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## Suspending ionic single-atom catalysts in porphyrinic frameworks for highly efficient aerobic oxidation at room temperature

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#### ABSTRACT

Room temperature and atmosphere pressure are highly desired catalytic conditions for aerobic oxidation of inert  $sp^3$  C—H bonds. To meet this challenge, we developed a simple strategy by suspending ionic single atoms (ISAs) inside the anionic pores of metal–organic frameworks (MOFs). CZJ-22-Cu, consisting of suspended ISA copper(II) inside the anionic pores, exhibits exceptionally high catalytic efficiency in aerobic oxidation of ethers to esters at room temperature and atmosphere pressure, in which turnover number (TON) 77,100 and turnover frequency (TOF) 7710 h<sup>-1</sup> have been realized for aerobic oxidation of isobenzofuran. The unmatched catalytic properties of CZJ-22-Cu are attributed to the unique features of suspended ISAs inside the anionic pores, which result in high surface free energy of redox-active centers, and the substrate-selective accumulation nature of the inside pores, which would significantly improve the reactivity and reaction rate.

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#### 1. Introduction

Catalysts, which can alter chemical reaction paths, are cornerstones in the chemical industry. Single-atom catalysts (SACs) are an emerging class of heterogeneous catalysts in which active metals, such as Pt, Ir, Rh, Pd, Au, and Ag atoms, are atomically dispersed onto solid surfaces [1,2]. Due to high metal atom usage and high surface free energy of active centers, SACs demonstrate superior catalytic properties in many chemical reactions [3–12]. To prevent single-atom mobility and sinter under realistic reaction conditions, SACs are fixed onto solid surfaces by strong interactions. This technique inevitably results in part of coordination sites being inaccessible to reactant molecules, which would compromise their catalytic efficiency. Additionally, low surface areas of nonporous solid supports would result in low loadings of active atoms and low spatial utility.

Metal-organic frameworks (MOFs) are an emerging class of porous materials with tunable framework structures and properties [13–15]. MOFs with high porosity, high surface areas, and tunable hydrophobic and hydrophilic pore nature have been targeted as a tunable class of crystalline porous supports for single-site catalysts by in situ synthesis or postmodification [16–21]. However, ligation

\* Corresponding author. E-mail address: cdwu@zju.edu.cn (C.-D. Wu). of metal coordination sites by organic ligands and/or counterions would reduce the activity of valence electrons, and thus significantly affect their catalytic efficiency. The challenge is how to decrease the coordination saturability and increase the surface free energy of SACs inside porous MOFs.

There are many anionic MOFs, consisting of endogenous cations inside the pore space, that are systematically exchangeable to tune their properties by ion exchange, and thus to realize applications in different fields [22–27]. Anionic MOFs provide an opportunity to develop ionic single-atom catalysts (ISCAs) inside the anionic pores by eliminating the ligation of counterions. Sequestered by the anionic pores, most of the coordination sites of ISACs would be vacant, resulting in very high surface free energy. Moreover, confining ISACs in negatively charged pores would solve the leaching and aggregation issues. Here, we report an anionic porphyrinic framework, [(CH<sub>3</sub>)<sub>2</sub>NH<sub>2</sub>]<sub>2</sub>[Y<sub>2</sub>(Cu-OCPP)(H<sub>2</sub>O)<sub>4</sub>]·8DMF·22H<sub>2</sub>O (CZJ-22; Cu-H<sub>8</sub>OCPP = Cu<sup>II</sup>-5,10,15,20-tetrakis(3,5-biscarboxylphenyl)p orphyrin), consisting of endogenous [(CH<sub>3</sub>)<sub>2</sub>NH<sub>2</sub>]<sup>+</sup> cations that are systematically exchangeable with redox-active metal ions to tune the catalytic properties. The copper (II)-encapsulated material Cu [Y<sub>2</sub>(Cu-OCPP)(H<sub>2</sub>O)<sub>4</sub>]·10DMF·18H<sub>2</sub>O (CZJ-22-Cu), consisting of suspended ionic single-atom (ISA) Cu<sup>II</sup> inside the anionic pores, demonstrates exceptionally high catalytic activity in aerobic oxidation of ethers to esters at room temperature and atmosphere pressure.





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#### 2. Experimental

#### 2.1. Materials and methods

All of the chemicals were obtained from commercial sources and were used without further purification, except that 5,10,15,2 0-tetrakis(3,5-biscarboxylphenyl)porphyrin was prepared according to the literature [28,29]. FT-IR spectra were collected from KBr pellets on an FTS-40 spectrophotometer. Thermogravimetric analyses (TGA) were carried out under N<sub>2</sub> on a NETZSCH STA 409PC/PG instrument at a heating rate of 10 °C min<sup>-1</sup>. Elemental analyses were performed on a ThermoFinnigan Flash EA 1112 element analyzer. GC-MS spectra were recorded on a SHIMADZU GCMS-QP2010. Powder X-ray diffraction (PXRD) data were recorded on a RIGAKU D/MAX 2550/PC for Cu K $\alpha$  radiation ( $\lambda$  = 1. 5406 Å). A Micromeritics ASAP 2020 surface area analyzer was used to measure N2 gas adsorption/desorption isotherms. Inductively coupled plasma mass spectrometry (ICP-MS) was performed on an X-Series II instrument. X-ray photoelectron spectra (XPS) were recorded on a VG ESCALAB MARK II machine. Transmission electron microscopy (TEM) with an energy-dispersive X-ray (EDX) detector was carried out on JEM 2100F equipment, and the samples were deposited onto ultrathin carbon films on carbon grids. Electron paramagnetic resonance (EPR) spectra were recorded on a Bruker ESRA-300 at room temperature.

#### 2.2. Synthesis of CZJ-22

Cu-H<sub>8</sub>OCPP (1 mg, 0.001 mmol) and Y(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O (100 mg, 0.26 mmol) were dissolved in a mixture of DMF (2 mL) and dilute HNO<sub>3</sub> (4 M, 0.5 mL). The mixture was sealed in a screw cap vial and heated at 80 °C for 1 week. Brown crystals of CZJ-22 were collected by filtration, washed with DMF, EtOH, and Et<sub>2</sub>O, and dried at room temperature. Yield: 83% (based on Cu-H<sub>8</sub>OCPP). Anal. calcd. for C<sub>80</sub>H<sub>144</sub>CuN<sub>14</sub>O<sub>50</sub>Y<sub>2</sub> (%): C, 41.00; H, 6.19; N, 8.37; Cu, 2.71; Y, 7.59. Found: C, 41.03; H, 5.97; N, 8.28; Cu, 2.39; Y, 7.71. FT-IR (KBr pellet, v/cm<sup>-1</sup>): 1692(w), 1610(s), 1547(s), 1437(s), 1371(s), 1251(w), 1148(w), 1114(w), 1080(w), 1008(m), 938(m), 781(m), 713(s), 614(w), 416(w).

#### 2.3. Synthesis of CZJ-22-Cu

Brown crystals of CZJ-22 (50 mg) were immersed in Cu(ClO<sub>4</sub>)<sub>2</sub> DMF solution (0.1 M, 2 mL) in a 5 mL screw cap vial and heated at 50 °C for 8 h. After the supernatant solution was decanted, the vial was refilled with fresh Cu(ClO<sub>4</sub>)<sub>2</sub> DMF solution. This procedure was repeated for 5 days. After cation exchange was completed, 2 mL MeOH was added to the vial to wash out excess Cu(ClO<sub>4</sub>)<sub>2</sub> in the solid sample for 3 days (3 times per day), and afforded CZJ-22-Cu as brown crystals. Anal. calcd. for  $C_{82}H_{136}Cu_2N_{14}O_{48}Y_2$  (%): C, 41.19; H, 5.73; N, 8.20; Cu, 5.32; Y, 7.44. Found: C, 40.37; H, 5.53; N, 8.36; Cu, 5.52; Y, 7.51. FT-IR (KBr pellet, v/cm<sup>-1</sup>): 1695(w), 1611(s), 1546(s), 1439(s), 1372(s), 1341(w), 1211(w), 1121(w), 1109(w), 1082(w), 1008(m), 939(m), 835(w), 780(m), 712(m), 623(w), 427(w).

#### 2.4. Synthesis of Zn-CZJ-22

The preparation procedure for Zn-CZJ-22 was the same as that for CZJ-22, except that Zn-H<sub>8</sub>OCPP was used instead of Cu-H<sub>8</sub>OCPP. Yield: 75% (based on Zn-H<sub>8</sub>OCPP). Anal. calcd. for C<sub>83</sub>H<sub>157</sub>N<sub>15</sub>O<sub>54</sub>Y<sub>2</sub>Zn (%): C, 40.32; H, 6.40; N, 8.50; Zn, 2.64; Y, 7.19. Found: C, 39.46; H, 6.19; N, 8.51; Zn, 2.38; Y, 7.09. FT-IR (KBr pellet, v/cm<sup>-1</sup>): 1697(m), 1605(s), 1547(s), 1433(s), 1374(s),

1231(w), 1208(w), 1149(w), 1112(w), 1074(m), 1002(m), 939(m), 920(w), 828(w), 778(m), 711(m), 686(s), 543(w), 416(w).

#### 2.5. Synthesis of Zn-CZJ-22-Cu

The preparation procedure for Zn-CZJ-22-Cu is the same as that for CZJ-22-Cu, except that Zn-CZJ-22 was used instead of CZJ-22. Anal. calcd. for  $C_{85}H_{145}N_{15}O_{50}Y_2ZnCu$  (%): C, 41.10; H, 5.88; N, 8.46; Cu, 2.56; Zn, 2.63; Y, 7.16. Found: C, 39.57; H, 5.65; N, 8.63; Cu, 2.43; Zn, 2.15; Y, 7.19. FT-IR (KBr pellet, v/cm<sup>-1</sup>): 1696(m), 1546(s), 1437(s), 1371(s), 1233(w), 1210(w), 1149(w), 1121(w), 1076(w), 1004(m), 939(m), 828(w), 796(w), 779(m), 713(m), 664(w), 623(w), 541(w), 421(w).

#### 2.6. X-ray crystallography

The determination of the unit cells and data collection for the crystals of CZJ-22, CZJ-22-Cu, and Zn-CZJ-22 were performed on an Oxford Xcalibur Gemini Ultra diffractometer with an Atlas detector. The data were collected using graphite-monochromatic enhanced ultra Cu radiation ( $\lambda$  = 1.54178 Å) at 293 K. The data sets were corrected by empirical absorption correction using spherical harmonics, implemented in the SCALE3 ABSPACK scaling algorithm [30]. The structures of all compounds were solved by direct methods and refined by full-matrix least-squares methods with the SHELX-97 program package [31]. Because the solvent molecules in these compounds are highly disordered, the SQUEEZE subroutine of the PLATON software suit was used to remove the scattering from the highly disordered guest molecules [32,33]. The resulting new files were used to further refine the structures. The H atoms on C atoms were generated geometrically. The X-ray crystallographic coordinates for structures reported in this paper have been deposited at the Cambridge Crystallographic Data Centre (CCDC) under deposition number CCDC 1569598-1569600. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data\_request/cif.

#### 2.7. A typical procedure for the aerobic oxidation of isobenzofuran

Isobenzofuran (0.3 mmol), CZJ-22-Cu (0.6  $\mu$ mol), and *N*-hydroxyphthalimide (NHPI) (0.015 mmol) in acetonitrile (2 mL) were stirred at room temperature (25 °C) under an atmosphere of oxygen (balloon) for 1 h. The solid was recovered by centrifugation and thoroughly washed several times with THF, CH<sub>3</sub>CN, and Et<sub>2</sub>O. The recovered solid was reused in the successive run. The identity of the product was determined by GC–MS and compared with that of the authentic samples analyzed under the same conditions, while the conversion of substrate, the yield, and the selectivity of product were obtained by GC analysis using a flame ionization detector (FID) with a capillary SE-54 column in the presence of an internal standard of naphthalene.

## 2.8. Study of the turnover numbers (TONs) for the aerobic oxidation of isobenzofuran catalyzed by CZI-22-Cu

Isobenzofuran (120 mmol), NHPI (1.2 mmol), and CZJ-22-Cu (1.5  $\mu$ mol) in acetonitrile (150 mL) were stirred at 25 °C under an atmosphere of oxygen (balloon) for 10 h. The solid catalyst was recovered by centrifugation and washed three times with acetonitrile. Aliquots were regularly taken out for GC analysis to determine the conversion of isobenzofuran, the yield of phthalide, and the turnover number (TON), which refers to mol of product per mol of catalyst.

#### 2.9. A typical procedure for substrate adsorption experiments

A sample of CZJ-22-Cu (5 mg) was treated under vacuum at 50 °C for 12 h. The activated sample was subsequently immersed in isobenzofuran (0.25 mL) at room temperature for 12 h and centrifuged. The recovered solid was thoroughly washed with ethyl ether to remove the surface-adsorbed molecules, which was subsequently submerged in CH<sub>3</sub>CN under stirring at room temperature for 18 h. The mixture was determined by analyzing an aliquot of



**Fig. 1.** (a) Ball-and-stick and polyhedron representations of the anionic framework of CZJ-22 viewed down the *b* axis. (b) A fragment structure of CZJ-22, highlighting the substrate-accessible nanocage. Color scheme: Y, green polyhedra; Cu, cyan; O, red; N, blue; C, deep gray; H, light gray. (c) Top view of the nanocage in CZJ-22-Cu (the top porphyrin was omitted for clarity), highlighting the porphyrin copper (cyan balls) and suspended ISA copper (violet balls) on the pore surfaces.

the bulk solution using GC in the presence of triphenylmethane as an internal standard and compared with the authentic sample analyzed under the same conditions.

# 2.10. A typical procedure for studying the chemical species adsorbed inside the pores of CZJ-22-Cu during aerobic oxidation of isobenzofuran

Isobenzofuran (0.3 mmol), CZJ-22-Cu (0.6  $\mu$ mol) and NHPI (0.015 mmol) in acetonitrile (2 mL) were stirred at 25 °C under an atmosphere of oxygen (balloon) for 0.5 h. The solid was subsequently collected by centrifugation and thoroughly washed with Et<sub>2</sub>O. The solid was immersed in acetonitrile for 12 h and centrifuged. The supernatant liquid was subjected to GC analysis and compared with the authentic samples analyzed under the same conditions.

#### 3. Results and discussion

CZJ-22 was synthesized by heating Cu<sup>II</sup>-H<sub>8</sub>OCPP and yttrium (III) nitrate in a mixture of DMF and nitric acid at 80 °C for 1 week. CZJ-22 crystallizes in the orthorhombic Cmca space group, consisting of one Cu-OCPP and two Y<sup>III</sup> ions per formula unit. To balance the anionic charge of the framework of CZJ-22, [(CH<sub>3</sub>)<sub>2</sub>NH<sub>2</sub>]<sup>+</sup> cations were encapsulated inside the anionic pores. CZJ-22 is a 3D noninterpenetrated anionic framework, building from fourconnected [Y(COO)<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>] nodes and octatopic Cu-OCPP metalloporphyrin linkers (Fig. 1a). The directional connections between these subunits resulted in nanocages with pore sizes of about 1.4 and 2.6 nm to accommodate [(CH<sub>3</sub>)<sub>2</sub>NH<sub>2</sub>]<sup>+</sup> cations and solvent molecules (Fig. 1b).

Since the pore window size (1.4 nm) in CZJ-22 is very large, the endogenous  $[(CH_3)_2NH_2]^+$  cations are readily exchanged with exogenous redox-active cations to develop ISACs. Treatment of CZJ-22 with a DMF solution of copper (II) perchlorate at 50 °C for five days resulted in a new MOF material, CZJ-22-Cu, in which the extra-framework  $[(CH_3)_2NH_2]^+$  cations were almost fully exchanged for copper (II) ions, as confirmed by ICP-MS, EDX spectroscopy, and elemental analysis. In the crystal structure of CZJ-22-Cu, ISA copper (II) is suspended in the anionic pores, which are weakly coordinated to two carboxyl oxygen atoms of Cu-OCPP with Cu—O distances of 2.28 and 2.44 Å (Fig. 1c). The long Cu—O bonds indicate that the coordination field of ISA copper is very



**Fig. 2.** Cu<sup>II</sup>2*p* XPS for Cu(CIO<sub>4</sub>)<sub>2</sub>, CZJ-22, Zn-CZJ-22-Cu, and CZJ-22-Cu in the solid state at room temperature.

weak. Accordingly, the surface free energy of copper species would be very high for activation of reactant molecules in catalysis. The permanent porosity of CZJ-22 and CZJ-22-Cu has been examined by N<sub>2</sub> adsorption experiments at 77 K. After the as-synthesized samples were heated at 50 °C under vacuum for 12 h, the activated solid samples of CZJ-22 and CZJ-22-Cu took up 452 and 545 cm<sup>3</sup> g<sup>-1</sup> N<sub>2</sub> at 77 K and 1 bar, resulting in BET surface areas of 242.4 m<sup>2</sup>/g and 236.8 m<sup>2</sup>/g, respectively (Figs. S16–S19 in the Supporting Information).

XPS of copper (II) perchlorate showed that the binding energies for Cu<sup>II</sup>2p<sub>3/2</sub> and 2p<sub>1/2</sub> are 935.98 and 955.68 eV, respectively [34]. In contrast, the signals for porphyrin Cu<sup>II</sup>2p<sub>3/2</sub> and 2p<sub>1/2</sub> in CZJ-22 are negatively shifted to 934.8 and 948.08 eV, respectively (Fig. 2). It is interesting that the binding energies for Cu2p<sub>3/2</sub> and 2p<sub>1/2</sub> in Zn-CZJ-22-Cu, consisting of suspended ISA copper(II), which are centered at 935.13 and 951.08 eV, respectively, are also



**Fig. 3.** Aerobic oxidation of isobenzofuran catalyzed by CZJ-22, CZJ-22-Cu, Zn-CZJ-22-Cu, Cu(ClO<sub>4</sub>)<sub>2</sub>, and a mixture of Cu-Me<sub>8</sub>OCPP and Cu(ClO<sub>4</sub>)<sub>2</sub> at room temperature and atmosphere pressure.

significantly negatively shifted. These results indicate that the coordination field of ISA copper is significantly affected by the special coordination environment. Indeed, the differences of the binding energies for porphyrin and ISA copper in CZJ-22-Cu are negligible, with the  $Cu2p_{3/2}$  signal centered at 934.75 eV. The solid-state EPR spectrum of CZJ-22 showed a typical monomer Cu<sup>II</sup>-porphyrin signal (g = 2.0664), which is identical to that of Cu-Me<sub>8</sub>OCPP (g = 2.0666) in acetonitrile (Fig. S24) [35]. However, the EPR signals for ISA Cu<sup>II</sup> in Zn-CZJ-22-Cu are significantly different from those of Cu(ClO<sub>4</sub>)<sub>2</sub> (g = 2.16676) in acetonitrile, indicating that the coordination field of ISA Cu<sup>II</sup> is significantly tuned by the anionic pore microenvironment. As expected, CZJ-22-Cu, consisting of both Cu<sup>II</sup>-porphryin and ISA copper(II) species, exhibits merged signals in the EPR spectrum.

Oxidation of ethers to esters offers straightforward access to high-value chemicals from less expensive raw materials, which is important and fundamental for the synthesis of natural products and bioactive molecules [36]. The use of molecular oxygen as an oxidant represents the most environmentally friendly pathway [37]. The practical barriers are the limited efficiency, low selectivity, limited scope, and extreme catalytic conditions. It is remarkable that CZJ-22-Cu is highly active in aerobic  $\alpha$ -oxidation of ethers to esters. As shown in Fig. 3, the heterogeneous catalyst CZJ-22-Cu afforded almost complete conversion of isobenzofuran (91%) for 0.5 h in the presence of *N*-hydroxyphthalimide (NHPI) at room temperature (25 °C) under 1 atm O<sub>2</sub> atmosphere. The heterogeneous catalyst CZJ-22, consisting of Cu<sup>II</sup>-porphyrins, exhibited much lower activity, with 9% isobenzofuran conversion, whereas the conversion is less than 1% catalyzed by homogeneous copper perchlorate under identical conditions. In other word, CZJ-22-Cu is 10 and 100 times more active than CZJ-22 and copper perchlorate, respectively. CZJ-22-Cu is also much superior to a simple mixture of its constituents of Cu-Me<sub>8</sub>OCPP and Cu(ClO<sub>4</sub>)<sub>2</sub> (3.8% conversion) under identical conditions.

We further studied the catalytic properties of Zn-CZJ-22-Cu, consisting of ISA Cu<sup>II</sup> only. As shown in Fig. 3, the isobenzofuran conversion is 36% after 0.5 h under identical conditions. These results indicate that the suspended ISA Cu<sup>II</sup> should be the main active site in the aerobic oxidation. Because the catalytic results



Fig. 4. Illustration of the sorption ability of CZJ-22-Cu as probed by GC.

of CZJ-22-Cu are not the simple additive effect of porphyrin copper and ISA copper, the superior catalytic efficiency should be the result of synergistic work between two kinds of redox-active copper sites. However, even though metalloporphyrins have been recognized as a class of highly efficient biomimetic catalysts, their catalytic properties are much inferior to those of ISACs in the aerobic oxidation reaction [21]. The super catalytic efficiency of CZJ-22-Cu should mainly be attributed to suspended ISAs with very weak coordination field, highly active valence electrons, and almost full availability of coordination sites.

To probe the accessibility of ISAs, we studied the solvent sorption properties of CZJ-22-Cu by immersing the activated solid samples in various solvents at room temperature for 12 h and centrifuging. GC analysis of the supernates indicates that CZJ-22-Cu takes up large numbers of different solvent molecules, such as ethanol, acetone, acetonitrile, toluene, isobenzofuran, phthalide, and isochroman (Fig. 4). We further studied the selective sorption capability of CZJ-22-Cu for reactant and product molecules. After an activated sample of CZJ-22-Cu was immersed in a mixture of



**Fig. 5.** Kinetic process for the aerobic oxidation of isobenzofuran catalyzed by CZJ-22-Cu at room temperature and atmosphere pressure.

isobenzofuran and phthalide (1:1 M ratio) at room temperature for 12 h, GC analysis of the supernate showed that CZJ-22-Cu preferably takes up isobenzofuran (35 molecules per formula unit) over phthalide (2 molecules per formula unit), suggesting that CZJ-22-Cu exhibits preferred sorption capability for reactant over product molecules. This property is very important for heterogeneous catalysts, which would enrich low-polar substrates and release high-polar products to improve the catalytic efficiency and reaction rate. To verify this hypothesis, we probed the included reactant and product molecules inside the pores of CZI-22-Cu during the aerobic oxidation of isobenzofuran. After the aerobic oxidation of isobenzofuran for 0.5 h, the catalysis was deliberately interrupted by centrifugation. The collected solid was immersed in acetonitrile to release the included guest molecules. GC analysis showed that there are about 3.5 isobenzofuran reactant molecules inside the pores of CZI-22-Cu per formula unit, whereas the encapsulated phthalide product is negligible, even though the conversion of isobenzofuran has been 91%.

Compared with homogeneous catalysts and SACs immobilized on solid surfaces, the selective accumulation property of CZJ-22-Cu is unique, which is one of the important factors illustrating the superior catalytic properties of CZJ-22-Cu in the aerobic oxidation. When additional isobenzofuran reactant (equal to the original) was added to the reaction mixture without separation of phthalide product after catalysis, the additional isobenzofuran can be fully oxidized for 1 h under the identical conditions. Isobenzofuran can also be fully oxidized for 1 h even in the presence of 10-fold phthalide. These results confirmed the distinctively selective accumulation of CZJ-22-Cu toward reactant over product molecules. The remarkable catalytic properties of CZJ-22-Cu further prompted us to study the kinetic process by using a large amount of substrate. As shown in Fig. 5, the turnover number (TON) reached 77,100 with an average turnover frequency (TOF) of 7710  $h^{-1}$  for 10 h with persistent high catalytic efficiency.

To check the stability of CZJ-22-Cu, we studied the leaching and recycling experiments. When the filtrate of the reaction mixture after catalysis was used instead of CZJ-22-Cu under the identical conditions, the oxidation of additional isobenzofuran is negligible. ICP-MS analysis indicates that copper species was not leached in the supernate. These results demonstrate the heterogeneous



Fig. 6. Catalytic aerobic oxidation of isobenzofuran by CZJ-22-Cu at different runs. The byproducts are phthalaldehyde and hemiacetal (Fig. S30). Color scheme: blue column, conversion of isobenzofuran; red column, selectivity of phthalide.

nature of the catalyst. CZJ-22-Cu can be recovered simply by centrifugation and reused in the successive run for eight cycles with almost retained high catalytic efficiency (Fig. 6). The PXRD pattern of the recovered solid is almost identical to that of the as-synthesized one, which proved the structural integrity of CZJ-22-Cu after catalysis (Fig. S10).

To evaluate the applicability of the ISAC system in aerobic oxidation, we investigated the catalytic  $\alpha$ -oxidation of isochroman and its derivatives. It is interesting that isochroman was almost fully oxidized, with 92% isochromanone selectivity for 2.5 h under 1 atm O<sub>2</sub> atmosphere at room temperature (Fig. 7). CZJ-22-Cu is also highly efficient and selective for the aerobic oxidation of a range of aromatic ethers to afford valuable esters with high conversions and significant functional group tolerance under the identical conditions. These results demonstrate that CZJ-22-Cu is a super catalyst for the production of synthetically and biologically valued isochromanones from readily available cheap raw materials with a broad substrate scope and functional group tolerance [37].

It has been suggested that such catalytic oxidation reactions often involved reactive radical and oxo-metal intermediates [38]. We first examined the radical intermediates in aerobic oxidation. When free radical scavengers such as hydroquinone and iodine were added to the reaction mixture, the conversion of isobenzofuran was drastically decreased to 3.1 and 0.9%, respectively. We further employed EPR spectroscopy to monitor the radical intermediates. When CZJ-22-Cu and NHPI were mixed in acetonitrile under N<sub>2</sub> at room temperature, the EPR spectrum of the supernate displayed a triplet hyperfine splitting signal for the phthalimido-*N*-oxyl (PINO) radical with g = 2.0087 and  $A^{N} = 4.72$ G (Fig. S25) [39,40]. When a diamagnetic spin trap agent, 5,5dimethyl-1-pyrroline-*N*-oxide (DMPO), was added to the reaction mixture during catalysis. The EPR spectrum of the supernate exhibits a four-line hyperfine pattern with the coupling constants of  $a^{N}$ = 12.9 G and  $a_{B}^{H}$  = 13.7 G with g = 2.0085, which is the characteristic signal for the spin adduct resulting from addition of  $O_2^-$  to DMPO (Fig. S26) [41].

It is known that hydrogen is easily abstracted from NHPI to form PINO and hydrogen radicals during catalytic aerobic oxidation [39,40]. The hydrogen radical is highly active for the reduction of Cu<sup>II</sup> species. It is interesting to note that the Cu<sup>II</sup> species in CZJ-22-Cu is much more easily activated (room temperature) than copper perchlorate (50 °C) and porphyrin copper, as revealed by EPR spectroscopy (Figs. S27–S29), suggesting that the Cu<sup>II</sup> species in CZJ-22-Cu is highly active. According to the free radical pathway, the Cu<sup>II</sup> species is first reduced by NHPI to form Cu<sup>I</sup>, which would bind with dioxygen to form the  $Cu^{I}-O_{2}$  species (Scheme 1). The complex is then reduced by H<sup>.</sup> derived from NHPI to result in a hydroperoxo intermediate, Cu<sup>II</sup>–O–OH, which would be further reduced by another H<sup>•</sup> to lead to heterolytic cleavage of the O–O bond, forming an oxo-metal intermediate, Cu<sup>III</sup>=0. Cu<sup>III</sup>=0 is highly reactive, which would insert the oxygen atom into the  $sp^3$ C–H bond to realize aerobic oxidation [42]. It is very clear that the present catalyst system is similar to the synergistic work between multiple active sites of enzymes [43]. Compared with enzymatic catalysis. H. acts as a combined proton and electron donor that is similar to reductases in the biological system.



**Scheme 1.** Proposed catalytic cycles for the aerobic oxidation of organic substrates by CZJ-22-Cu in the presence of the co-catalyst NHPI.



Fig. 7. Aerobic oxidation of aromatic ethers catalyzed by CZJ-22-Cu at room temperature and atmosphere pressure. The numbers in the parenthesis represent the reaction time (h). Color scheme: green column, conversion of ether; red column, selectivity of ester.

whereas ISA Cu<sup>II</sup> in CZJ-22-Cu performs as a redox-active center, corresponding to the prosthetic groups in enzymes. Additionally, PINO would abstract hydrogen atoms from organic substrates to initiate aerobic oxidation in a radical propagation mechanism [39,40]. In other words, there are two parallel pathways in the catalytic aerobic oxidation, in which NHPI would initiate aerobic oxidation by ISAs to form PINO, whereas PINO can abstract hydrogen from organic substrates to initiate radical aerobic oxidation. The synergistic work between these parallel pathways would significantly improve the catalytic efficiency and the reaction rate of the aerobic oxidation reaction. Compared with enzymes, the coupled catalyst system is more economical in terms of oxygen usage, because both oxygen atoms of O<sub>2</sub> are participated in the oxidation reaction (RCH<sub>2</sub>R' +  $O_2 \rightarrow RCOR' + H_2O$ ), whereas one oxygen of  $O_2$  is sacrificed in enzymatic catalysis (RCH<sub>2</sub>R' + 2O<sub>2</sub> + 4H<sup>+</sup> + 4e  $\rightarrow$  $RCOR' + 3H_2O$ ).

#### 4. Conclusions

In summary, to make use of eight-branched metalloporphyrin Cu<sup>II</sup>-OCPP connecting with four-connected Y<sup>III</sup> ions, we successfully constructed an anionic porphyrinic framework, CZJ-22, in which the extra-framework [(CH<sub>3</sub>)<sub>2</sub>NH<sub>2</sub>]<sup>+</sup> cations inside the anionic pores are easily exchanged to synthesize porous ISACs. The single-crystal structure of CZJ-22-Cu shows that the encapsulated ISA copper is suspended on the pore surfaces and almost fully available at the coordination sites, which results in the largest number of dangling bonds and empty d atomic orbitals to maximize the surface free energy for activation of molecular oxygen. CZJ-22-Cu demonstrates exceptionally high catalytic efficiency in aerobic oxidation of ethers to esters at room temperature and atmosphere pressure. The operational simplicity and environmental friendliness of this methodology afford a new pathway for the development of porous ISACs as promising alternatives to traditional catalysts, and thus a way to tackle the challenge issue of activation of inert reactants.

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#### **Appendix A. Supplementary material**

Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.jcat.2017.11.022.

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