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Encapsulation of Bis(ethylenediamine) Copper(II) Complex in Zeolite Matrices
- Comparison with Encapsulation of Natural Enzymes Like Cytochrome-C and Vitamin-B_{12} -

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Abstract−Bis(ethylenediamine) copper(II) complex was encapsulated in NaY, KL, Naβ and NaZSM-5 zeolite. The redox properties of metal complexes in neat and encapsulated state were studied by cyclic voltammetry. The redox potential of metal complex is altered towards negative value upon encapsulation in various zeolites. This may be due to axial interaction with various zeolite matrix. The redox properties of biological systems are also altered (cytochrome-C, and Vitamin-B_{12}) when they are immobilized on NaAlMCM-41 materials. The copper ethylenediamine complex in constrained environment shows higher activity for the oxidation of dimethyl sulfide compared to that of neat complex.

Key words: Encapsulation, Zeozymes, Redox Potential, Cyclic Voltammetry, Cytochrome-C, Zeolites, Oxidation

INTRODUCTION

The catalytic properties of transition metal complexes encapsulated in various zeolites have been examined exclusively [Viswanathan, 1996]. These materials hold the promise of combining the advantages of homogeneous and heterogeneous catalytic systems. The active transition metal site differs from the solution species in that the species are constrained by the zeolites [Chavan et al., 2000]. It allows reactions to occur under milder conditions.

The lifetime of the catalyst can be influenced by its encapsulation, since degradation pathways involving reactions such as dimerization of catalysts can be prevented. Due to these features the zeolite encaged metal complexes resemble to a certain extent enzymes where the catalytic center might be a transition metal ion, and the protein provides the stability and stearic constraints. Inorganic complexes encapsulated in such porous systems can therefore be termed as zeozymes [Deshpande et al., 1999].

The biomimetic process requires a system, which exhibits multifunctional properties such as charge separation, electron transport and multi electron transfer. One of the possible ways of obtaining this type of multifunctional property is by encapsulating metal complexes in various zeolites. Selectivity is imposed in natural systems by virtue of altering redox potential of metal complexes in various protein mantles [Clark, 1960]. As in the biological systems, one can alter the redox potential of synthetic complexes by encapsulating them in various zeolites. By knowing the redox potential of metal complexes in various zeolites, one can choose a good system for a particular reaction. The reasons for the alteration of redox potential of metal complexes in biological systems as well as in zeozymes are not well known. By using the physical properties of various zeolites, one can correlate the redox potential of metal complexes with various properties of zeolites. In this present work, bis(ethylenediamine) copper(II) (Cu-en) was encapsulated in NaY, KL, Naβ, NaZSM-5 and NaAlMCM-41 materials. The redox properties of metal complexes were studied by using cyclic voltammetry. In order to compare biological system with zeozymes, cytochrome-C and Vitamin B_{12} were immobilized in NaAlMCM-41 materials. The oxidation of dimethyl sulfide was carried out using neat and zeolite-encapsulated copper ethylenediamine complex.

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EXPERIMENTAL

Neat bis(ethylenediamine) copper(II) nitrate complex and copper exchanged zeolites and NaAl-MCM-41 were prepared according to the method given in literature [Vogel, 1964; Herman and Flentge, 1978; Basab, 1998]. Encapsulation of copper ethylenediamine complexes in various zeolites was done as follows: Copper exchanged zeolites were calcined at 473 K. About 1 g of dried copper exchanged zeolites were suspended in 25 ml of ethylenediamine in a sealed round bottom flask and stirred for 24 hours. The resulting violet colour material was filtered, washed with excess water and dried at room temperature.

Immobilization of cytochrome-C was done by taking 10 mg of cytochrome-C in 5 mL of 0.1 M phosphate buffer (pH=6) and stirred with 100 mg of MCM-41 for 2 hours in an ice bath. The red coloured solid was filtered, washed with excess phosphate buffer and dried at room temperature in air.

Immobilization of vitamin B_{12} was done by taking 100 mg of vitamin B_{12} in 10 ml of 0.1 M phosphate buffer (pH=9) and stirred with 100 mg of MCM-41 material for 24 hours at room temperature. The red coloured solid was filtered, washed with excess phosphate buffer and dried at room temperature.

The cyclic voltammograms of neat and encapsulated complexes were recorded on a Wenking potentioscan POS73 with digital 2000 X-Y recorder. The working electrode was prepared by taking 1 : 1 weight ratio of zeolite-encapsulated metal complexes/MCM-41-immobilized biological system and vulcanXC-72 carbon and dispersed in 1 ml of water. This suspension was ultrasonicated for fifteen minutes. 10 μL of this dispersion was coated on glassy carbon and 5 μL of 5% nafion (Aldrich, binder) was added on these coatings and dried. This glassy carbon was used as working electrode.

Pt foil was used as counter electrode and Ag/AgCl/KCl (saturated) as reference electrode. A cyclic voltammogram of neat Cu-en complex was taken in solution mode by dissolving 0.01 M of metal complex in 0.1 M phosphate buffer (pH=7). The cyclic voltammaogram for neat cytochrome-C and neat Vitamin B_{12} was recorded in phosphate buffer (pH=6 and 9 respectively).

Liquid phase oxidation of dimethyl sulfide was carried out in a glass reactor (double necked round bottom flask (50 mL). The reactor was equipped with reflux condenser. In a typical experiment, 100 mg of the desired catalysts was dispersed in 5 ml of water and 1 : 1 mole ratio of DMS and 30% hydrogen peroxide were added and stirred for 24 hours. At the end, the reaction mixture was centrifuged and the products were analyzed in a gas chromatograph (Nucon) equipped with OV 17 column.

RESULTS AND DISCUSSION

The cyclic voltammogram of neat complex shows a couple of peaks with values of E_{pc} peak (cathodic) at 238 mV and E_{pa} peak (anodic) at 4 mV (Fig. 1(a)). This redox process associated with the cathodic peak is reduction of copper ethylenediamine to copper ($Cu(en)_2^{2+}/Cu$) and the anodic peak is oxidation of deposited copper metal to copper cation (Cu/Cu^{2+}) [Senaratne et al., 1996] (Fig. 1(a)). A summary of these measurements is given in Table 1. The peak potential altered with respect to scan rate and plot of peak current with respect to square root of scan rate shows linear behavior. This shows that redox process ($Cu(en)_2^{2+}/Cu$) is quasi-reversible in nature. Upon encapsulation in various zeolites, the reduction potential ($Cu(en)_2^{2+}/Cu$) is altered towards more negative value and peaks are broadened (Fig. 1(b)). The alteration of peak potential towards more negative value upon encapsulation indicates the stabilization of Cu^{2+} oxidation state in zeolite cages. This may be due to axial interaction with zeolite matrix. The alteration of peak potentials indicates that the metal complex is not having the same geometry as in the neat complex but undergoes distortion inside the zeolite matrix. In the case of NaY and KL zeolites, different electrochemical responses were observed. In order to ascertain whether different electrochemical responses were due to uncomplexed copper cations or copper complexes present on the external surface, a cyclic voltammogram was recorded for copper exchanged NaY, KL and Naβ zeolites and physical mixture of copper ethylenediamine and NaY zeolites. The peak potentials for copper exchanged NaY, KL, Naβ and physical mixture of copper ethylenediamine and NaY zeolites (Cu^{2+}/Cu redox

Table 1. Cyclic voltammetric data for neat and zeolite-encapsulated Cu-en complexes

Catalyst	E_{pc} (mV)	E_{pa} (mV)
Cu-en	−238	−4
Cu-en-NaY	−672	−96
	−308	
Cu-en-KL	−268	−64
	−504	
Cu-en-Naβ	−516	−96
Cu-en- MCM-41	−504	−20
Cu-en- NaZSM-5	−397	+86
Cu-NaY	−252	276
Cu-KL	−240	−36
Cu-Naβ	−268	172

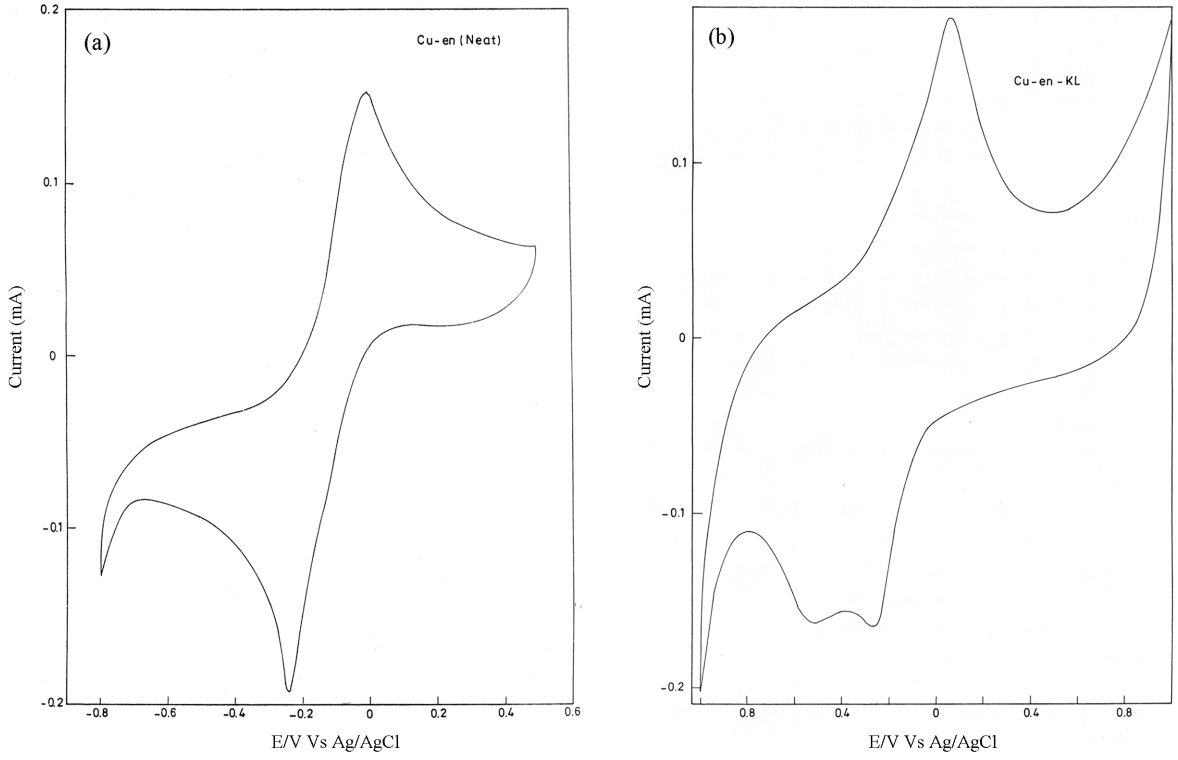

Fig. 1. Cyclic voltammogram of (a) Cu-en (Neat) (b) Cu-en-NaY.

process) are totally different from that of copper ethylenediamine complex encapsulated in various zeolites. This indicates that copper ethylenediamine complex is encapsulated inside the zeolite matrix and not present on the external surface. When copper exchanged zeolites were treated with ethylenediamine, the redox potential of Cu^{2+}/Cu shifted towards a more negative value. This is due to the increase of crystal field stabilization energy as one goes from hexa aqua copper complex to bis ethylenediamine copper complex. Due to axial interaction with various zeolites and distortion of metal complexes inside the zeolite matrix, peak potentials are altered in various zeolites. Different electrochemical responses are due to copper ethylenediamine complex present in different positions of zeolites. Because of the partial covalent character of the aluminosilicate crystals, electrons are not localized on the framework atoms, rather they are partially delocalized [Sauer, 1989]. When a metal complex interacts with an active site, it will perturb all the active sites present within the zeolite, so that the complex will have different interaction energy and altered redox potential at different places of zeolite. Charge distribution along the framework owing to the partial ionic character of the aluminosilicate crystal generates a strong columbic field inside the cavities, which might activate the metal complex. Field gradients exist because of the zeolite geometry, cages, channels, side packets and charge distribution [Utterhoeven et al., 1992]. This may alter the energy levels of the metal complex so that metal complexes present at different locations of zeolite have altered redox potentials.

The redox potential of a metal complex is altered when it is encapsulated in zeolite matrix. In order to determine the redox properties of biological system in constrained environments, cytochrome-C and Vitamin B_{12} were immobilized on MCM-41 materials. The electrochemical data for neat and encapsulated cytochrome-C are given in Table 2. The redox potential of cytochrome-C is altered towards more positive value upon encapsulation in MCM-41. This is further supported by the observation reported in the literature where cytochrome-C is immobilized on MCM-48 [Kriel et al., 2000]. In the literature, this shift is attributed to the conformational change of the protein mantle. These observations can be explained as follows. There are two possible interactions when the cytochrome-C is encapsulated in zeolite matrix. The protein mantle can interact with Bronsted acid site of the zeolite matrix, which may alter the geometry of the iron porphyrin active site. Moreover, the axial position of iron porphyrin moiety can also interact with surface hydroxyl groups of zeolite matrix. The net effect leads to the alteration of the redox potential. The redox potential of biological enzyme can also be altered in zeolites as in the metal complexes.

The vitamin B_{12} undergoes redox process at E_{pa} of −790 mV and E_{pc} of −958 mV. The redox process corresponds to Co(II)/Co(I) (Fig. 2(a)). Upon encapsulation in NaAl-MCM-41 the reduction potential is shifted towards more positive values (Table 2) while the anodic peak potential is not affected (Fig. 2(b)). This may be due to change of axial coordination inside the zeolite matrix as in the zeozymes.

Table 2. Electrochemical properties of neat and immobilized biological systems

Catalyst	E_{pa} (mV)	E_{pc} (mV)	$E_{1/2}$ (mV)
Cytochrome-C	93	26	59.5
Cytochrome-C	150	110	130
Cytochrome-C	170	130	150
Vitamin-B_{12}	−790	−958	-
Vitamin-B_{12}/MCM-41	−791	−841	−816

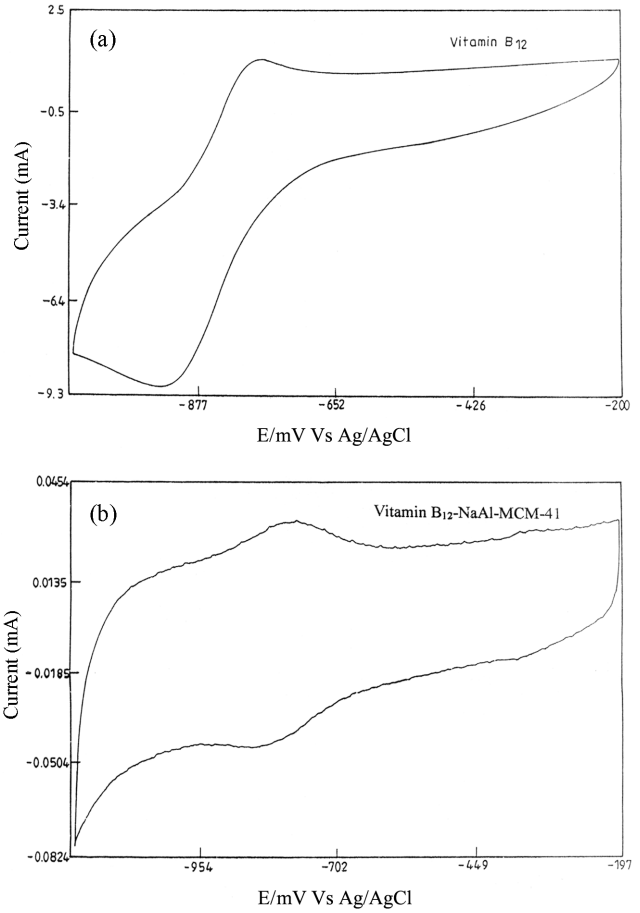

Fig. 2. Cyclic voltammogram of (a) Vitamin-B_{12} (Neat) (b) Vitamin-B_{12}-NaAlMCM-41.

CATALYTIC ACTIVITY

The catalytic activity towards oxidation of dimethyl sulfide was carried out by using neat and encapsulated copper ethylenediamine complexes. The results are given in Table 3. The neat complex is showing lower activity for the oxidation of dimethyl sulfide. Turn

Table 3. Catalytic activities towards oxidation of DMS by neat and encapsulated Cu-en complexes

Catalyst	Conversion dimethyl sulfoxide mole (%)	TON
Cu-en	0	0
Cu-en-NaY	75.1	466
Cu-en-KL	99.3	1,383
Cu-en-Naβ	95.0	1,050
Cu-en-ZSM-5	98.8	1,597
Cu-en-MCM-41	81.3	1,313

over number increases upon encapsulation of copper ethylenediasmine complex in various zeolites. This may be due to alteration of redox potential of copper ethylenediamine complex in various zeolites.

CONCLUSION

Copper ethylenediamine complexes are encapsulated in NaY, KI, MCM-41, Naβ and NaZSM-5 zeolites. Alterations in redox properties of zeolite-encapsulated complexes can be accounted for on the basis of physical properties of zeolites employed. The redox potential of cytochrome-C can be altered in the zeolites as in the metal complexes. Catalytic activity of copper ethylenediamine complex shows higher TON upon encapsulation in various zeolites.

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