

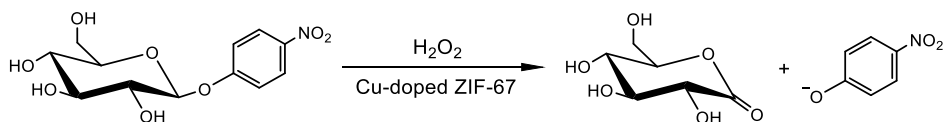
Synthesis and Redox Reaction of Copper- and Cobalt-Containing Zeolitic Imidazolate Frameworks

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There are many enzymes containing copper ions in the active center, including lytic polysaccharide monooxygenase (LPMO), dopamine β -monooxygenase, peptidylglycine α -hydroxylating monooxygenase, which reductively activate oxygen and oxidize C–H bonds, laccase, which couples phenols with oxidation to reduce oxygen to water by four electrons, and superoxide dismutase, which disproportionates superoxide anion radicals. The copper ions present in these enzymes are mainly coordinated with imidazole in the histidine side chain, and there is also a vacant coordination position in which oxygen or superoxide anion radicals are coordinated. In addition, these copper ions have a redox cycle that goes back and forth between monovalent and divalent copper in the enzyme catalytic cycle. For these reasons, a number of copper complexes with vacant coordination positions have been synthesized to reproduce the function of these copper-containing enzymes.

Previously we reported that Cu-doped ZIF-8, which is one of zeolitic imidazolate frameworks and composed of 2-methylimidazole and zinc ion, exhibits excellent superoxide dismutase-like activity. In this study, we focused on ZIF-67, which is a cobalt analog of ZIF-8 and is more stable than ZIF-8 [1]. Cu-doped ZIF-67 was prepared by mixing a methanol solution containing copper(II) acetate and cobalt(II) nitrate and a methanol solution of 2-methylimidazole, followed by standing at 50°C for 6 ~24 hours. In this study, we evaluated LPMO-like activity of Cu-doped ZIF-67. LPMOs are mononuclear copper-containing enzymes that catalyze oxidative depolymerization of crystalline polysaccharides, such as cellulose and chitin, in a reaction that depends on an electron donor and dioxygen or hydrogen peroxide on the mononuclear copper site located at the surface of the enzymes [2]. The LPMO-like reactivity of Cu-doped ZIF-67 was evaluated using the oxidation reaction of *p*-nitrophenyl- β -D-glucopyranoside [3], which is a model compound of polysaccharides, with hydrogen peroxide as an oxidant in aqueous media.



References

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