, 5). As shown in Table 2, (entry 9, 11), 9,10-dihydroacridine gave a higher yield (up to 99 %) than the other substrates. While 9,10-dihydroanthracene as reactant gave the product, anthracen-9(10H)-one, slightly lower than other substrate due to the generation of almost 10% anthracene-9,10-dione. This phenomenon showed that electron-donating group played an important role, which makes oxidation reaction more easily.

(**Table 2** here)

The good catalytic performance can be attributed to their specialized structures, which can be ascribed to the following four reasons: (i) metal centers in **1** and **2** were unsaturated and these sites can well catalyze synthesis of products, (ii) the channels of **1** are 7 ×17 Å and 10 × 17Å, and the channel of **2** is 14 × 8 Å, which are large enough for various substrate to transform into the desired product, (iii) the ($Cu_6(CN)(H_2O)$) nods in **1** and the copper chains in **2** provide high density of copper sites as active centers to promote the oxidation of C-H bond of substrates to synthesize oxidation products, (iv) there's a long distance between adjacent active centers in the channels, which ensure the active sites as single catalytic sites to synthesize mono-oxidation products without synergistic interactions.[40-43]

The valence variation of active site was supervised by XPS (See Figure S3) during the reaction process. Before the catalytic process, the binding energy (BE) peak of Cu $2p_{3/2}$ was at 929 eV, which was assigned to Cu(I) in **1** and **2**. After 1 h reaction, the BE peaks were at 929 eV and 931eV, the higher BE peak at 931 eV was assigned to Cu(II), accompanied by the characteristic Cu(II) satellite peaks (942 eV). After catalysis, the characteristic Cu(II) peak disappeared that only 929 eV peak was found. The results indicated that there was a reversible oxidation/reduction transformation of central metal ions. On the basis of above experimental results, we proposed plausible mechanism for the benzo-cyclanes into cyclanone as shown in Figure 4. Firstly, the Cu(I)-based MOFs were activated by oxygen to generate Cu(II) and tert-butyl alcohol peroxide was used to generate free radical t-BuO•. Secondly, the t-BuO• radicals reacted with benzo-cyclanes to generate carbon-centered radicals. Lastly, carbon-centered radicals were converted to desired products and the Cu(II) turned back to Cu(I).[44-46] To verify the generation of free radicals, we used tetrahydronaphthalene as substrate and butylated hydroxytoluene (BHT) as radical-trapping reagent in the reaction. As we expected, only the 5 % yield was given, which was much lower than entry 1 (Table 1). This result demonstrated that free radicals must be generated in this oxidation system.[47-49]

(Figure 4 here**)**

To confirm heterogeneous property of **1** and **2**, the leaching of copper of **1** and **2** during the oxidation reaction were examined by atomic absorption spectroscopy analysis, and slight leaching (<1 ppm) were presented. Then filtering test was performed by removing the solid catalysts after 1 h and the filtrate were continued reaction for another 4 h. It was noticed that the yield of the supernatant remained nearly unchanged in next 4 h. Therefore, these results unambiguously demonstrated that **1** and **2** were heterogeneous catalysts.

The stabilities and reusabilities of heterogeneous catalysts are key parameters for practical use. The recycle experiments for **1** and **2** indicated there was no significant decline of activity and selectivity for the oxidation reaction after five cycles (Figures 5b and 5d). The PXRD patterns of the catalysts after cycling demonstrated that the structural integrity and crystallinity of **1** and **2** were maintained well (Figures 5a and 5c), suggesting their excellent activities and recyclabilities under catalytic conditions.

(Figure 5 here**)**

Conclusions

In summary, we successfully synthesized two stable Cu(I)-based MOFs materials condition with different amines as template agents. Such MOFs materials with unsaturated metal sites were used as heterogeneous catalysts for C-H activation in aqueous medium and **1** and **2** showed highly catalytic activity and selectivity. More importantly, these MOFs can be easily reused several times without loss of obvious catalytic efficiency advantages. The excellent catalytic activity and good chemical stability prove **1** and **2** to be efficient catalyst for the formation C=O bond.

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.cgd.xxxxxxx.

Crystallographic parameters, structure figures, TGA plots and XPS pattern. (PDF)

Crystallographic data for **1** and **2** in CIF format (CIF)

Accession Code

CCDC 1858008 and 1858009 contain the supplementary crystallographic data for this paper. This data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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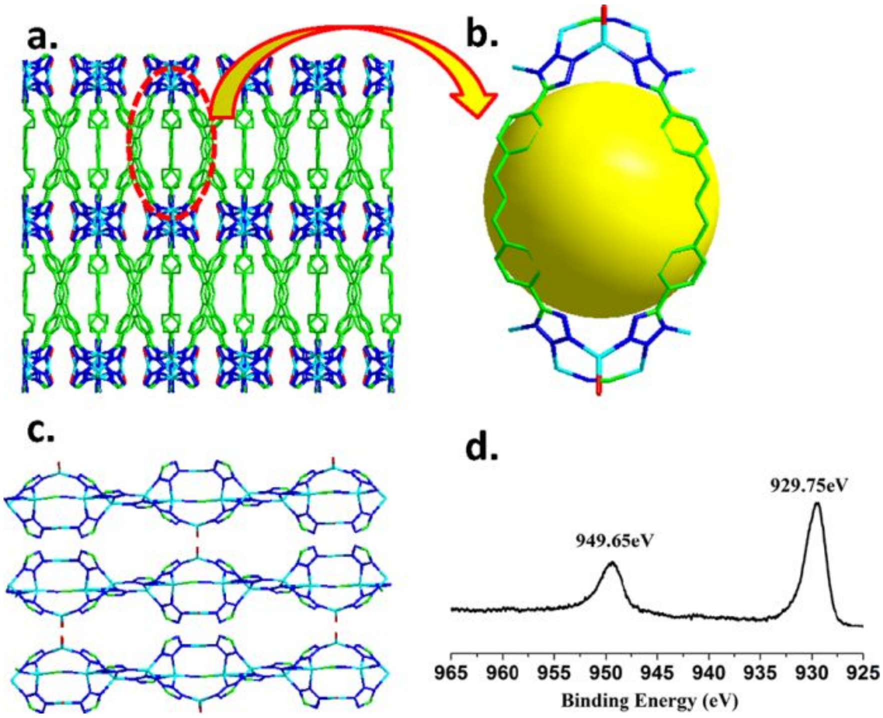


Figure 1. Crystal structure of **1** (a) 3D cage framework along a-axis. (b) The detail of cage structure. (c) Copper chain in 1 (d) Cu $2p_{3/2}$ XP spectra of **1**. The solvent molecules and all hydrogen atoms are omitted for clarity (C, green; N, dark blue; O, red; Cu, light blue).

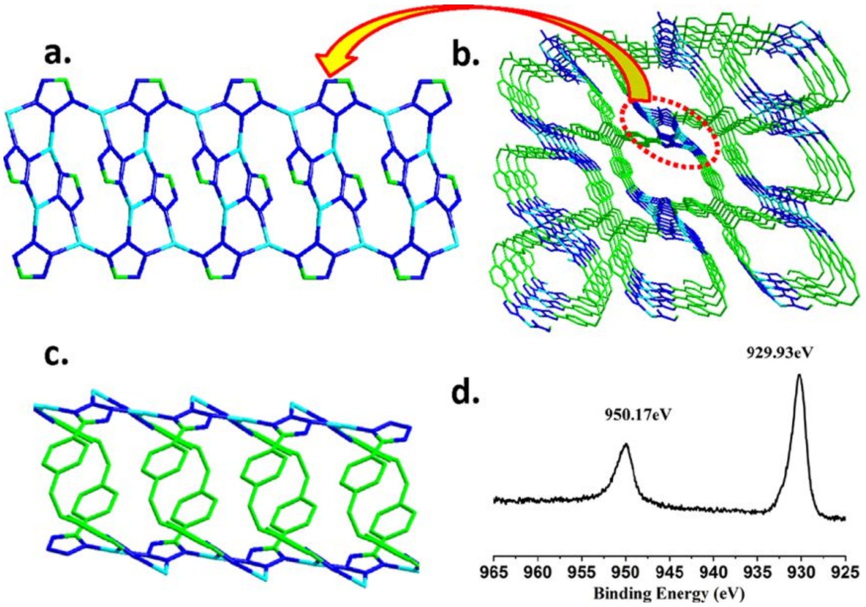


Figure 2. Crystal structure of MOF **2** (a) The detail of copper chain. (b) 3D pore space framework along a-axis. (c) The detail of channel structure. (d) Cu $2p_{3/2}$ XP spectra of **2**. The solvent molecules and all hydrogen atoms are omitted for clarity (C, green; N, dark blue; O, red; Cu, light blue).

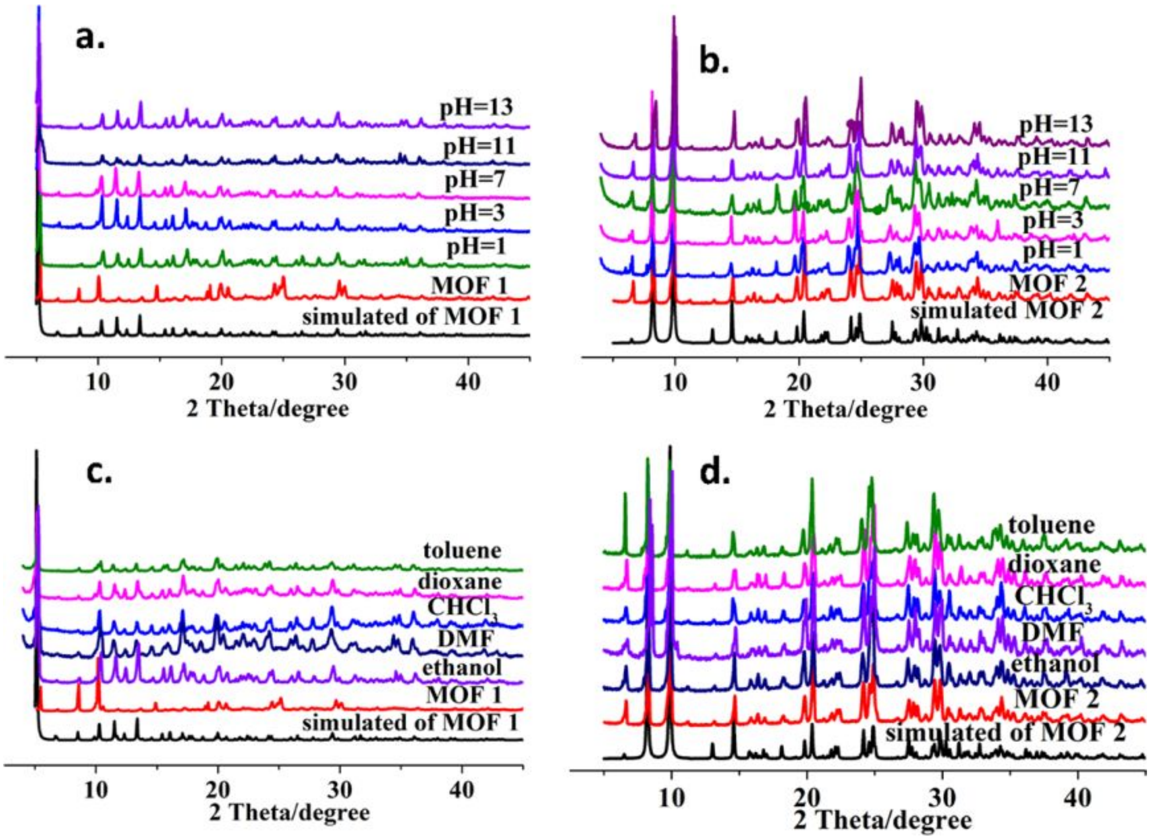
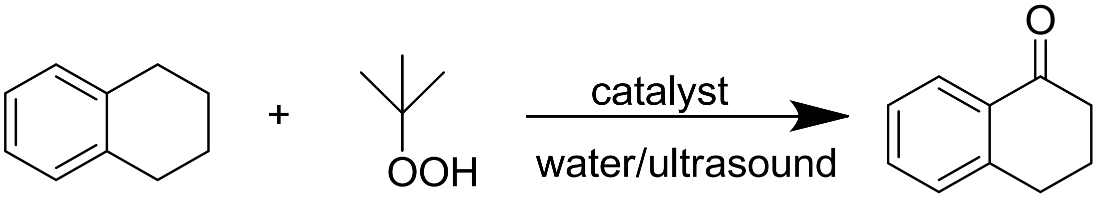
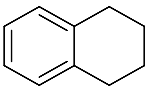
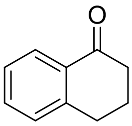


Figure 3. PXRD of MOF **1** in (a) a wide pH ranged of aqueous solutions. (b) a series of organic solvents. PXRD of MOF **2** (c) in a wide pH ranged of aqueous solutions and (d) a series of solvents

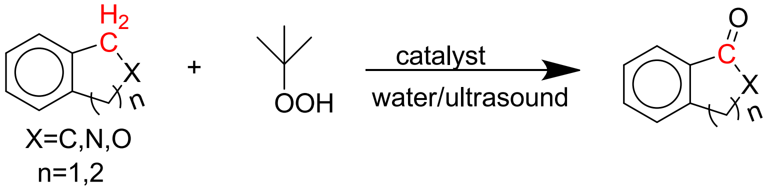
Table 1. Reaction of tetrahydronaphthalene with tert-butyl hydroperoxide(TBHP) in the presence of Cu(I)-MOFs: effect of reaction atmosphere.

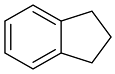
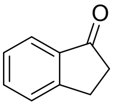
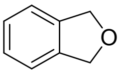
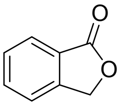
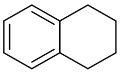
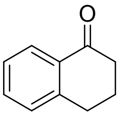
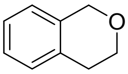
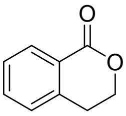
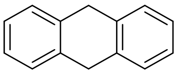
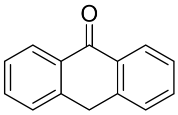
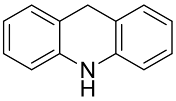
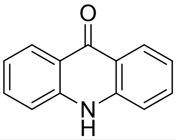


entry	catalyst	atmosphere	substrate	product	yield%
1	**1**	N_2			<10
2	**2**				<10
3	**1**	Air			$80^a.92^b$
4	**2**				$86^a,95^b$
5	**1**	O_2			$81^a,90^b$
6	**2**				$88^a,96^b$

[a]Reagents and conditions: tetrahydronaphthalene (1.0 mmol), TBHP (1.5 mmol), catalyst (0.05 mmol), H_2O (2 mL), ultrasound, room temperature, 4h, [b]6h

Table 2. Oxidation of arylacycloalkane catalyzed by Cu(I)-based MOFs



entry	catalyst	substrate	product	Yield%
1	**1**			92
2	**2**			97
3	**1**			78[a],93[b]
4	**2**			83[a],97[b]
5	**1**			80[a],92[b]
6	**2**			86[a],95[b]
7	**1**			93
8	**2**			98
9	**1**			85
10	**2**			87
11	**1**			95
12	**2**			99

[a] Reagents and conditions: substrate (1.0mmol), TBHP (1.5mmol), catalyst (0.05mmol), H_2O (2mL), ultrasound, room temperature, air atmosphere, 4h ,[b]6h.

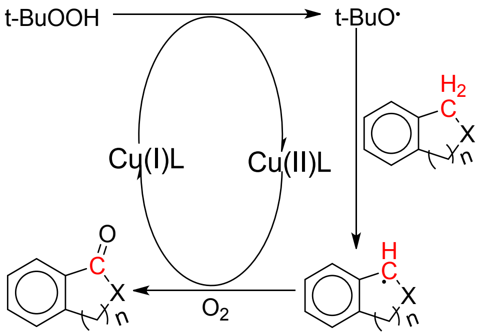


Figure 4. Proposed mechanism for the oxidation reaction

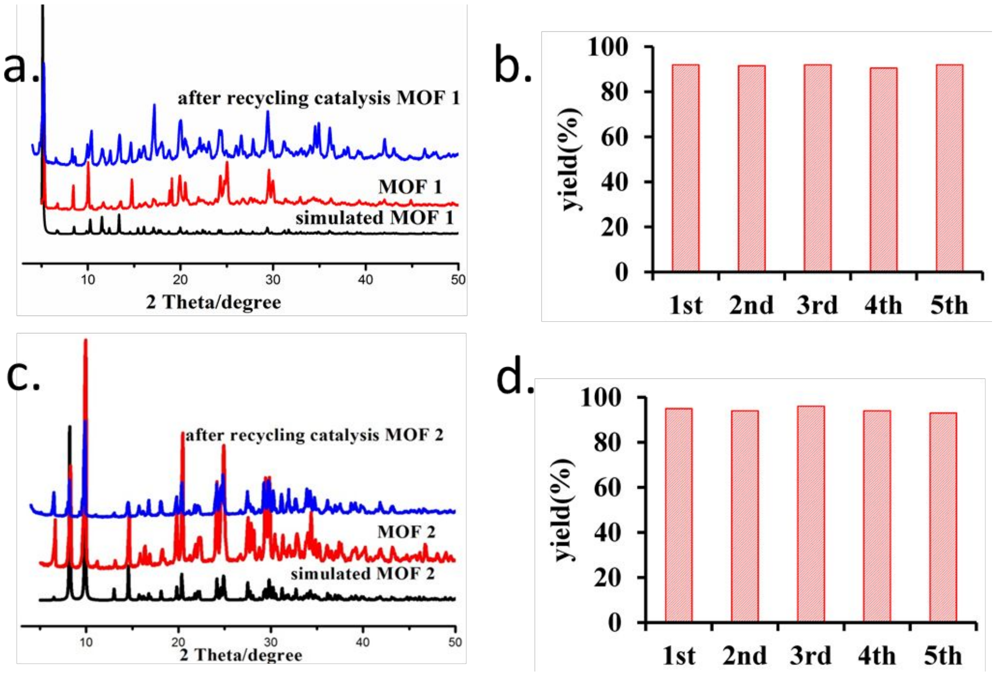


Figure 5. (a) Comparison of the PXRD patterns of **1** before and after catalysis. (b) Recycling test for oxidation catalyzed by **1**. (c) Comparison of the PXRD patterns of **2** before and after catalysis. (d) Recycling test for oxidation catalyzed by **2.**

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Cu(I)-based Metal-organic Frameworks as Efficient and Recyclable Heterogeneous Catalysts for Aqueous-medium C-H Oxidation

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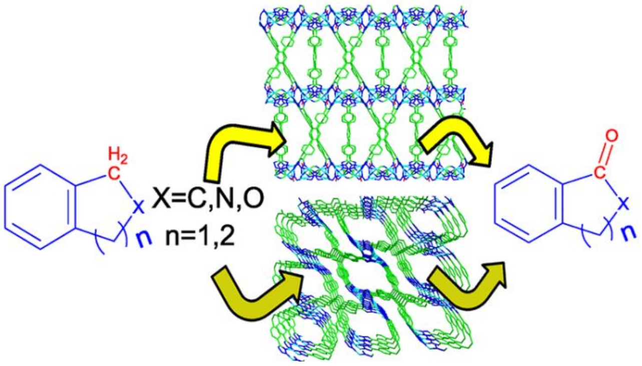

Two Cu(I)-MOFs were synthesized and employed as heterogeneous catalysts to selectively catalyze oxidation of C-H. Excellent catalytic activity and good stability give the two MOFs great potential for practical use in heterogeneous catalysis.