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Microcapsule-supported binuclear manganese complex as an efficient and reusable oxidation catalyst

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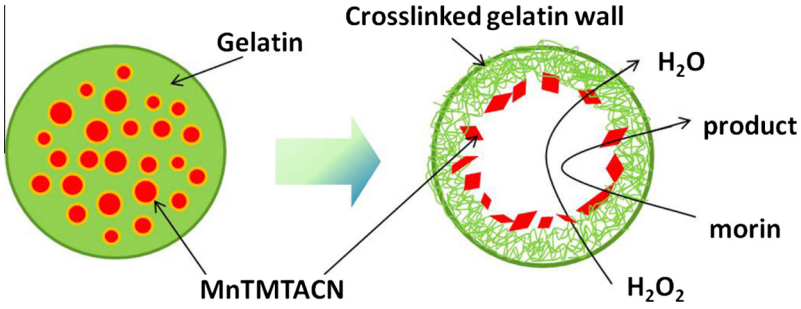
HIGHLIGHTS

- The heterogenization of a catalyst MnTMTACN was realized by microencapsulation technology.
- MnTMTACN well crystallized within the amorphous matrix.
- The microencapsulated MnTMTACN exhibited excellent catalytic activity and reusability.

GRAPHICAL ABSTRACT



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ABSTRACT

Heterogenization of a biomimetic catalyst $[Mn^{IV}_2\ (\mu\text{-}O)_3\ (TMTACN)_2][PF_6]_2{\cdot}H_2O$ (MnTMTACN) was realized by entrapping the manganese complex within biopolymer microspheres via an emulsification solvent extraction method. Elementary analysis and ultra violet-visible spectroscopy confirmed the successful encapsulation of MnTMTACN in the biopolymer microspheres. The surface and interior morphologies of the MnTMTACN-loaded microspheres were characterized with optical microscopy (OM), scanning electron microscopy (SEM) and transmission electron microscopy (TEM), respectively. High resolution transmission electron microscopy (HRTEM) revealed not only a confined crystallization of MnTMTACN but also a good dispersion of these nanocrystals within the biopolymer microspheres. The encapsulated MnTMTACN exhibited a high catalytic activity and could be reused at least 7 times in catalyzing the oxidation of 2′,3,4′,5,7-pentahydroxyflavone (morin) with hydrogen peroxide.

1. Introduction

Many studies described the design of complexes between transition metals and organic ligands, which structurally mimic the active centers of oxidoreductase [1–3]. Many biomimetic systems such as porphyrins, phthalocyanines or Schiff bases have been proposed as functional models of oxidoreductase. Among these systems, manganese-triazacyclononane complexes have received considerable attention [1,4–6]. 1,4,7-Triazacyclononane (TACN) and its related ligands are facially coordinating tridentate ligands. Dimanganese complexes derived from TACN and its substituted derivatives, such as 1,4-dimethyl-1,4,7-triazacyclononane (DMTACN), 1,2-bis(4,7-dimethyl-1,4,7-triazacyclonon-1-yl)ethane (DTNE) and tris(2-methylpyridyl)amine (TPA) ligands were proven to be H_2O_2 activators. The complex derived from the ligand 1,4,7-trimethyl-1,4,7-triazacyclononane (TMTACN), $[Mn^{IV}_2\ (\mu\text{-}O)_3\ (TMTACN)_2][PF_6]_2{\cdot}H_2O$ (MnTMTACN) (Fig. 1a) was found to be very active in catalyzing the decomposition of H_2O_2 at relatively low temperature [7–11]. Moreover, a variety of model oxidation processes, such as epoxidation [12–15], dihydroxylation of alkenes [16,17], oxidation of azo-dyes [18,19], oxidation of phenols [20,21], and C–H activation [22] could proceed under similar conditions.

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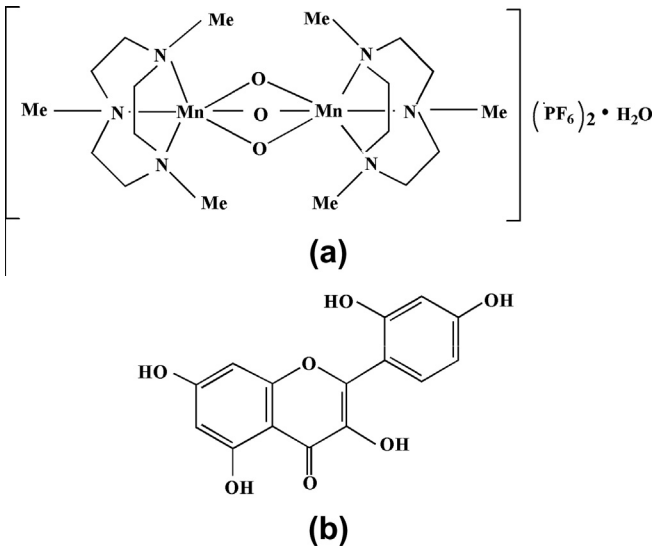

Fig. 1. (a) Structure of MnTMTACN ($[Mn^{IV}_2(\mu\text{-}O)_3(TM\text{-}TACN)_2][PF_6]_2 \cdot H_2O$); (b) structure of morin (2′,3,4′,5,7-pentahydroxyflavone).

However, as an efficient and homogeneous catalyst, MnTMTACN is expensive and not easy to be separated from the constituents of the reaction mixture. Separating and recycling of the catalysts are still major challenges, and this has stimulated the study of heterogenization of these catalysts by a variety of routes. One common method for creating a heterogeneous catalyst is by covalent attachment to a support material. For example, TACN or DMTACN has been linked to a support material such as SiO_2, and then the metal ions were binded to the immobilized ligands, affording the heterogeneous systems [23,24]. However, such a method does not apply to the TMTACN ligand. When TMTACN reacts with a functional group such as oxirane or haloalkyl group, its chelating properties would be affected or even lost. Thus, a feasible immobilization strategy allowing the maintenance of the positive attributes of the "free" MnTMTACN system is still needed. Also, the catalysts on the support usually diffuse very slowly and experience a different solution environment from that of the homogeneous catalysts, which often rendering them less active than their homogeneous counterparts. It thus should be better to construct a system which could retain a solution-like environment for the heterogenized catalysts.

Microencapsulation technology has been widely used in many fields [25–27]. Inspired by some work in entrapping active materials in soluble polymer supports [28–31], we reported here a simple method to heterogenize MnTMTACN within gelatin microspheres of core self-diffusion and shell cross-linked. Gelatin is a biodegradable natural polymer derived from collagen, which is commonly used in drug delivery systems as a carrier matrix. Gelatin crosslinking is utilized in order to insolubilize the carrier in water, improve the thermal and mechanical stability of the carrier under application conditions, as well as control the rate of degradation [32,33]. The catalytic property of the MnTMTACN-loaded gelatin microspheres was investigated by catalyzing the oxidation of 2′,3,4′,5,7-pentahydroxyflavone (morin) (Fig. 1b) with hydrogen peroxide.

2. Experimental

2.1. Materials

All chemicals and reagents were purchased from Sinopharm Chemical Reagent Co., Ltd., Shanghai, China. They were analytical grade and used as received without further purification unless noted otherwise.

2.2. Synthesis of MnTMTACN

The synthesis of MnTMTACN was carried out by coordination of TMTACN using a procedure common for the preparation of such type compounds [34]. The ligand TMTACN (1 mmol) was dissolved in 9 ml EtOH/H_2O (2/1 v/v). Then $MnCl_2$·aq (1 mmol) and KPF_6 (1.5 mmol) were added simultaneously and stirred under N_2 at room temperature for 10 min. The mixture was then cooled to 0 °C and stirred for 10 min. 1 mL aqueous solution of hydrogen peroxide (1 M) was mixed with 1 mL aqueous solution of NaOH (2 M). The mixture was then added dropwise into the reaction mixture over a period of 3 min. And the resulting mixture was stirred for another 10 min in ice bath. After that, pH of the mixture was neutralized to 7–8 with sulfuric acid solution (2 M). Then the solid was filtered and washed with CH_3CN. The filtrate was recrystallized in CH_3CN. Finally, a red solid product was obtained (2.3 g, corresponding to 57% yield). Elemental analyses were calculated as follows: C, 26.73 wt.%; H, 5.45 wt.%; N, 10.40 wt.%. Elements found were C, 26.62 wt.%; H, 5.46 wt.%; N, 10.44 wt.%. Mn content was estimated using inductively coupled plasma-atomic emission spectroscopy (ICP): Mn, 12.47 wt.% (calculated: 13.61 wt.%).

2.3. Microencapsulation of MnTMTACN in gelatin spheres

Encapsulation of as-synthesized MnTMTACN into gelatin microspheres (GS) was realized via an emulsification solvent extraction method (Fig. 2). Briefly, 10 ml aqueous solution of gelatin (10% w/v) and MnTMTACN (5 g/L, 7 g/L, 10 g/L, 15 g/L) was added to 50 ml of paraffin oil which was preheated to 60 °C. The two phases were emulsified for 30 min using an overhead stirrer (IKA RW20) at 400 rpm. The emulsion was then rapidly cooled to 5 °C in an ice bath and stirred continuously for 20 min to allow the spontaneous gelation of the gelatin aqueous solution.

The crosslinking of GS was carried out using glutaraldehyde as the crosslinker. The entire process of crosslinking was kept at 5 °C. The microspheres formed were dehydrated by adding isopropanol precooled at 5 °C and stirred for further 30 min. The microspheres were then collected from the suspension by filtration and washed several times with isopropanol and petroleum ether to remove the residual oil on the surface. The washed microspheres were finally dried as a free flowing powder and stored in dry environment.

2.4. Cumulative release property of MnTMTACN-loaded GS

The cumulative release test was conducted by immersing 0.3 g MnTMTACN-loaded GS (60% loading determined by ICP) in 50 ml deionized water under stirring. 2 ml of the solution was taken out at predetermined time intervals and replaced with 2 ml fresh water. Then the released MnTMTACN was determined by measuring Mn contents in the solution with ICP.

2.5. Catalytic activity and recycle of MnTMTACN-loaded GS

The catalytic activity and recycle of MnTMTACN-loaded GS (60% loading determined by ICP) was tested by oxidations of a model substrate (morin) with hydrogen peroxide as oxidant. MnTMTACN-loaded GS (20 mg) were added into 10 ml of freshly prepared buffered stock solution (morin, 70 μM; H_2O_2, 1 mM; carbonate buffer, 10 mM, pH = 10.0; T = 40 °C) under constant agitation for 3 min. Then the MnTMTACN-loaded GS were separated by filtration, washed with deionized water and put into another 10 ml of the stock solution for recycling.