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Electro- and magneto-electrochemistry of zeolite Y- and MCM-41-associated bipyrylium ion

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Abstract

The electrochemical response of bipyrylium bication [1,4-bis(3,5-diphenyl-4-pyrylium)phenylene] associated with Y and MCM-41 aluminosilicates (BTP@Y and BTP@MCM, respectively) is described using polymer-film electrodes immersed into Et_4N^+ + MeCN and Bu_4N^+ + MeCN electrolytes. BTP@MCM provides a solution-like response in all electrolytes consisting in two successive strongly comproportionation mediated one-electron reduction processes near to +0.05 and −0.12 V vs. Ag|AgCl. The response of BTP@Y in Bu_4N^+ + MeCN is restricted to a unique reduction process near to −0.40 V, while in Et_4N^+ + MeCN, it differs significantly: here, two reduction processes at −0.22 and −0.36 V appear. This response suggests the presence of different boundary-associated topological redox isomers for which no significant comproportionation reaction occurs. Under the application of a static magnetic field, the electrochemical response of BTP@MCM remains almost unchanged while that of BTP@Y in contact with Et_4N^+ + MeCN is sensitive to changes in the orientation and strength of the external magnetic field. Such magnetoelectrochemical effects are consistent with the idea that different boundary-associated orientation isomers of BTP@Y exist.

Keywords: Bipyrylium ion; Magnetoelectrochemistry; Y and MCM-41 aluminosilicates; Redox isomers

1. Introduction

Encapsulation of organic guests inside microporous solids has proved to be a general methodology for modulating their physicochemical properties. In particular, incorporation of electrochemically active ions into zeolites is of interest with regard to the development of electrocatalytic systems [1] and in the design of analytical sensors [2].

The mechanism of charge transfer at zeolite-modified electrodes, however, has been the subject of discussion [3–6]. Three basic models, extrazeolitic, intrazeolitic, and surface-mediated have been proposed [7,8]. Following Shaw et al. [9], in the extrazeolitic mechanism, the electron transfer process takes place outside of the zeolite being preceded by the ion exchange of electroactive species with electrolyte cations, whereas in the intrazeolitic mechanism the electroactive species remains in the supercages of the outer cavities or subsurface zones of the zeolite. In the surface mediated electron transfer mechanism, electroactive species of the zeolite surface undergo initial electron transfer and subsequently experience outer-sphere electron transfer processes with intrazeolite species [10–12].

The occurrence of extrazeolitic processes has been claimed by Baker and co-workers [13–16] from studies on silver zeolite-modified electrodes, and zeolite-associated methyl viologen [17]. The occurrence of intrazeolitic processes has been advocated by Bedioui and co-workers [18–20] on studying the voltammetric response of different zeolite-encapsulated transition metal complexes.

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Calzaferri et al. [21] have discussed the electrochemistry of methyl viologen-zeolite electrodes and silver and copper zeolite-modified electrodes [22–24], to describe the possibility of intrazeolite electron transport and intrazeolite ion transport mechanisms [24].

Upon examination of the electrochemistry of zeolite-modified electrodes and heterogeneous dispersions of zeolite-encapsulated transition metal complexes, Bessel and Rolison [25,26] developed the idea that electroactive species are restricted to a boundary region of zeolite grains. Electrochemical data consistent with the presence of different topological redox isomers in the case of the Mn(salen)N_3 complex (salen = *trans*-(*R*,*R*)-1,2-bis(salicyldeneamino)cyclohexane) and 2,4,6-triphenylthiopyrylium ion associated with zeolite Y have been previously reported [27,28]. This response can be interpreted within the models of Lovric and Scholz [29,29] and Oldham [30] on the redox conductivity of solid microparticles. As discussed elsewhere [31], voltammetric and chronoamperometric data on Y zeolite-associated Mn(salen)N_3 agree with the more recent formulation of such modelizations due to Schröder et al. [32].

It should be emphasized that the electrochemical pathway must be strongly dependent on the ease of migration of electroactive species from the zeolite matrix to the solution phase; thus, whereas single cations such as Ag^+ are able to pass to the electrolyte solution, bulky organic cations may remain entrapped into small cages of zeolites. Accordingly, it appears to be potentially interesting to explore the electrochemistry of large size organic cations unable to be exchanged with electrolyte cations. This is the case of bipyrylium bication, BTP^{2+} (=[1,4-bis(3,5-diphenyl-4-pyrylium)phenylene]), which can be prepared in zeolite Y cavities through a ship-in-a-bottle synthesis [33]. The crystalline structure of faujasite-type zeolite Y is formed by almost spherical supercages (14 Å diameter) interconnected tetrahedrally through smaller openings (diameter 7.4 Å). Accordingly, BTP^{2+} ions cannot be accommodated inside a single zeolite Y supercage and would require two neighbour supercages as indicated by molecular modelizations [33]. The synthesis, characterization and some preliminary electrochemical data of BTP@Y have been previously reported [33]. In the solution phase, BTP^{2+} ions display two consecutive one-electron reduction processes mediated by comproportionation, as depicted in Fig. 1.

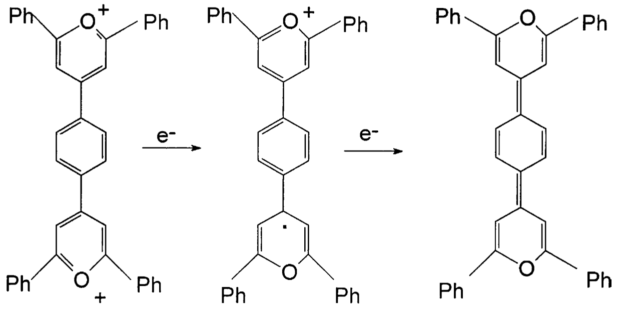

Fig. 1. Scheme of electron transfer processes involving BTP^{2+} in the solution phase.

In this context, Bessel and Rolison [25] suggested that, following the proposal of Turro and García-Garibay [34] in the study of zeolite-associated photochemical probes, different topological redox isomers; i.e., electroactive molecules located at different sites in the zeolite matrix, can exhibit distinctive electrochemical responses. Consistently, Dutta and Turbeville [35], on studying intrazeolitic photoinduced redox reactions between $Ru(bpy)_3^{2+}$ and methylviologen, proposed that there are particular orientations of the methylviologen molecules favouring the electron hopping. From such formulations, it is possible to assume that different orientation isomers are possible in the case of bulky molecules entrapped within the voids of zeolites.

The purpose of the current work is to describe the electrochemistry of bipyrylium bication associated with zeolite Y (BTP@Y) and to compare it with that of such an ion adsorbed on mesoporous MCM-41 aluminosilicate (BTP@MCM). Since MCM-41 has a channel diameter of 30 Å [36,37], the incorporation of BTP^{2+} should not be impeded by size. Since electron transfer processes in zeolite-associated species involves the ingress/issue of charge-compensating electrolyte cations on/to the zeolite pore and channel system, size exclusion-effects have been studied in comparing the electrochemistry of zeolite-modified electrodes in Et_4N^+ + MeCN and Bu_4N^+ + MeCN.

In order to assess the presence of boundary-associated species, and eventually orientation isomers, a series of magnetoelectrochemical experiments was performed. The study of electrochemical phenomena under the application of a magnetic field in solution electrochemistry can be considered as an increasingly growing research area. The effect of magnetic fields on electrochemical processes is threefold [38]: (i) they may cause energy level splitting in radicals (Zeeman effect); (ii) they may bring about diamagnetic orientation of aromatic molecules and, (iii) they may cause convection in the electrolytic solution (magnetohydrodynamic effect).

The magnetohydrodynamic effect has been studied by Fahidy [39,40], Waskaas [41–43], O'Brien and Santhanam [44], and Ragsdale et al. [45,46]. This effect is explained in terms of a gradient of paramagnetic ions in the vicinity of an electrode surface, i.e., in terms of magnetoconvection. More recently, Waskaas and Kharkats [47], have suggested that the magnetic field causes a transport of all ions because of the difference in the magnetic susceptibility in the solution at the electrode surface.