

# Cobalt Porphyrin Immobilized on Montmorillonite: A Highly Efficient and Reusable Catalyst for Aerobic Oxidation of Alcohols to Carbonyl Compounds

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**Abstract:** The highly efficient aerobic oxidation of alcohols to carbonyl compounds was achieved catalyzed by cationic *meso*-tetrakis (1-methyl-4-pyridyl, TM4PyP) metalloporphyrins immobilized in montmorillonite interlayers. Cobalt porphyrin (CoTM4PyP-MT) showed excellent activity and selectivity in the aerobic oxidation of benzyl alcohol, where 90% yield of benzaldehyde was obtained. CoTM4PyP-MT can be five times reused without significant loss of activity.

**Key words:** metalloporphyrins; montmorillonite; oxidation; alcohol; dioxygen

Selective catalytic oxidation of alcohols to corresponding aldehydes is of great importance for both laboratory and synthetic industrial applications [1]. A variety of transition metal-based catalysts has been intensively investigated for the oxidation of alcohols so far [2–6]. As models of cytochrome P450, metalloporphyrins are used as oxygen carrier intermediates and widely as homogeneous catalysts for various biomimetic oxidation reactions as well [7,8]. The homogeneous oxidation of alcohols catalyzed by metalloporphyrins has been well investigated with PhIO [9], Cl<sub>2</sub>PyNO [10], KHSO<sub>5</sub> [11], and *m*-chloroperbenzoic acid [12] as oxidants. However, metalloporphyrins catalysts decompose easily in the oxidation process and the difficulty of recovery is a major weakness.

Great efforts have been made to immobilize metalloporphyrins onto supports such as organic polymer materials, chemically modified silica surfaces, and mesoporous molecular sieves to promote stability [13–19]. Montmorillonite is preferable to be used as the support for immobilizing metalloporphyrins due to its large specific surface area, chemical and mechanical stability, layered structure, and high cation exchange capacity [20]. So far, only oxidations of alkanes, cyclohexene, and 2-mercaptoethanol have been reported over by montmorillonite-supported cationic metalloporphyrins

[21–24]. To our knowledge, the aerobic oxidation of alcohols catalyzed by montmorillonite-supported metalloporphyrins is still unknown.

In continuation of our ongoing research on the metalloporphyrin-based aerobic oxidation of alcohols [25,26] we demonstrate herein the first successful example of the efficient aerobic oxidation of alcohols catalyzed by montmorillonite-supported metalloporphyrins. This heterogeneous catalyst presents excellent activity and can be five times consecutively reused without significant loss of activity.

## 1 Experimental

### 1.1 Materials

Alcohols and carbonyl compounds were of analytical grade and purchased from Alfa Aesar or Aldrich. They were used without further purification unless indicated. Pyrrole and isobutyraldehyde were redistilled before use. All other solvents were analytical grade. The montmorillonite was purchased from Aladdin Reagents.

### 1.2 Synthesis of *meso*-tetrakis (1-methyl-4-pyridyl) met-

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## alloporphyrin [26]

Pyrrole (20 ml) and 4-pyridinecarbaldehyde (20 ml) were refluxed in propionic acid (200 ml) for 1 h to produce *meso*-tetrakis(4-pyridyl) porphyrin (T4PyP) with a yield of 24%. Next, T4PyP (0.25 g) and cobalt acetate (1 g) were refluxed in dimethylformamide (35 ml) for 6 h under nitrogen atmosphere to form *meso*-tetrakis (4-pyridyl) cobalt porphyrin (CoT4PyP) with a yield of 88%.

In the following step, CoT4PyP (0.2 g) and methyl *p*-toluenesulfonate (12 g) were added to 100 ml dimethylformamide solution. The mixture was stirred for 12 h at 90 °C, and the solution was cooled to room temperature. Ethyl ether (20 ml) was added to the mixture and it was kept overnight. After filtration, the filter cake was washed thoroughly with ethyl ether and purified by recrystallization in water/acetone (1:2) to obtain *meso*-tetrakis (1-methyl-4-pyridyl) cobalt porphyrin (CoTM4PyP) with 80% yield. The other metalloporphyrins could be synthesized in similar procedures by replacing Co with both metal ions. The spectral and analysis data of metalloporphyrins catalysts were listed as following. [CoTM4PyP]<sup>4+</sup>: EI-MS: *m/z* 735. UV-Vis (H<sub>2</sub>O):  $\lambda_{\max}$ , nm (log $\epsilon$ ) 418 (2.47), 539 (0.93). IR (KBr, cm<sup>-1</sup>): 1640, 1005. Anal. calcd. for C<sub>44</sub>H<sub>28</sub>N<sub>8</sub>Co: C, 71.83; H, 4.93; N, 15.23. Found: C, 71.43; H, 4.72; N, 14.96. [MnTM4PyP]<sup>4+</sup>: EI-MS: *m/z* 731. UV-Vis (H<sub>2</sub>O):  $\lambda_{\max}$ , nm (log $\epsilon$ ) 464 (2.48), 559 (1.25). IR (KBr, cm<sup>-1</sup>): 1640, 1009. Anal. calcd. for C<sub>44</sub>H<sub>28</sub>N<sub>8</sub>Mn: C, 72.22; H, 4.96; N, 15.31. Found: C, 71.79; H, 4.92; N, 15.16. [FeTM4PyP]<sup>4+</sup>: EI-MS: *m/z* 732. UV-Vis (H<sub>2</sub>O):  $\lambda_{\max}$ , nm (log $\epsilon$ ) 415 (2.84), 543 (1.23). IR (KBr, cm<sup>-1</sup>): 1638, 1002. Anal. calcd. for C<sub>44</sub>H<sub>28</sub>N<sub>8</sub>Fe: C, 72.13; H, 4.95; N, 15.29. Found: C, 72.32; H, 4.95; N, 15.31.

### 1.3 Preparation of montmorillonite interlayer-fixed metalloporphyrins

A mixture of *meso*-tetrakis (1-methyl-4-pyridyl) metalloporphyrin (Mn, Co, Fe) (100 mg) and montmorillonite (1 g) in 0.1 mol/L nitric acid (100 ml) was submitted to reflux and stirred for 5 h. Then, the mixture was slowly cooled to room temperature. The solid was filtered and washed with water and ethanol for several times. The solid was dried in vacuum at 80 °C. The amount of metalloporphyrin adsorbed into clay was quantified by measuring the amount of MTM4PyP (M = Mn, Co, and Fe) in the nitric acid and filtrate on an Atomic Absorption Spectrometer (Shimadzu AA2580).

### 1.4 Characterization

The UV-visible spectra of metalloporphyrins were recorded on a Shimadzu UV-2450 UV-Vis spectrophotometer in the range of 200 to 700 nm, using water as solvent. Fourier transform infrared (FT-IR) spectra of the samples were recorded in

the range of 4000–400 cm<sup>-1</sup> on an FT-IR spectrometer (Bruker, VERTEX 70) using the KBr pellet technique. X-ray diffraction measurements were performed on a D-MAX diffractometer with a Cu K $\alpha$  source operated at 40 kV and 30 mA. The specific surface area and pore volume of the montmorillonite was determined from nitrogen adsorption-desorption isotherms (Micromeritics ASAP-2010) before and after immobilization of metalloporphyrins

## 1.5 Catalytic oxidation of alcohols

A 20 ml Schlenk tube was charged with benzyl alcohol (1 mmol), catalyst (0.015 g), acetonitrile (4 ml), isobutyraldehyde (3 mmol), and naphthalene (0.2 mmol, inert internal standard) and then the mixture was stirred at 70 °C. Dioxigen was bubbled through the solution. The consumption of the starting benzyl alcohol and formation of products was monitored by GC (Shimadzu GC-2010 plus) or GC-MS (Shimadzu GCMS-QP2010).

For the recycling experiments, the catalyst was recovered by centrifugation and first washed with water (5 ml) for five times, and then with acetonitrile (10 ml) to remove the occluded reactants and products. After washing, the acetonitrile solution was checked for the presence of reactants/products using gas chromatography. The recycled catalysts were then dried in vacuum at 80 °C for 6 h. The recycled catalyst was reused under the same reaction conditions by compensating the lost amount of catalyst.

## 2 Results and discussion

### 2.1 Supported catalyst characterization

In this work, montmorillonite is used for the immobilization of cationic metalloporphyrins because it is an easily commercially available clay with interlayer surface. It is also easily exchanged with solute ions by varying the cationic composition of the solution. In the adsorption process, pyridyl ions of metalloporphyrins are bound to the clay surface by sharing one or several ligands with adsorbent cations as isolated complexes. Consequently, *meso*-tetrakis (1-methyl-4-pyridyl) metalloporphyrins can be firmly anchored onto its surface. In all immobilization procedures nearly all metalloporphyrins were transferred to the solids and low quantities were spectrometrically detected in solution by atomic absorption analyses. Thus, the loaded amounts of the MnTM4PyP, CoTM4PyP, and FeTM4PyP was  $4.7 \times 10^{-5}$  mol/g,  $3.8 \times 10^{-5}$  mol/g, and  $3.5 \times 10^{-5}$  mol/g, respectively.

The immobilization process could also be characterized by the color change of the clays. For MnTM4PyP a change was observed from light green to brown, with a final color of dark brown in the case of the dry solid. The presence of metalloporphyrins in the solid clay was determined by the diffuse

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