

Synthesis and Characterization of the Host-Guest Nanocomposite Material Zeolite Y-Iron Bipyridine

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Abstract: This paper reports the synthesis of host-guest nanocomposite material $[\text{Fe}(\text{bpy})_3]^{2+}\text{Y}$ (where bpy=2,2'-bipyridine) using the flexible ligand method. X-ray diffraction analysis, adsorption technique, and cyclic voltammetry were used to characterize the material. The results show that $[\text{Fe}(\text{bpy})_3]^{2+}$ has been entrapped in the supercage of zeolite, its electron transfer is realized by electron hopping of $[\text{Fe}(\text{bpy})_3]^{2+}$ within the supercage of zeolite.

Keywords: Host-guest nanocomposite material, zeolite Y, iron bipyridine, intrazeolite electron transfer.

Zeolites have the defined crystalline structures with the channels or cages of nanoscale dimensions. These channels or cages of zeolites can offer the loading sites to self-assemble and stabilize the entrapped guest within the zeolites that can be used for useful matrixes to produce nanoguests materials¹. Because this kind of materials showed some special property², it has aroused much interest³. A new field of investigation for the entrapped metal complexes has been developed in electro-assisted catalysis of organic reaction⁴. At present, there are three approaches to the preparation of these ship-in-a-bottle chelate complexes, namely (i) the flexible ligand method, (ii) the template synthesis method, and (iii) the zeolite synthesis method. In the first approach, the flexible ligand must be able to diffuse freely through the zeolite pores, where it coordinated to the previously exchanged transition metal cations to form the ship-in-a-bottle complex. The complex has kinetic diameter greater than 0.74 nm (the diameter of channel of zeolite) and is not capable to escape from the interior of the zeolite readily, and has been generally characterized by UV-Vis, IR, XRD, and XPS. A few papers^{5,6,7} have reported the characterization of intrazeolite complex using voltammetry, all preformed in organic phase. Meanwhile, intrazeolite or extraelectron electron transfer of the complexes entrapped in the supercage formed by flexible ligand method is a focal point of discussion in the field of zeolite modified electrodes^{7,8}. Moreover, the electrochemical characterization of intrazeolite transition metal complexes in aqueous solutions has not been reported (to our knowledge). Our results demonstrate that the complex formed by flexible ligand method has been entrapped in supercage and its electron transfer belongs to intrazeolite electron transfer realized by electron hopping

of $[\text{Fe}(\text{bpy})_3]^{2+}$.

Experimental

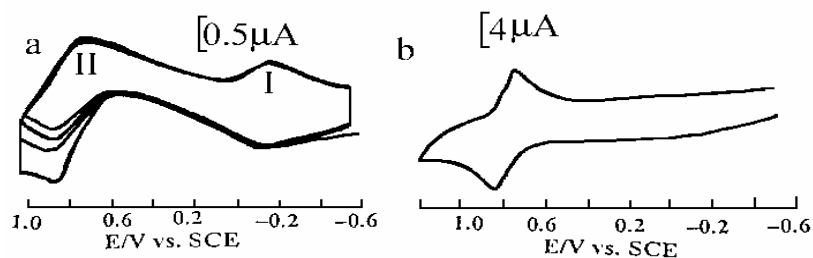
X-ray diffraction analysis was carried out on a Rigaku D/MAX IIIA diffractometer. Adsorption experiment was made using CAHN200 adsorption instrument. Cyclic voltammetric experiments were performed on a Model 79-1 Voltammetric Analyzer. Cyclic voltammograms were recorded on an RDK-RW-117 X-Y recorder (Japan). NaY was supplied by Lanzhou Refinery. Other reagents in the experiment were of reagent grade and used as received. All solutions were prepared with doubly distilled water.

Fe^{2+} was introduced into NaY *via* ion exchange using the ammonium ferrous sulfate. $[\text{Fe}(\text{bpy})_3]^{2+}\text{Y}$ was prepared by combining 1.0 g of Fe^{2+}Y with 91 mg of bipyridine at 120 °C for 65 h, during which the zeolite developed a pink color. The zeolite was then washed with 10 ml portions of H_2O for three times, and dried at 110 °C for 2 h. This zeolite was Soxhlet extracted with dichloroethane until no bipyridine could be eluted for *ca.* 48 h. The dried product was characterized by XRD and adsorption technique. $[\text{Fe}(\text{bpy})_3]^{2+}\text{Y}$ Zeolite-modified electrode ($[\text{Fe}(\text{bpy})_3]^{2+}\text{Y-ZME}$) was prepared by adding a 20 : 1 suspension formed by 50 mg $[\text{Fe}(\text{bpy})_3]^{2+}\text{Y}$, 5 mg polyvinyl chloride and 0.3 ml dichloroethane to blank glassy carbon electrode and drying in the air.

Results and Discussion

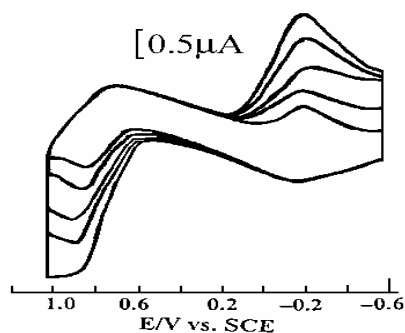
No loss of crystallinity is observed after entrapping complex from XRD analysis. The adsorptive capacity of NaY for water is 50.4%; that of $[\text{Fe}(\text{bpy})_3]^{2+}\text{Y}$ is 12.2%. This shows the volumes of the pores of the zeolite Y obviously decreased, proving that the complex may mainly locate in the supercage of zeolite Y. **Figure. 1a** shows cyclic voltammogram of $[\text{Fe}(\text{bpy})_3]^{2+}\text{Y-ZME}$ in 0.1 mol/L Na_2SO_4 , in which two pairs of peaks denoted I and II are observed. The intensity of the peak I does not decay with either immersion time or number of redox cycles, neither does the peak II after equilibrium having been built (*ca.* after four cyclic voltammetric scans).

Figure. 1. Voltammograms of (a) $[\text{Fe}(\text{bpy})_3]^{2+}\text{Y-ZME}$ in 0.1 mol/L Na_2SO_4 (from outer to inner curve: first, second, third, and fourth cycle), and (b) the glassy carbon electrode in 0.1 mol/L Na_2SO_4 solution containing 1×10^{-3} mol/L $[\text{Fe}(\text{bpy})_3]^{2+}$.



When electrode was immersed in 0.1 mol/L Na_2SO_4 for 14 d, no color is observed in neutral solution, whereas, a pale pink color is observed in acidic solution after immersing for only 2 h. This fact shows the complex can not leak from supercage in neutral medium, and can readily leak from supercage realized by ion-exchanged between H^+ and Fe^{2+} . **Figure. 1b** shows cyclic voltammogram of the glassy carbon electrode in 0.1 mol/L Na_2SO_4 solution containing 1×10^{-3} mol/L $[\text{Fe}(\text{bpy})_3]^{2+}$. From **Fig. 1b**, it can be seen that there is only one pair of redox peaks of 0.86 V of E_{pa} , and 0.78 V of E_{pc} . Comparison of the results obtained from **Figure. 1a** and **Figure. 1b**, we conclude that the process characterized by peaks II has been ascribed to the redox system $[\text{Fe}(\text{bpy})_3]^{3+}/[\text{Fe}(\text{bpy})_3]^{2+}$. From literature⁹, we know that the $[\text{Fe}(\text{bpy})_3]^{2+}$ has mono-, bis-, tri-coordination, and that the $[\text{Fe}(\text{bpy})_3]^{3+}$ only has a mixed ligand complex with hydroxyl that is more stable than $[\text{Fe}(\text{bpy})_3]^{3+}$. Therefore, we infer peak I is evoked by the mixed ligand complexes with hydroxyl formed by the combining the complex and hydroxyl of zeolite internal surface. Furthermore, the $[\text{Fe}(\text{bpy})_3]^{2+}$ -Y-ZME can conduct current in the absence of electron transfer mediators, namely, $[\text{Fe}(\text{bpy})_3]^{2+}$ entrapped in the supercage of zeolite can produce current by electron hopping of $[\text{Fe}(\text{bpy})_3]^{2+}$. **Figure. 2** shows cyclic voltammogram of potassium bichromate in 0.1 mol/L Na_2SO_4 at $[\text{Fe}(\text{bpy})_3]^{2+}$ -Y-ZME. It is also obvious that the responding current increased with concentration of potassium bichromate. Bichromate anion can not cross thick zeolite film to base electrode; therefore, in the absence of electron transfer mediator, current conduction of bichromate anion is realized by electron hopping of $[\text{Fe}(\text{bpy})_3]^{2+}$ within the supercage. All experimental results illustrate that $[\text{Fe}(\text{bpy})_3]^{2+}$ -Y-ZME can realize intrazeolite electron transfer.

Figure. 2. Voltammogram of potassium bichromate at $[\text{Fe}(\text{bpy})_3]^{2+}$ -Y-ZME (from inner to outer curve: base electrolyte, 0.17, 0.34, 0.51 and 0.68×10^{-3} mol/L potassium bichromate)



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