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Catalysis of structure-like macromolecules supported manganese tetraphenylporphyrin for cyclohexane oxidation

Guan Huang *, Shang-Yue Liu, Ai-Ping Wang, Yong-An Guo, Hong Zhou

College of Chemistry and Chemical Engineering, Guangxi University, Nanning 530004, China

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Abstract

Manganese tetraphenylporphyrin (Mn TPP) has been successfully supported on chitosan (CTS), chitin (CTN) and cellulose (CLS) by means of physical adsorption, and they are characterized by UV–Vis spectroscopy. The supported catalysts exhibit enhanced activity and effective recycle (except for Mn TPP/CLS) for oxidation of cyclohexane in the presence of air as oxidant. Both Mn TPP/CTS and Mn TPP/CTN show higher selectivity for cyclohexanone and cyclohexanol, whereas Mn TPP/CLS shows lower selectivity. The kind of support influences the catalytic activities and the selectivity for the supported catalysts. Appearance of the catalytic differences is attributed to the presence of the microenvironment differences for the supports.

Keywords: Macromolecule; Manganese tetraphenylporphyrin; Cyclohexane oxidation; Air

1. Introduction

Biomimetic oxidation of hydrocarbon with molecular oxygen and metalloporphyrins as catalysts has been attracting much attention in the last two decades [1–3]. It is evident that the use of oxygen (or air), which is inexpensive, abundant and readily available oxidants in place of oxygen donors, is desirable on economic and environmental grounds. However, instability of metalloporphyrin towards oxidative degradation and difficulty in recovery of the expensive catalysts limit the practical application of metalloporphyrins in both synthetic chemistry and industrial process. Supported metalloporphyrins have received much more attention [4–8]. Because their use can not only enhance stability of metalloporphyrins and keep the high-efficient catalytic activity of metalloporphyrins on hydrocarbon oxidation, but they can also be easily separated from the reaction mixture and reused [6]. To date, there are many approaches of supporting metalloporphyrins. The most convenient method is intercalation, adsorption or entrapment of porphyrin between layer of clays or within the pores, surface or matrices of solid. In this way, we have successfully supported iron or cobalt tetraphenylporphyrin on chitosan and have employed them as catalysts for aerobic oxidation of cyclohexane respectively [9,10]. At present, industrial oxidation of cyclohexane to cyclohexanone and cyclohexanol is still carried out using soluble cobalt catalyst or no catalyst, in which cyclohexane conversion is less than 3.9% and the selectivity to cyclohexanol and cyclohexanone is 78% [11]. Recently, Guo et al. [12] used simple metalloporphyrins to catalyze aerobic oxidation of cyclohexane into cyclohexanol and cyclohexanone in the absence of solvent and assistant catalyst at 8% conversion and 85% selectivity, but this technology exhibited disadvantages in that metalloporphyrins could not be used repeatedly. In continuous search for new supported metalloporphyrin catalysts, here we first report the investigation concerning manganese(III) tetraphenylporphyrin immobilized on structure-like macromolecules, such as chitosan, chitin and cellulose, as catalysts for aerobic oxidation of cyclohexane in the absence of

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* Corresponding author. Tel.: +86 771 3237868; fax: +86 771 2851043.
E-mail address: huangg66@126.com (G. Huang).

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any solvents or reductants. The research results show that Mn TPP/CTS, CTN and CLS could be reused four, three and one time, respectively, with average cyclohexane conversion of 5.45%, 4.17% and 11.40%, average selectivity of 93.22%, 92.29% and 82.72%, and average catalyst turnovers of 2.31×10^4, 2.10×10^4 and 4.80×10^4, respectively. The performance of the solid catalysts affected by three structure-like supports has been studied.

2. Experimental

2.1. Materials

All reagents and solvents used were analytical grade and were obtained commercially. No impurities were found in cyclohexane by GC analysis before use. Manganese TPP was synthesized according to the documented procedures [13,14]. Manganese TPP supported on chitosan and chitin (i.e. Mn TPP/CTS and Mn TPP/CTN) respectively, were prepared according to the procedure previously described [9,15].

2.2. Preparation of Mn TPP/CLS

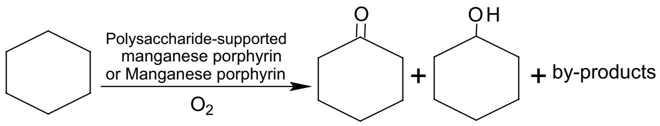
Microcrystal cellulose (2 g) was added into 100 ml of saturated zinc chloride solution and stirred for 1.5 h. Then, 0.1000 g of manganese tetraphenylporphyrin solved in 100 ml of chloroform and 10 ml of distilled water were dropped into the reaction mixture and stirred for 2 h, at room temperature. The shallow-green solid was collected by filtration, rinsed with alcohol and dried in air. The amount of Mn TPP anchored on the support was determined by UV–Vis spectroscopy of the solution left after impregnation [16].

2.3. Characterization of the supported catalysts

The supported catalysts were characterized by UV–Vis spectroscopy, using the similar method [4]. The electronic spectra of the supported Mn TPPs were obtained in glycerol mull in quartz vessel, and the UV–Vis spectra of Mn TPP/CTS, Mn TPP/CTN and Mn TPP/CLS were compared with that of Mn TPP in the region of 280–580 nm (Fig. 1). The chloroform extractions from the powder of the solid catalysts were measured using UV–Vis spectrophotometry, with the results shown in Fig. 1a.

2.4. Catalytic oxidation

The cyclohexane oxidation catalyzed by four catalysts with air, respectively, was as follows:



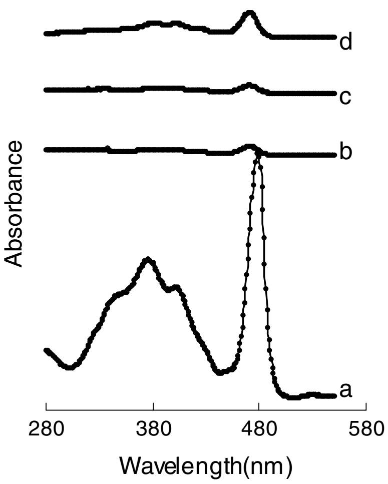


Fig. 1. UV–Vis spectra at room temperature: (a) chloroform solution of Mn TPP and (b–d) in glycerol mull Mn TPP on cellulose, chitin and chitosan, respectively.

The main oxidation products were cyclohexanone and cyclohexanol, with the by-products, cyclohexyl hydrogen peroxide, hexanedioic acid and esters, as confirmed by GC–MS analysis.

The catalytic oxidation of cyclohexane has been carried out in a 500 ml autoclave equipped with a magnetic stirrer and a Model CYS-1 digital oxygen-detector at the optimum temperature of 418 K and under the optimum air pressure of 0.8 MPa.

In the typical experimental, the catalyst having the concentration of 2.0×10^{-5} M of manganese porphyrin or its equivalent for the supported manganese complexes was introduced into the reaction mixture when the required reaction condition was attained. The air was continuously pumped into the reaction system and the pressure was kept at 0.8 MPa. The flow of air was measured by means of rotameter, and the oxygen concentration of tail gas was determined by a Model CYS-1 digital oxygen-detector. The reaction mixture samples adopted were identified by GC–MS and quantified by GC with internal standard method, using chlorobenzene as the standard substance [17]. After oxidation reaction was stopped, the supported catalysts were recovered by means of simply separating from the reaction mixture, washed with alcohol, and dried by cool gas. The supported manganese complexes were consecutively reused as catalysts for next oxidation of cyclohexane with a little catalyst leaching (especially in reuse) or without a significant loss of its activity.

3. Results and discussion

Manganese TPP was supported on chitosan, chitin and cellulose (which were all in white originally) and different green solids were obtained, respectively. It may indicate the presence of manganese porphyrin on the supports. The presence of Mn TPP on the supports can be further