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Zeolite-encapsulated M(Co, Fe, Mn)(SALEN) complexes modified glassy carbon electrodes and their application in oxygen reduction

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ABSTRACT

Zeolite-encapsulated transition metal complexes of SALEN [N, N′-bis(salicylidene) ethylenediamine] have been used as catalysts of oxidation reactions of hydrocarbons with oxidants including dioxygen. But in these processes molecular oxygen as oxidant did not show good activity compared with other oxidants such as TBHP, PhIO and H_2O_2. In order to evaluate the catalytical effect of the hybrid materials on the process of activating molecular oxygen, zeolite-encapsulated M(Co, Fe, Mn)(SALEN) complexes modified glassy carbon electrodes [M(SALEN)/Y/GCEs (M = Mn, Fe, Co)] were prepared and used as electrocatalysts of oxygen reduction reaction (ORR). The electrocatalytic reduction of dioxygen, thus, was investigated by cyclic voltammetry (CV) and chronocoulometry (CC) at glassy carbon electrodes (GCEs) modified with metal (Co, Fe, Mn) complexes of SALEN encapsulated inside NaY in pH 6.90 aqueous solutions. The results have shown that the M(SALEN)/Y/GCEs (M = Mn, Fe, Co) exhibited efficient electrocatalytic activity towards dioxygen reduction with reduced overpotentials of about 505 mV, 393 mV and 397 mV for Co(SALEN)/Y, Fe(SALEN)/Y and Mn(SALEN)/Y, respectively, lower than bare GC electrode and enhanced peak currents. The electroreduction of O_2 on these modified GCEs is an irreversible and diffusion-controlled process. The transferred number of electrons and the transfer coefficient for dioxygen reduction reaction were determined by CV and CC. These results suggest that zeolite-encapsulated M(Co, Fe, Mn)-SALEN complexes can efficiently activate molecular oxygen by decreasing the overpotential and increasing current of oxygen reduction reaction. And dioxygen is reduced to form water in the process. The significance of this work lies in evaluating the catalysis of the hybrid catalysts for oxidation reaction by electrochemical techniques.

1. Introduction

Up to the present, there have been many reports on the preparation and characterization of zeolite-encapsulated, ship-in-a-bottle metal complexes of SALEN [N, N′-bis(salicylidene) ethylenediamine] [1–6]. The encapsulation of metallosalen complexes is usually carried out by the flexible ligand method, in which a flexible ligand, able to freely diffuse through the zeolite pores, complexes with a pre-exchanged metal ion. The resultant complex becomes too large and rigid to leave the cages. It is well known that cytochrome P-450, containing iron metal in the prosthetic active site, is capable of activating dioxygen, forming active species capable of oxidizing alkanes [7]. Therefore, the zeolite-encapsulated metallosalen complexes, a kind of biomimetic system, have been proposed as functional models of cytochrome P-450 [1,5,8,9]. They have been studied extensively as biomimetic catalysts for hydrocarbon hydroxylation/epoxidation and alcohol carbonylation with a variety of oxidants including hydrogen peroxide [1,3,4,10], tert-butylhydroperoxide (TBHP) [1,10–12,6], and iodosylbenzenes (PhIO) [9,10], and with less frequent use of O_2 as oxidant [2,5,8]. Molecular oxygen was proven not to be a good oxidant for oxidation reactions of organic compound compared with the other oxidants mentioned above [10,11] because of its higher chemical stability. Can or to what extent the zeolite-encapsulated metallosalen complexes activate molecular oxygen as cytochrome P-450 in biological process? How does the oxygen reduction reaction (ORR) conduct in the presence of these hybrid catalysts of zeolite-encapsulated metallosalen complexes as electrocatalysts? We would like to know if the zeolite-encapsulated metallosalen complexes modified glassy carbon electrodes are capable of promoting the oxygen reduction reaction in aqueous solution.

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On the other hand, oxygen reduction has been of great theoretical and practical importance in power sources, biological processes and chemical syntheses. In particular, the design and development of new catalysts for the multielectron reduction of dioxygen has received a great deal of attention for practical applications such as biological reactions and fuel cells [13–16]. There have been extensive investigations on electrochemical reduction of O_2 with electrocatalysts such as noble-metal materials such as Pt [17–20], Au [21], Ru [22], non-noble materials including inorganic oxide compounds [23,24], organic compounds such as anthraquinone and its derivatives [25–28], biological enzyme such as catalase [29,30], vitamin B [31,32] and riboflavin [33], and metal macrocyclic complexes of phthalocyanines [34,35] and porphyrins [13,36–40]. In addition, transition metal complexes of Schiff-base ligands, especially SALEN complexes [8,41–43] which may mimic the catalytic cycle of cytochrome P-450, have attracted much research interest with their easy preparation in experimental lab. As electrocatalysts for the ORR process, the complexes are often coated on the surface of glassy carbon electrode, forming modified electrodes by either electropolymerizing the complexes to obtain conducting polymer film [39,44,45] on the surface of glassy carbon electrodes, or immobilizing them into some polymer compounds, such as polypyrrole [27], polyacrylamide [30], Nafion [40,46,47] and polyaniline [48], followed by the absorption of these polymer compound on glassy carbon electrodes. In fact, chemically modified electrodes (CMEs) have continued to be of major concern during the last decade. And a relatively large amount of electrochemical research has been devoted to the development and application of different types of CMEs [49]. Zeolite-modified electrodes are a kind of important chemically modified electrodes in studying the redox behavior of the metal complexes encapsulated in zeolite. The electrochemical properties of the CMEs of zeolite-immobilized metallosalen complexes were much investigated in 1990s [50–52]. But there are only a few papers on ORR using zeolite-encapsulated metallosalen complexes as electrocatalysts [53].

In the present contribution, the NaY zeolite-encapsulated M(SALEN) modified electrodes, denoted as M(SALEN)/Y/GCEs (M = Mn, Fe, Co), were prepared and used as electrocatalysts for the ORR process. The electrochemical behavior and catalytic efficiency of these modified electrodes for ORR were examined by CV and CC.

2. Experimental

2.1. Reagents and chemicals

All chemicals and reagents used in present work were of analytical grade and used as received without further purification. All aqueous solutions for electrochemical experiments were prepared using doubly deionized water. The supporting electrolyte in organic system used for electrochemical experiments, tetra-*n*-butylammonium perchlorate (TBAP), was prepared according to literature procedure [54] and recrystallized three times, 0.025 mol l^{-1} phosphate buffer solution (pH 6.90) was purchased from Tianjin Guangfu Fine Chemicals Company in China. The used NaY was purchased from the China Petroleum and Chemical Corporation. Its SiO_2/Al_2O_3 ratio is 5.80.

2.2. Preparation of the M(SALEN)/Y(M = Co, Fe, Mn)

NaY zeolite was subjected to ion-exchange in water solutions (0.01 mol l^{-1}) of $Co(CH_3COO)_2$, $FeCl_3$ or $Mn(CH_3COO)_2$ at room temperature for two times. Washed with water several times and dried in the air, the NaMY(M = Co, Fe, Mn) was then obtained. The metallosalen complexes were synthesized inside the faujasite structure through reaction between the ion-exchanged zeolite Y (NaMY) and the SALEN ligand by flexible ligand method [55]. Typically, 0.5 g of the $NaCo^{II}Y$ and 1.5 g H_2SALEN were intimately mixed and placed in a crucible with cover. The crucible was then heated to 170 °C and kept for 24 h in air. The molten slurry was cooled to room temperature and extracted with methylene chloride, acetone and acetonitrile until the solvent was colorless to obtain the brown powder of Co^{III}(SALEN)/Y. Using the same method, Fe^{III}(SALEN)/Y (brown red) and Mn^{III}(SALEN)/Y (earth yellow) were obtained by replacing $NaCo^{II}Y$ with $NaFe^{III}Y$ or $NaMn^{II}Y$.

2.3. Preparation of working electrodes

Prior to modification, the GC electrode was polished to a mirror-like surface with alumina and water slurry on polishing cloth and rinsed with doubly distilled water. Then, it was cleaned ultrasonically in acetone, absolute ethanol, HNO_{3-} H_2O (1:1, v/v) solution and distilled water in the sequence, then dried in air before use.

The modified electrodes were prepared according to the literature [56]. To obtain the best voltammetric responses of M(SALEN)/Y composite film, the experimental conditions for film casting, such as the mass ratio of M(SALEN)/Y to graphite, the concentration of the suspension of M(SALEN)/Y and graphite in tetrahydrofuran (THF), the concentration of the solution of PS in THF, and the total volume of suspension of M(SALEN)/Y and graphite, were optimized. Typically, 30 mg of M(SALEN)/Y and 30 mg of high purity graphite were dispersed in 1 ml THF ultrasonically to form a black suspension. Four microlitres of this black suspension was pipetted directly on the freshly polished surface of glassy carbon electrode (GCE), forming M(SALEN)/Y composite film. Dried subsequently in air at room temperature for approximately 1 h, the composite film was further coated by 10 μl of polystyrene solution in THF solution (8 g/l) and then dried overnight at room temperature. Thus, the M(SALEN)/Y/GC modified electrode was obtained. Similarly, the MnY/GC modified electrode was obtained by replacing M(SALEN)/Y with MnY Zeolite. The graphite/GCE was prepared using only high purity graphite as the modifier by above approach. The M(SALEN)/Y/GCE, MnY/GCE, graphite/GCE and bare GCE were all used for working electrode in electrochemical experiments.

2.4. Apparatus and procedure

Electrochemical experiments were performed on a CHI model 600B (Shanghai, China) electrochemical workstation with a three-electrode system: bare GCEs or modified GCEs, working electrode; Pt plate (2 mm × 7 mm), counter electrode; saturated calomel electrode (SCE), reference electrode. The glassy carbon electrodes (geometric area, 0.0707 cm^2) were purchased from LK Co. (Tianjin, China). The buffer solution used was 0.025 mol l^{-1} Na_2HPO_4–0.025 mol l^{-1} NaH_2PO_4 (pH 6.90, 15 °C). Electrochemical experiments were performed in a one-compartment cell closed with a Teflon cap, through which the electrodes and gas bubbling system were fitted. High purity O_2 and N_2 regulated by two flowmeters (equipped with needle valves) were used to maintain dioxygen saturation and deoxygenate in the measurement cell.

Voltammetric experiments on M(SALEN)/Y modified electrodes were performed in phosphate buffer solution of pH 6.90. The buffer was purged with highly purified nitrogen for approximately 15 min before experiments. A nitrogen environment was then kept over solutions in the cell during the electrochemical experiments of M(SALEN)/Y. In the experiments of electrocatalytic reduction of dioxygen, O_2 was bubbled for 15 min before recording the voltammograms and chronocoulometric responses. All experiments were done at ambient temperature of 15 ±1 °C.