Selective oxidation over a metalloporphyrinic metal–organic framework catalyst and insights into the mechanism of bicarbonate ion as co-catalyst

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HIGHLIGHTS

- A metalloporphyrinic metal–organic framework catalyst was very active for selective oxidation.
- The crystal structure and catalysis-promoted environment facilitates the selective oxidation.
- An insight into the catalytic mechanism of HCO_3^- was gained according to a theoretical study.

GRAPHICAL ABSTRACT
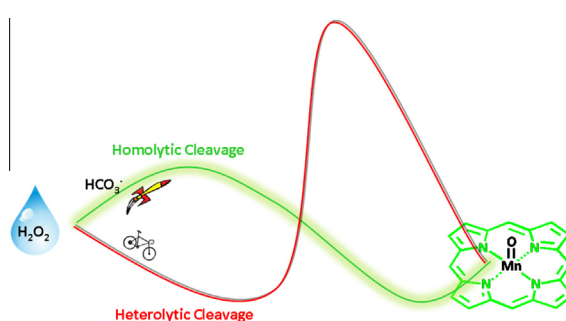
ABSTRACT

A biomimetic oxidation catalyst, metalloporphyrinic metal–organic framework, was successfully constructed by manganese tetrakis (4-carboxyphenyl) porphyrin as a bridging ligand and Fe ions with a stable 3D framework. The X-ray diffraction (XRD) spectra and X-ray photoelectron spectroscopy (XPS) details demonstrated its structure formed by channels and cavities and a catalysis-promoted electronic environment, which provides a fundamental understanding of this heterogeneous catalyst. Afterwards, it was found that Fe-MMOF can be capable of catalyzing the selective oxidation of versatile natural substrates, acting as an effective peroxidase mimic. The accessibility of the open channels to substrate molecules was also discussed to reveal the steric effect of substrate on catalytic activity. Here, we divided the epoxidation process into three parts, involving formation of HCO_4^-, the activation of HCO_4^- to form porMn^V = O and the nucleophilic attack of substrate at the electrophilic oxygen of porMn^V = O. Remarkably, an insight into the role of HCO_3^- was gained from the proposed mechanism based on the general idea about homolytic peroxide oxidation reaction.

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1. Introduction

Epoxidation of unsaturated compounds is a widely used process. These epoxides are valuable intermediates and building blocks for chemical manufacturing as well as laboratory synthesis, because they can be transformed into a large variety of compounds due to the high activity of oxirane ring. Nonetheless, a catalytic process with high conversion and desirable selectivity whose presence may be detrimental for multiple applications is not easy [1–3]. In this regard, developing efficient catalysts is becoming a research hotspot. Since 1980s, synthetic metalloporphyrins have been widely utilized by many researchers in olefin epoxidation to mimic cytochrome P-450 as biomimetic catalyst due to their

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rarely high performance on conversion and selectivity under mild condition [4,5]. However, these metalloporphyrins as homogeneous catalysts have some drawbacks compared with insoluble catalysts due to the formation of catalytically inactive dimers and fast degradation in homogeneous, molecular catalysis [6]. One promising strategy is to combine homogenous catalyst with insoluble materials [7–10]. Another approach is to incorporate a bulky substituent on the phenyl groups of the tetraphenylporphyrin ligand in order to produce molecular crystals or dendrimers, which could prevent the inactivation of heme-based catalysts by bimolecular interaction to form the M-O-O-M unit [11,12]. Consequently, there is an urgent need to achieve efficient heterogeneous catalysts with high-density active sites, structures formed by channels and cavities of strictly regular dimensions and catalysis-promoted electronic environment, remaining a grand challenge.

Metal–organic frameworks (MOFs), a new class of coordination polymers, emerged approximately two decades ago and constructed from organic bridging ligands and metal ions/clusters, which constitutes a large and steadily expanding group of porous crystalline materials with 3D structures. Among them, the designed bridging ligands lead to a variety of MOFs with golden opportunities for a huge domain of applications, especially in the fields of catalysis [13–15]. Therefore, MOF materials have been greatly encouraged as an effective platform for highly tunable catalyst designs through incorporating the active sites into frameworks. Recently, several MOFs with uncoordinated metalloporphyrin-based building synthons including carboxylic acid groups or pyridyl moieties have been applied to mimic properties of cytochrome P450 [16–22]. In terms of catalytic functions, metalloporphyrinic MOFs succeed to possess coordinating moieties at their peripheries, along with incorporating enzyme catalysis into heterogeneous materials. Therefore, these metalloporphyrinic MOFs (MMOFs) can be considered as self-supported catalysts with an enhanced performance due to their high-density active sites into frameworks. In order to address aforementioned challenge, these motivated us to use MMOF approach to target efficient heterogeneous catalysts with open coordination frameworks.

To data, the use of green oxidant-hydrogen peroxide (H_2O_2) has received remarkable attention, because H_2O_2 is inexpensive and less-toxic [23–25]. It is pertinent to mention that bicarbonate ions (HCO_3^-) has been routinely used as co-catalyst in enhancing the metalloporphyrin-catalyst efficiency and utilization of H_2O_2 compared to H_2O_2 alone, because of the formation of peroxymonocarbonate (HCO_4^-) [26–28]. Although it is generally believed that HCO_4^- is a more reactive nucleophile than H_2O_2 and speeds up the reaction, the process of formation of HCO_4^- has not been clearly confirmed. Therefore, it is of great significance to gain insights into reaction route for the formation of HCO_4^- over the porphyrinic catalysts. Recently, a number of computer simulations have achieved great success on reaction mechanisms [29–31] and gas adsorption or storage [32–34]. Theoretical calculations are being used as a powerful characterization method and tool to prove proposed mechanisms and predict reaction phenomena. Among them, the computational studies has been demonstrated that side chains of iron porphyrins, axial ligand, substrates with versatile substitutions were related to reactivity trends [31]. Hence, computational simulation makes it possible to analyze the catalytic role of HCO_3^-.

Herein, we reported a novel metal–organic framework catalyst with an enhanced activity, which was denoted as Fe-MMOF (Fe-MMOF denotes iron-based metalloporphyrinic metal organic framework). Catalytic studies have demonstrated that Fe-MMOF can catalyse the epoxidation of a variety of natural substrates, acting as an effective peroxidase mimic. A detailed research about substrate sorption was beneficial for understanding the steric effect from the substrate dimensions. Of further significance, our

strategy for mechanism study of co-catalyst focused on the formation of HCO_4^- from the perspectives of homolytic or heterolytic cleavage of H_2O_2. In addition, the activation of HCO_4^- to form catalytic intermediate and the nucleophilic attack of substrate at the electrophilic oxygen were also computationally discussed. It should be mentioned here that the model this article employed here was ethylene which was one of the most common substrates in computer simulations and manganese(III) porphyrin as referenced catalyst.

2. Experimental and theoretical methods

2.1. Chemicals

Methyl 4-formylbenzoate, pyrrole, propionic acid, N,N-dimethylformamide (DMF), iron(II) chloride tetrahydrate (FeCl$_2$·4H$_2$O), manganese(II) chloride tetrahydrate (MnCl$_2$·4H$_2$O), 5, 10, 15, 20-Tetrakis (4-methoxycarbonylphenyl) porphyrin (TPPCOOMe) was prepared according to procedures described in Scheme S1. All commercial chemicals were used without further purification unless otherwise mentioned.

2.2. Porphyrin synthesis

The 5, 10, 15, 20-tetrakis (4-carboxyphenyl) porphyrin (H$_2$TCPP) was synthesized by the modified Lindsey method [35], involving NaOH hydrolysis of the corresponding carbomethoxyphenyl intermediate.

Thus, 1.22 g (7.46 mol) of 4-carbomethoxybenzaldehyde and 0.50 g of distilled pyrrole (7.46 mol) were added to 750 mL of dry CH$_2$Cl$_2$ for 30 min. Then, BF$_3$ etherate (92 μL) was added via syringe, and the reaction mixture was protected from light. After stirring at room temperature for 1 h, 1.37 g (5.62 mmol) of p-chloranil was added in the solid form and the solution was stirred overnight. The solution was concentrated to a small volume using a rotary evaporator. To this solution, silica gel (60–200 mesh) was added and the slurry was evaporated to give a dry black powder, which was loaded on a silica column using CHCl$_3$. First CHCl$_3$ fraction removed any poly (pyrrole) impurity and the porphyrin was eluted with 2–4% acetone in CHCl$_3$. It was then further purified by recrystallization from a 1:4 CHCl$_3$/methanol mixture (v/v). Yield: 0.55 g (35%). ^{1}H NMR (400 MHz, CDCl$_3$) δ 9.08–8.64 (m, 8H), 8.62–8.37 (m, 8H), 8.39–8.13 (m, 8H), 4.34–3.88 (m, 12H), −2.79 (s, 2H). The ^{1}H NMR details could be obtained form the Fig. S1 in the Supplementary Information.

5,10,15,20-Tetrakis (4-methoxycarbonylphenyl) porphyrin-Mn(III) chloride (Mn-TPP-COOMe). A solution of H$_2$TCPP 0.42 g (0.50 mmol) and MnCl$_2$·4H$_2$O (0.24 g, 1.00 mmol) in 50 mL of DMF was refluxed for 12 h. After the mixture was cooled to room temperature, 500 mL of H$_2$O was added. The resultant precipitate was filtered and washed with 200 mL of H$_2$O for three times. The obtained solid was dissolved in CHCl$_3$, followed by washing three times with water. The organic layer was dried over anhydrous magnesium sulfate and evaporated to afford quantitative dark green crystals [36].

In the next stage, 0.45 g (0.50 mmol) of the latter product was dissolved in 20 mL of THF. To this, 1.60 g of NaOH in 20 mL of water was added and the solution was stirred at room temperature for 3 days. At the end of this period, THF was removed by rotary evaporation. The crude porphyrin was treated with 20 mL of 2 N HCl solutions, yielding a green precipitate, which was filtered, washed with water, and dried. Protonated porphyrin was neutralized by adding 10 mL of pyridine and subsequently removed by vacuum distillation. Then, purple solid was washed with water and dried under a vacuum. Yield: 0.39 g (88%). FTIR (KBr): 3414