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Metallosalen complexes immobilized in zeolite NaX as catalysts of aerobic oxidation of cyclooctane

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Abstract

Physicochemical properties of metallosalen complexes entrapped within NaX zeolite and their catalytic activities in the oxidation of cyclooctane with dioxygen in the absence of a reducing agent were studied, and compared with free metallocomplexes.

Broadening of the zeolite structure-sensitive vibrations observed after the encapsulation gives the evidence of the zeolite framework changes due to the presence of the ‘‘ship-in-the-bottle’’ species. EPR spectroscopy evidences the inclusion of metallosalen complexes since it distinguishes between encapsulated metallocomplexes and those adsorbed on the zeolite external surface. UV–vis spectra confirm the immobilization and stabilization of the metallocomplexes inside the zeolite structure.

The most active catalysts are free metallosalen complexes. We have found that the activity of these complexes increases in the order Ni(salen), Fe(salen), Mn(salen), Cu(salen) and Co(salen) with triple difference in the catalytic activity between the most and the least active catalyst. Upon encapsulation their activity drops about two times. Only Ni(salen) after heterogenization does not change its catalytic activity. The reduction of catalytic activity of the encapsulated catalysts is probably governed by two factors: constraints in the formation of the intermediate complex and change of the redox potential of the metal in the salen complex.

Keywords: Metallosalen complexes; Cyclooctane oxidation; Encapsulated metallocomplexes; Transition metal ions; Zeolite X

1. Introduction

Transition metallocomplexes encapsulated within the pores of zeolites receive special attention as inorganic mimics of enzymes [1–3]. A wide variety of metal complexes have been successfully immobilized in a range of different zeolites. Such hybrid materials have numerous potential applications including catalysis, gas separation, artificial photosynthesis and photocatalysis [4a,4b].

Cytochrome P-450 is an example of a biologically important compound with iron porphyrin as active center and is an efficient catalyst for the selective oxidation of organic compounds [5]. In the case of enzymes their high activity and selectivity is connected with the fact that the active complex is surrounded by a protein mantle assisting in spatial organization of reactants reducing thereby entropic constraints of the reaction. Enzymes also may give rise to stabilization of the transition state through supramolecular interactions, guiding desired reaction along a specific pathway. Many of such functionalities of enzymes can successfully be reproduced in chemically simpler mimetic systems, such as zeozymes. In this case the metal complex imitates the role of the active site, whereas the zeolite host replaces the surrounding protein.

The catalytic activity of model systems based on transition metallocomplexes of porphyrins, phthalocyanines and Schiff bases in homogeneous media decreases due to the formation of μ-oxo dimers or bimolecular self-oxidation of the macrocyclic complex [6]. Active phases should be immobilized on different supports to tailor the catalyst for desired performance, recover the catalysts after a reaction in an easy way, or to prepare catalysts that are benign to the environment (catalytically active phases are sometimes toxic). The immobilization of metallocomplexes on different supports is a good method to satisfy environmental demands and to obtain catalysts which preserve

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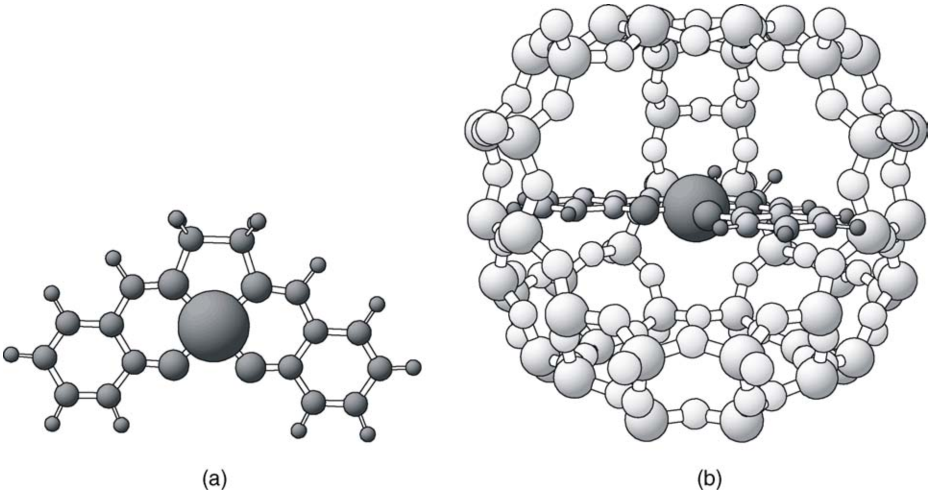

Scheme 1. Co(salen) complex (a) and Co(salen) complex entrapped inside of zeolite NaX (b).

the properties of homogeneous systems, but are more stable and can easily be recovered.

Heterogenization of metal complexes with ligands that are known to be active in homogeneous catalysis inside of zeolite pores can be achieved via ship-in-the-bottle synthesis. The three-dimensional large pore zeolites X and, with the pore of 7.4 Å, are often chosen as a host framework. The size of the zeolite supercages enables the synthesis and accommodation of bulky metallocomplexes inside those cavities, whereas their window openings do not allow the synthesized complex to diffuse away (Scheme 1). When encapsulation of metallocomplexes is carried out through the flexible ligand method all individual components like the metal ion and ligand can easily pass in and out of the zeolite but the final coordination complex is too large and rigid to go out once assembled inside. The isolated complex immobilized in this way acquires also some new properties. When confined in the zeolite voids, the complex may lose some of its degrees of freedom and adopt a unique geometry, which may differ from that existing in the solution. The surrounding zeolite framework may also affect the selectivity of catalytic reactions by influencing in a different way the transition states of parallel processes [6].

The salen ligand (*N*,*N*′-bis(salicylidene) ethylenediamine) was selected to synthesize all metallocomplexes used in our work. Its minimum kinetic diameter reaches 6.5 Å but after the complexation of a metal cation it increases to about 9 Å [7]. It is an example of a tetradentate ligand, which contains two oxygen and two nitrogen atoms. It is also known that salen can form stable complexes with a variety of transition metals, among them Mn, Co, Fe, Cu and Ni, which are often used in oxidation reactions. These metals were chosen to synthesize complexes with salen ligand as analogues of metalloporphyrins, mimicking the activity of the cytochrome P-450 [8].

In our paper, we describe for the first time the application of the immobilized salen metallocomplexes for high pressure oxidation of cyclooctane with dioxygen in the absence of a reducing agent. We also will try to answer the question how the structure and catalytic activity of free metallocomplexes changes upon the immobilization of these complexes within the faujasite supercages. Metallosalen complexes and their counterparts encapsulated in zeolite NaX were thoroughly characterized by FT-IR, UV–vis and EPR techniques, in order to prove the encapsulation and to understand how structure of the zeozymes influences the catalytic activity and selectivity in this reaction.

2. Experimental

2.1. Materials

Manganese, iron, cobalt, nickel and copper complexes with *N*,*N*′-bis(salicylidene) ethylenediamine (salen) were synthesized according to the procedure described elsewhere [9]. Three series of samples were prepared: metallosalen complexes, metallosalen complexes encapsulated in the zeolite NaX (i.e. M(salen)/NaX) and, as a reference, zeolite X exchanged with the corresponding metal ions (i.e. MNaX). Additionally, for the sake of EPR measurements the adduct of Co(salen) with pyridine was synthesized [10].

The sodium form of the zeolite X was subjected to ion-exchange in water solutions of appropriate metal cations [10–12]. After the exchange, the zeolite was washed several times with water and dried. Manganese, iron, cobalt, nickel and copper exchanged zeolites were coloured after the synthesis. According to the flexible ligand method, metallosalen complexes were synthesized inside the faujasite structure through reaction between the ion-exchanged zeolite X and the salen ligand. Samples of the zeolite X containing the incorporated complexes were Soxhlet extracted with dichloromethane to remove the complexes from the external surface of the zeolite. Once the extracting solution became colourless, the samples were dried and stirred with a saturated solution of NaCl for 1 h at room temperature, to remove metal cations, which remained uncomplexed.