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Electrochemical study with cavity microelectrode containing clay-supported $Mn^{(III)}$salen complex – Dioxygen activation with cytochrome P450 model

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ABSTRACT

$Mn^{III}Cl$–salen complex of tetradentate Schiff base ligand was incorporated into layers of clay montmorillonite by using an *in situ* flexible ligand method. The obtained modified clay was examined by X-ray diffraction, FT-IR and by using a cavity microelectrode (CME) to perform the electrochemical studies of the catalyst in the supported solid phase. Experiments show a well-defined and chemically reversible redox system of the manganese complex incorporated into the clay, similar to that observed in solution but with apparent diffusion coefficient around $2.3 \times 10^{-9}\ cm^{-2}\ s^{-1}$. Dioxygen activation in catalytic conditions that was found to be efficient in the modified material is studied with the CME. It demonstrates the absence of formation of μ-oxo dimers and peroxo-bridged compounds and a good penetration of the different reactants into the clay. Moreover, this analysis illustrates the interest of CME as a powerful tool for the study of similar supported catalyst implying the biomimetic activation of molecular oxygen.

1. Introduction

Synthetic metal complexes, such as metalloporphyrins, phtalocyanines, and transition metals by Schiff bases are commonly used in catalytic or electrocatalytic systems as for the oxygenation of organic molecules, epoxidation of alkenes, oxidation of hydrocarbons, mimicking cytochromes P-450 enzymes [1–8]. A particular attention has been devoted to catalysts for olefins epoxidation taking into account their low cost and large availability. According to the catalytic cycle proposed by Murray and co-workers [9], the metal catalyst serves as a relay for oxygen atom transfer to the substrate and involves a high-valent metal-oxo intermediate such as $Mn^{V}{=}O$ [10]. In this way, the well-known Kochi's $Mn^{III}Cl$–salen catalyst (salen: salicylaldehyde ethylenediamine) (Fig. 1), modified later by Jacobson and Katsuki [11–13] and for which the preparation and handling are relatively easy, was found to be a suitable candidate for the homogeneous epoxidation of cyclooctene both in chemical [14,15] and electrochemical catalytic systems [16,17].

For practical use, the catalyst requires a good stability against self-oxidation that leads to the formation of μ-oxo dimers and peroxo-bridged compounds. Indeed, when molecular oxygen is used as oxygen atoms donor in homogeneous catalysis, μ-oxo dimers are systematically formed in the medium causing a neat weakening of the oxidation reaction evolution due to their inactive catalytic character [18–21]. To overcome these difficulties, heterogenization of the catalyst have received considerable attention by using different immobilization methods such as (i) intercalation into clays [14,21–26], (ii) encapsulation onto zeolites or mesoporous molecular sieves [8,14,27–32] and (iii) electropolymerization or grafting on polymer matrices [33–36] or silicates [37,38]. It was concluded that the formation of μ-oxo dimers is limited by the immobilization, which consequently increases the turnover frequencies of the catalytic reaction. [17,39–41].

Most of the electrochemical studies concerning the intercalation of Schiff base complexes were carried out using "classical" inert millimetric electrode (glassy carbon, platinum) covered with a thin film of the modified materials (see the example a modified clay [42,43]), or using carbon paste electrodes made by pressing a mixture of the powder material with graphite, carbon black and a blinder substance [44,45]. Because of the limitations inherent to these methods, the electrochemical response generally consisted of broad signals making difficult detailed investigations. In this relation, the use of cavity microelectrodes (CME), also called powder microelectrodes (Fig. 2) combines the advantages of the above-mentioned techniques with the properties of microelectrodes. Especially, the ohmic drop and the double layer capacitance are notably reduced in transient electrochemical experiments,

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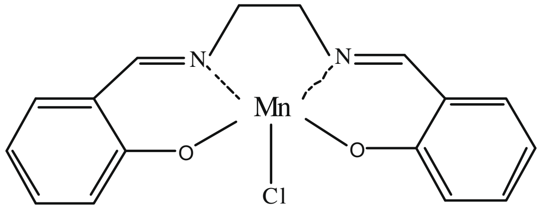

Fig. 1. Manganese (III) [*N*,*N*′-bis(salicylaldene) ethylenediamine] chloride.

which allow the use of shorter experimental times. In cyclic voltammetry, curves with a minimum of distortion could easily be recorded for scan rates up to few tens V s^{-1}. These possibilities have to be compared with the performances of carbon paste macro-electrodes for which the range of available scan rates are typically limited to values lower than 1 mV s^{-1} [46]. Moreover, CME requires only microquantities of material, around 10^{-8} g that could be a great advantage in the preparation of the sample. Since the initial developments of the CME method in the 1990s, originally for improving the performances of enzyme electrodes [47], the technique was used with success in a series of electrochemical investigations of electroactive materials such as those related to corrosion [49], electrochemical detection [48], batteries and composite materials [50–57]. CME was also used to perform electrochemical synthesis of hybrid materials with carbon nanotubes [58] or to evaluate potentialities of redox mediators in the electrical wiring of enzymes [59].

Considering the advantages of CME, we used this method for investigating the catalytic activity of Mn^{III}Cl–salen complex immobilized into an inexpensive, highly available, non-toxic and inactive material, Algerian montmorillonite that could be considered as an alternative to other commercially available supports. Montmorillonite is a hydrous lamellar compound with a structure consisting of negatively charged Si—Al—Mg—O sheets between which the adsorption properties are induced by the presence of exchangeable cations that facilitates the immobilization of molecular materials. Taking advantages of clays with this ability, the use of an *in situ* flexible ligand method [25] allows the heterogeneization of Mn(salen) complexes. The purpose of the present study was both to evaluate the possibilities of such inactive material in electrocatalytic applications, but also to demonstrate the advantages and interests of CME in similar investigations of relatively complicated reactive scheme, here the biomimetic activation of molecular oxygen by a metal–salen complex. In complement, the material was also characterized by XRD diffraction, UV–Vis and FT-IR spectroscopy.

2. Experimental

2.1. Chemicals and reagents

Montmorillonite used in this work is originated from the mining of Maghnia (West Algeria). Before use, the clay was purified and Na-exchanged according to the literature procedure [60]. Acetonitrile (Fluka), ethanol and methanol (Prolabo) were HPLC-grade and used as received. Tetraethylammonium perchlorate (TEAP) was recrystallised in water and dried at 80 °C before use.

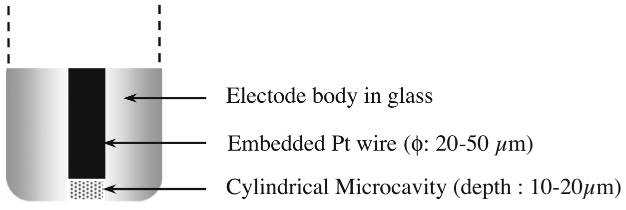

Fig. 2. Representation of the head of a cavity microelectrode.

2.2. Apparatus

High quality powder diffraction data of the Na–montmorillonite and catalyst–montmorillonite were obtained using a Siemens D500 diffractometer with the parafocusing Bragg–Brentano geometry, using monochromatic Cu $K\alpha_1$ radiation (λ = 1.5406 Å) selected with an incident beam curved-crystal germanium monochromator. The patterns were scanned at room temperature, over the angular range 1.5–20.01° (2θ), with a step length of 0.03° (2θ) and counting times of 15 and 20 s step^{-1} for Na- and Mn-based compounds respectively. Line profile fitting and extraction of the peak positions were carried out with the Socabim fitting program, available in the PC software package DIFFRAC^{plus} supplied by Bruker AXS.

IR spectra were recorded on a FT-IR-Equinox 55 Bruker spectrometer by using the conventional KBr pellet method (2 wt.%), spectra were collected at room temperature with a resolution of 4 cm^{-1} and 32 scans. Electronic spectra in the range of 320–700 nm were measured in methanol solutions on a Shimadzu 1605 UV–Vis spectrophotometer. ^{1}H NMR spectrum of the ligand was recorded in acetone d_6 on a 400 MHz Bruker nuclear magnetic resonance spectrometer. The Mn contained in clay material was determined using a Varian atomic absorption spectrometer (AAS) model SpectAA-10 Plus. Cyclic voltammetry was performed with an EG&G Princeton Applied Research potentiostat/galvanostat (model 263A) using the M270 Electrochemical Analysis Software and a conventional 5 mL three-electrodes cell. A cavity microelectrode (50 μm diameter and 17 μm depth) was the working electrode, an Ag/AgCl as a reference electrode and a platinum wire was the auxiliary electrode. The electrochemical experiments were carried out at 20 °C under a nitrogen atmosphere after 10 min of desaeration or under oxygen atmosphere after bubbling of pure dry oxygen gas during 10 min in the case of the catalysis study following the cytochrome P450 model.

2.3. Preparation of the ligand salen

The ligand *N*,*N*′-bis(salicylaldene) ethylenediamine (salen) was synthesized by refluxing 2-hydroxybenzaldehyde (Aldrich) and ethylenediamine (Fluka) in 1:2 M ratio respectively in absolute ethanol. Bright yellow spangles were obtained, filtered, washed by diethyl oxide then, with ethanol and dried at 50 °C under vacuum (84% yield).

IR (KBr): ν(C═N) 1635 cm^{-1}, ν(C—O) 648 cm^{-1}. ^{1}H NMR: δ: .96 CH_2—CH_2 (s, 4H); 7.32 CH_{arom} (m, 8H); 8,53 N═CH (s, 2H); 13,16 OH_{phenol} (s, 2H).

2.4. Preparation of the supported catalyst

The complex Mn^{III}Cl–salen was prepared *in situ* within the Algerian montmorillonite according to the flexible ligand method described by Fraile et al. [25]. Five gram of the Na–montmorillonite were slowly added to an aqueous solution of manganese (II) acetate tetrahydrated (Fluka, 1.837 g, 7.5 mmol) in 125 mL of methanol and the suspension was stirred for 24 h at room temperature. The solid obtained was filtered, washed with methanol and dried at 50 °C under vacuum. 1 g of this solid was added to 160 mL of methanol containing the ligand *salen* previously prepared (0.214 g, 0.8 mmol) and lithium chloride (Aldrich, 0.064 g, 1.5 mmol). The mixture was stirred and refluxed for 24 h. The obtained dark brown powder was filtered, washed with methanol and dried at 50 °C for 24 h. Mn^{III}Cl–salen (72% yield): IR (KBr) ν(C═N): 1628 cm^{-1}; ν(C═C): 1595 and 1530 cm^{-1}, ν(C—O):