



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^{-1} 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

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 (ISACs) 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, $[(\text{CH}_3)_2\text{NH}_2]_2[\text{Y}_2(\text{Cu-OCPP})(\text{H}_2\text{O})_4]\cdot 8\text{DMF}\cdot 22\text{H}_2\text{O}$ (CZJ-22; $\text{Cu-H}_8\text{OCPP} = \text{Cu}^{\text{II}}\text{-5,10,15,20-tetrakis}(3,5\text{-biscarboxylphenyl})\text{porphyrin}$), consisting of endogenous $[(\text{CH}_3)_2\text{NH}_2]^+$ cations that are systematically exchangeable with redox-active metal ions to tune the catalytic properties. The copper (II)-encapsulated material $[\text{Y}_2(\text{Cu-OCPP})(\text{H}_2\text{O})_4]\cdot 10\text{DMF}\cdot 18\text{H}_2\text{O}$ (CZJ-22-Cu), consisting of suspended ionic single-atom (ISA) Cu^{II} 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 5,10,15,20-tetrakis(3,5-bis(carboxy)phenyl)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 N₂ on a NETZSCH STA 409PC/PG instrument at a heating rate of 10 °C min⁻¹. 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 α radiation ($\lambda = 1.5406 \text{ \AA}$). 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-H₈OCP (1 mg, 0.001 mmol) and Y(NO₃)₃·6H₂O (100 mg, 0.26 mmol) were dissolved in a mixture of DMF (2 mL) and dilute HNO₃ (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 Et₂O, and dried at room temperature. Yield: 83% (based on Cu-H₈OCP). Anal. calcd. for C₈₀H₁₄₄CuN₁₄O₅₀Y₂ (%): 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⁻¹): 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(ClO₄)₂ 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(ClO₄)₂ 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(ClO₄)₂ in the solid sample for 3 days (3 times per day), and afforded CZJ-22-Cu as brown crystals. Anal. calcd. for C₈₂H₁₃₆Cu₂N₁₄O₄₈Y₂ (%): 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⁻¹): 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-H₈OCP was used instead of Cu-H₈OCP. Yield: 75% (based on Zn-H₈OCP). Anal. calcd. for C₈₃H₁₅₇N₁₅O₅₄Y₂Zn (%): 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⁻¹): 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 C₈₅H₁₄₅N₁₅O₅₀Y₂ZnCu (%): 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⁻¹): 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 ($\lambda = 1.54178 \text{ \AA}$) 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 μ 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, CH₃CN, and Et₂O. 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 CZJ-22-Cu

Isobenzofuran (120 mmol), NHPI (1.2 mmol), and CZJ-22-Cu (1.5 μ 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.

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