

Ship-in-a-bottle synthesis, characterization and catalytic oxidation of styrene by host (nanopores of zeolite-Y)/guest ([bis(2-hydroxyanil)acetylacetonato manganese(III)]) nanocomposite materials (HGNM)

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Abstract

A series of manganese(III) complexes with Schiff-base tetradentate ligands, [bis(2-hydroxyanil)acetylacetonato manganese(III)] (X = H, CH₃, Cl and NO₂) have been synthesized and characterized as homogeneous and encapsulated into the nanopores of zeolite-Y by the flexible ligand method (FLM). The new materials were characterized by several techniques: chemical analysis and spectroscopic methods (FT-IR, UV/VIS, XRD, BET and DRS). The analytical data indicated a composition corresponding to the mononuclear complex of Schiff-base ligand ([Mn(X₂-haacac)Cl]). The characterization data showed the absence of extraneous complexes, retention of zeolite crystalline structure and encapsulation in the nanopores. Substitution of the aromatic hydrogen atoms of the Schiff-base ligand by electron withdrawing groups like –Cl, and –NO₂ has two major effects: (1) retention and concentration of the Mn(III) complex in the zeolite cavities is enhanced (due to the larger size of the substituents) and (2) the electronic and spectral properties of the encapsulated complex are modified. The aerobic oxidation of styrene to benzaldehyde, styrene oxide and phenylacetaldehyde over these catalysts is also reported. Reaction conditions have been optimized by considering the amount of catalyst, effect of time and temperature. Under the optimized reaction conditions, [Mn((NO₂)₂-haacac)Cl]-NaY has shown the highest conversion of 95.8% after 12 h. Encapsulated Mn(III) complex is catalytically very efficient as compared to other neat complexes for the oxidation of styrene and is stable to be recycled without much deterioration.

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1. Introduction

Cytochrome P450, a monooxygenase, found in almost all living organisms, catalyzes the selective oxidation of C–H bonds to an alcohol functionality, a reaction difficult to achieve by conventional methods of chemical synthesis [1]. This class of enzymes also catalyzes a wide variety of other reactions, including oxygen transfer to heteroatoms, epoxidation of olefins, hydroxylation of aromatic hydro-

carbons and oxidative degradation of chemically inert xenobiotics such as drugs and environmental contaminants. The substrate range of P450 enzymes is very broad, ranging from simple alkanes to the most complex of hormones and their precursors [1]. This remarkable activity of cytochrome P450 arises from the highly activated transition metal complexes present in them. Many model systems based on transition metal complexes of porphyrins, phthalocyanines and Schiff-bases that can mimic monooxygenase enzymes have been widely investigated [2]. The catalytic activity of the model complexes in homogeneous medium decreases with time due to ligand oxidation or

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formation of dimeric oxo- and peroxobridged complexes. Heterogenization of the homogeneous catalysts (metal complexes) has been sought to isolate the metal complexes to prevent their dimerization, increase their ruggedness and separability and to benefit from the synergistic catalytically beneficial interaction between the complexes and the support [3–8].

Heterogenization is achieved either by encapsulating the metal complex inside the nanopores of zeolites or by anchoring or tethering them to inert supports [4]. Grafting and tethering refer to covalent attachment of the metal complex, either directly (grafting) or through a spacer ligand (tethering). The encapsulation (ship-in-a-bottle) approach is convenient and ideal because the complex, once formed inside the cages of the zeolite, is too large to diffuse out and is not lost into the liquid phase during the reaction. As these composite materials mimic biological enzymes, they are also called “zeozymes” (acronym for zeolite mimics of enzymes). On confinement in the zeolite matrix, the metal complex may lose some of its degrees of freedom and adopt unusual geometries that are stabilized by coordination to the zeolite-surface functional groups. In a general sense, the encapsulated complexes mimic enzyme systems in that the porous inorganic mantle (similar to the protein mantle in enzymes) provides (hopefully) the right steric requirement for the metal complex and imposes certain requirements (based on size and shape) to the access of the active site by the substrate molecules (substrate selectivity). Though many porous materials have been used, the most popular ones have been zeolites Y possessing large cages (12 Å diameters).

Co(salen) complexes encapsulated in zeolite-Y were found to form more stable dioxygen adducts than the complexes in homogeneous solutions, mimicking hemoglobin [9]. In a similar attempt to prepare analogs of cytochrome P450, Fe-phthalocyanine complexes were encapsulated in zeolite-Y, which exhibited remarkable substrate- and regio-selectivities in the oxidation of unactivated alkanes [10–14]. Jacobs and co-workers [10] reported a composite catalyst system that achieved realistic mimicry of cyto-

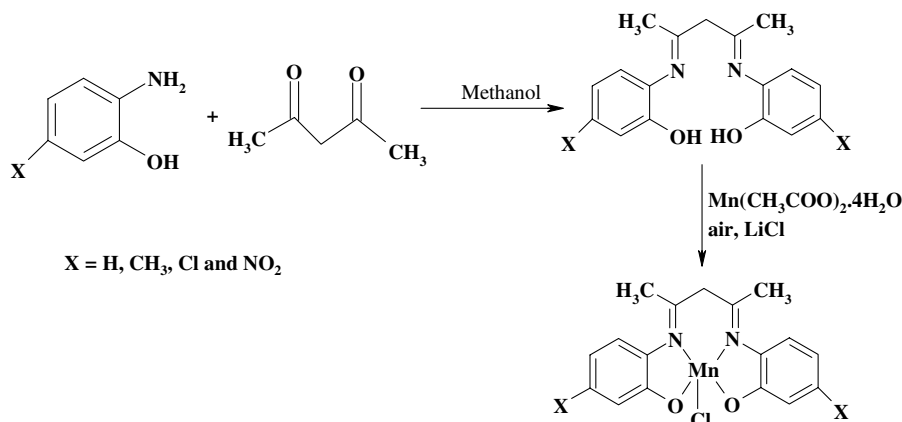
chrome P450 by incorporating Fe-phthalocyanine complex in the crystals of zeolite-Y, which were in turn embedded in a polydimethylsiloxane membrane. This system oxidized cyclohexane, at room temperature, at rates comparable to those of the enzymes. Jacobs et al. have encapsulated manganese complexes of 2,2-bipyridine [15], 1,10-phenanthroline and triazacyclononane [16,17] in faujasite, HMS and MCM-41, as models for the methane monooxygenases. Mn porphyrin complexes embedded in polydimethylsiloxane (PDMS) exhibited high activity in the selective oxidation of cyclic alcohols to ketones with TBHP as the oxidant [18]. Ogunwumi and Bein [19] and Sabater et al. [20] have investigated enantioselective epoxidation using encapsulated metal complexes. Piaggio et al. [21] have found that a manganese(III) chiral salen complex immobilized in Al-MCM-41 is an effective epoxidation catalyst for *cis*-stilbene. In our laboratory, we have been working in the area of heterogenized homogeneous catalysts [22–25].

Most frequently inside the large pores of the zeolites metalloporphyrins and their analogues as phthalocyanines and Schiff bases [26] were prepared. They have been studied extensively as biomimetic catalysts for alkene epoxidation and alkane hydroxylation with variety of oxidants including hydrogen peroxide, *tert*-butylhydroperoxide (TBHP), iodosylbenzene and hypochlorite [27]. There are only a few papers on oxidation of hydrocarbons with dioxygen in the presence of zeolite-encapsulated metallocomplexes as catalysts [28]. The present paper describes the synthesis, characterization and catalytic activity in the aerobic oxidation of styrene of various Schiff-base complexes containing, on the 5-positions, electron-withdrawing groups like –Cl, or –NO₂ and encapsulated in nanocavity of zeolite-Y by the flexible ligand method Schemes 1 and 2).

2. Experimental

2.1. Materials and physical measurements

All other reagents and solvent were purchased from Merck (pro-analysis) and dried using molecular sieves



Scheme 1.

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