First Observation That Electroinactively Bound Cations in Clay Can Participate in Electrocatalytic Reaction

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The electrocatalytic oxidation of guanine by nontronite-bound electroinactive $Fe(bpy)_3^{2+}$ has been identified with a catalytic rate constant of 5.84×10^4 M s^{-1}.

One way to improve the charge transport in clay-modified electrode is to use the clay lattice acceptor/donor sites as relays to transfer electrons from the adsorbed cationic catalyst to the conductive substrates. Indeed, iron atoms in clay minerals have been known to act as electron donor/acceptor sites.[1,2] A serious problem encountered in such approach is the electroinactivation of the incorporated cationic catalyst. About 80% of the incorporated catalyst, which is roughly equivalent to the cation exchange capacity (CEC) of the clay, suffer this setback. While, only around 20% of the catalyst, present as ion pairs in excess of CEC respond to the applied potential, which limits the usefulness of clays as electrode surface modifiers.[3] For the first time we have observed that such electroinactively bound cations can be used as catalytic centers. Our results indicate that the nontronite-bound electroinactive $Fe(bpy)_3^{2+}$ together with the iron sites of nontronite can catalyze the guanine oxidation. Obviously, it would be highly beneficial if the stable, major electroinactive fractions can be used in chemical applications.

Cyclic voltammogram (CV) of the $Fe(bpy)_3^{2+}$-exchanged nontronite-modified glassy carbon electrode (NMGCE) prepared by the static ion-exchange method in pH 7.4 phosphate buffer showed well-defined reversible redox peaks at +0.85 V and +0.93 V (vs. Ag/AgCl). When the NMGCE is dipped into a solution containing $Fe(bpy)_3^{2+}$, Na^+ present in the clay structure is exchanged with $Fe(bpy)_3^{2+}$ to the extent of CEC by ion exchange mechanism. As reported earlier,[4] in the case of montmorillonite, the cation complex is exchanged in excess of the CEC as ion pairs and the $Fe(bpy)_3^{2+}$ bound in the CE sites are electroinactive due to the kinetic inertness. While, the intercalated ion pairs in excess of the CEC were proved electroactive. In effect, the CV obtained corresponds only to the small fraction of ion pairs present in the lamellar face to face channels of the phyllosilicates. Note that the CEC is relatively higher for nontronite (100 meq/100 g) than montmorillonite (87 meq/100 g).[1] Figure 1 shows the CV of the $Fe(bpy)_3^{2+}$-exchanged NMGCE in 100 μM guanine solution. As can be seen, in the presence of guanine, there is an additional peak A1 at +0.75 V apart from the redox peaks C2 and A2 of $Fe(bpy)_3^{2+}$-ion pairs. Note that there was no discernible direct oxidation peak for guanine on NMGCE noticed in this concentration. Thus, the additional wave-shaped peak A1, arises from the catalytic oxidation of guanine. The oxidation of guanine at A1 is probably mediated by the electroinactively bound $Fe(bpy)_3^{2+}$ for the following reasons. First, the peak current ratio of A1 to A2 increases as the scan rate decreases, i.e., this ratio is inversely proportional to the scan rate. Second, the peak A1 is wave-shaped. These observations lead to the conclusion that this new peak is due to a catalytic process.[5] Third, more importantly, the cathodic to anodic peak current ratio for the C2/A2 process is retained at a value close to unity in all scan rates studied. These results imply that the intercalated electroactive ion pairs of $Fe(bpy)_3^{2+}$ are oxidized reversibly, and does not involve in the guanine oxidation. It seems that the only candidate involving in the catalysis is the $Fe(bpy)_3^{2+}$ bound to the CE site of the clay, which is electroinactive.

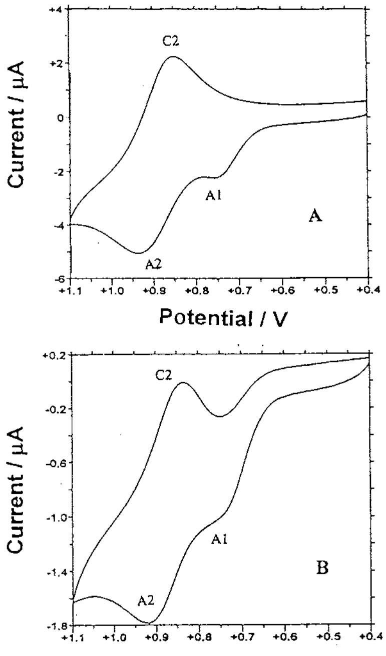

Figure 1. Cyclic voltammograms of the $[Fe(bpy)_3]^{2+}$ exchanged NMGCE in 100μ M guanine + pH 7.4 phosphate buffer solution at a scan rate of (A) 100 mV s^{-1} and (B) 10 mV s^{-1}.

To confirm the above proposition, the $Fe(bpy)_3^{2+}$-exchanged NMGCE was dipped into the buffer solution. After 24 h, no peak could be observed indicating that all the electroactive ion pairs have leached out of the clay.[4b] Then, this electrode was transferred to the guanine containing solution and the CV obtained is shown in Figure 2. Compared to the CV of the NMGCE, the oxidation current for guanine oxidation was very high. This confirms that the electrocatalysis observed is due to the participation of the bound $Fe(bpy)_3^{2+}$ in the interlayer space. The removal of the electroactive ion pairs and the strong binding of electroinactive $Fe(bpy)_3^{2+}$ at CE site was further confirmed from the spectral studies. The electronic spectrum for $Fe(bpy)_3^{2+}$-exchanged clay cast on optically transparent ITO electrode showed two overlapped shoulders at 498 nm and 532 nm, respectively.[6] Note that the modified ITO

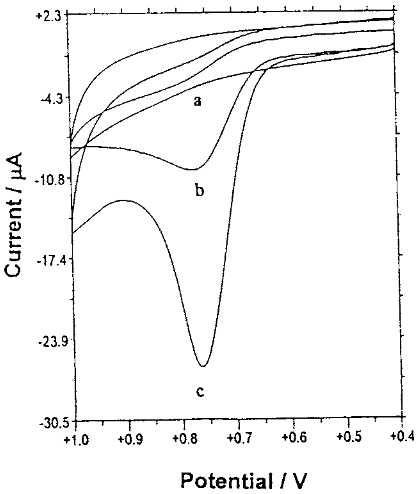

Figure 2.(a) Cyclic voltammogram of the $[Fe(bpy)_3]^{2+}$ exchanged NMGCE recorded after dipping it in pH 7.4 phosphate buffer solution for 24 h. (b) The NMGCE in 200 μM guanine containing pH 7.4 phosphate buffer solution. (c) same as (a) but the CV was recorded in the presence of 200 μM guanine.

electrode showed CV similar to that of the $Fe(bpy)_3^{2+}$-incorporated NMGCE. Next, the electrode was allowed to stand in buffer solution for 24 h and then the CV was performed. It failed to give any voltammetric response. Interestingly, the same electrode gave visible spectrum with 498 nm and 532 nm bands but with little decrease in optical density.

In effect, the $Fe(bpy)_3^{2+}$ adsorbed in the CE sites in concomitant with the Fe^{3+} in nontronite catalyze the reaction (Figure 3). In the scheme, the electroinactive $Fe(bpy)_3^{2+}$ chemically reacts with Fe^{3+} centers of nontronite to form Fe^{2+} and $Fe(bpy)_3^{3+}$.[7] The $Fe(bpy)_3^{3+}$ formed subsequently oxidizes guanine as it is well known to involve in the electron transfer in the guanine moiety of DNA.[8] The Fe^{2+} formed in nontronite is instantaneously oxidized to Fe^{3+} through the initial applied potential of +0.4 V, which is more positive than the E^0 of $Fe^{2+/3+}$ couple of nontronite clay,[1] and thus forms a perfect catalytic cycle. In the absence of guanine, the electroinactive $Fe(bpy)_3^{2+}$ may be expected to yield redox peaks according to the reaction mechanism. However, in such a case, the electroinactive $Fe(bpy)_3^{2+}$ should act as the substrate instead. As it is well known that the electrocatalytic reaction is pseudo-first order, the concentration of electroinactively bound $Fe(bpy)_3^{2+}$ is too little to act as substrate for such a catalytic process and to give any observable catalytic peak. The catalytic reaction scheme for guanine oxidation is typical of surface-modified electrode catalyzing the solution phase substrate.[9] The amount of $Fe(bpy)_3^{2+}$-exchanged can be calculated from the CEC of the total amount of clay coated. Since the chelate bears +2 charge, the number of gathered $Fe(bpy)_3^{2+}$ would be equal to one-half of the cation exchange sites of the clay.[6b] The 0.07 cm^2 GCE surface was covered with 6 μl of 0.1 wt% clay suspension yielding 6.42×10^{-12} molar equivalents of exchange sites on the electrode surface. This gives a notion that 100% exchange of the clay will acquire 4.58×10^{-11} mole cm^{-2} of the surface concentration of the chelate, which is reminiscent of monolayer surface coverage. The dimensionless peak current function, $i_p/[nFACA(DAnFv/RT)^{1/2}]$, was found to be a constant value of 0.498 for various concentration of guanine studied. The catalytic rate constant, k_{cat}, can then be estimated as done in previous studies.[10] Briefly, the dimensionless current function is given as a function of $\log[lk_{cat}t/(DAnFv/RT)^{1/2}]$, where l is the number of layer and other symbols assume usual significance. The average k_{cat} value calculated, with l = 1 for monolayer, is found to be 5.84×10^4 M s^{-1}. The observed catalytic constant is comparable to the rate constant of electron transfer to NADH from the surface confined quinone.[10]

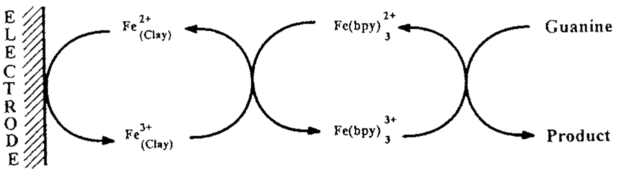

Figure 3. The reaction mechanism of the electrocatalytic oxidation of guanine on the $[Fe(bpy)_3]^{2+}$-incorporated NMGCE.

References and Notes

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7 Chemical reaction between $Fe(bpy)_3^{2+}$ and Fe^{3+} of clay and oxidation of Fe^{2+} through initial applied potential occur as coupled events, since, in the open circuit conditions, there is no chemical reaction between Fe^{3+} in clay and clay bound $Fe(bpy)_3^{2+}$ observed.
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