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Zeolite-Encapsulated Zinc (II)-Amino Acid Complex: Synthesis and Spectroscopy

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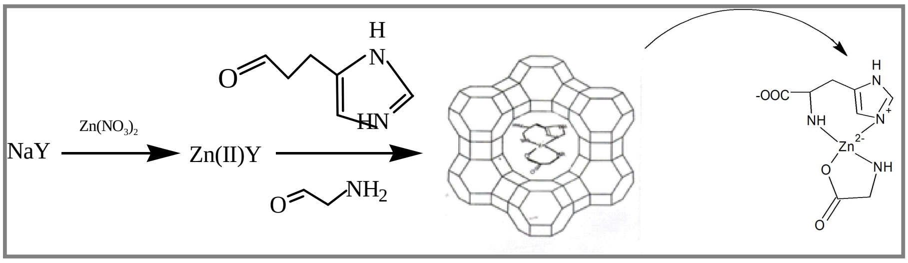
ABSTRACT

Nanocavity Zeolite Y encapsulated Zn(II) complexes of Histidine and Glycine is synthesized insitu in Na-Y-Zeolite by the reaction of ion exchanged metal ions, with the flexible ligand molecules that had diffused into the cavities. The encapsulated complex is characterized by SEM, XRD, FTIR spectroscopy with a view to confirm the encapsulation of the complex and to arrive at the composition, structure and geometry of encapsulated complex. Analysis of data indicates the formation of complexes in the cavities without effecting Zeolite frame work structure (XRD). The absence of any extraneous species is obtained from SEM.

Graphical Abstract



Flexible ligand Synthesis

Keywords: Na-Y Zeolite, Glycine, L-Histidine, Ion-Exchange, Flexible ligand Synthesis.

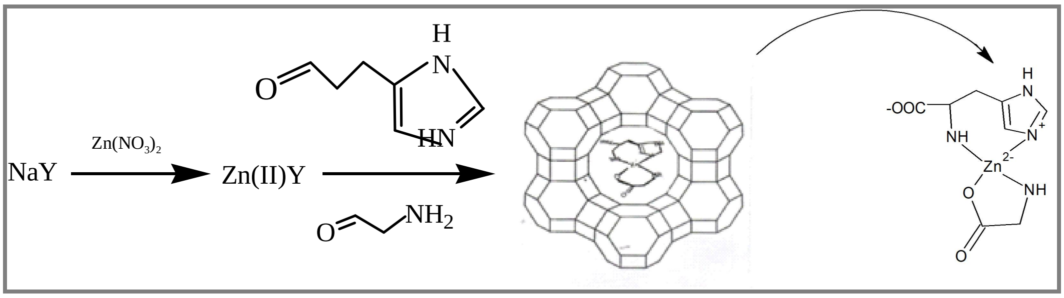
INTRODUCTION

Zeolites are hydrated aluminosilicates of the alkali and alkaline-earth metals with fully cross-linked open framework structures made up of corner sharing SiO_4 and AlO_4tetrahedra[1]. Both natural (analcime, chabazite, clinoptilolite) and synthetic zeolites (A, X, Y and ZSM-5) are used commercially because of their unique adsorption, ion-exchange, molecular sieve and catalytic properties. The encapsulation of transition metal coordination complexes [2] and organometallics within the voids of nanoporous zeolite has attracted attention since it provides a simple way of coupling the reactivity of the metal complex with the robustness and stereochemistry of the host zeolite [3–5]. Encapsulation provides a convenient route for the heterogenization of homogeneous catalytic processes, and indeed, these compounds have found application in catalysis and gas purification [6–19]. Nanodimensional pores of zeolite -Y are attractive hosts for encapsulation as they combine a high thermal and chemical stability with a quite regular, crystalline framework structure. Zeolite complexes posses a number of structural similarities to metalloenzymes and therefore they are expected to mimic enzyme active sites for the catalytic reactions, they are Oxidation, Hydrogenation, dehalogenation, friedal-craft alkylation. This study describes the synthesis and characterization of Zn(II) complex of histidine and glycine ligands. Encapsulation of the metal and the ligands in the nanocage of zeolite-Y generates the ternary complex. The complex was synthesized employing the flexible ligand method encapsulation technique. The structures of these encapsulated complexes were established on the basis of various physico-chemical and spectroscopic studies. The results indicated that the complexes did not hinder or modify the framework or structure of the zeolite, confirming successful immobilization of ligands through the voids of zeolite Y.

MATERIALS AND METHODS

$Zn(NO_3)_2$ is obtained from Merck co. Na-Y with Si:Al ratio of 2.53 were purchased from Aldrich. Glycine and L-Histidine were purchased from TCI. Tetrahydrofuran and DMF purchased from Merck. Methanol and ethanol were purchased from TCI. Hydrogen peroxide was purchased from Aldrich.

Preparation of zeolite encapsulated Zn(II) complex: The synthetic route of encapsulated complex is presented in scheme 1. The synthesis was carried out in two steps employing the general flexible ligand method, preparation of metal exchanged zeolite, M-Y (M=Zn(II)) and synthesis of zeolite-Y encapsulated metal complex.



Scheme 1. Flexible ligand Synthesis.

Preparation of metal exchanged zeolite, Zn (II)-Y: Zn(II) exchanged-Na-Y zeolites was synthesized according to the method described by Xavier *et.al* [20]. To 2.0 g Na-Y suspended in 100 cm^3 deionized water was added Zn $(NO)_3$ (0.025 m) in order to exchange Na-ions of Na-Y with Zn(II) ions. The reaction mixture was stirred gently at 90°C for 24 h, filtered, precipitate washed with copious amount of hot deionized water until the filtrate was freed from any metal ion content. The resulting precipitate was dried at 80°C in hot -air oven for 10 h.

Synthesis of $[HIS\text{-}Zn\text{-}GLY]^{+2}$-Y Complex: Encapsulated complex was prepared using the flexible ligand method (scheme 1). To a stirred Methanol solution of Zn(II)Y (4g) was added 0.45 g of L-Histidine suspended in 100 cm^3 of MeOH and then refluxed for 8 h. The solid consisting of $[Zn(C_6H_9N_3)_2]^{+2}$ denoted as $[Zn(C_6H_9N_3)_2]^{+2}$-Y was collected by filtration, washed with ethanol, and dried at 80°C under hot air oven for 14 h. To a stirred MeOH suspension (100 cm^3) of $[Zn(C_6H_9N_3)_2]^{+2}$ -Y (2 g) were slowly added 40% glycine (0.632 g). The mixture was heated to reflux for 24 h. The solution was filtered and the resulting zeolite was soxhlet extracted with N,N-Dimethyl Formamide (for 4 h), and then Ethanol (for 3 h) to remove excess of unreacted products and any free metal complexes absorbed by on to the external surface of the zeolite crystallites. The resulting solids were dried at 90°C under hot air oven for 12 h [20].

RESULTS AND DISCUSSION

Scanning electron microscopy (SEM): In situ flexible ligand synthesis method (Scheme 1), leads to the encapsulation of Zn(II) Complexes of Histidine and glycine ligands within the nanocavity pores of zeolite. The ligands, which are flexible enough to diffuse through the zeolite channels, react with the pre exchanged metal ions in the supercage to afford the encapsulated complex. The product material was purified by extensive soxhlet-extraction with suitable solvent to remove unreacted ligand and surface complexes. The samples did not change their color on purification, indicating that the complexation has occurred in the cavities and that the resulting complexes are too large to diffuse out of zeolite through channels (figure 1). The SEM photographs of the samples taken before soxhlet extraction show the deposition of complexes on the external surface. However, the absence of extraneous materials in the SEM photographs of finished products indicates the complete removal of surface complexes and the particle boundaries on the external surface of are clearly distinguishable which could be accomplished by extended extraction procedure.

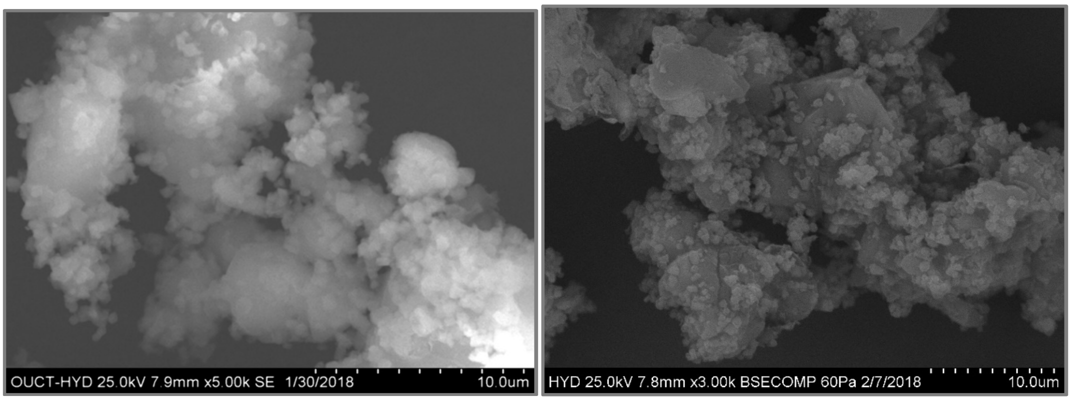


Figure 1. SEM photograph before and after soxhlet.

X-ray diffraction (XRD): The X-ray diffraction (XRD) patterns of zeolite containing histidine, glycine ligands complexes are similar to those of Zn(II) Y and the parent NaY. It shows that the zeolite crystallinity is retained on metal exchange and encapsulating conditions have little impact on the crystallinity of zeolite host [20]. Crystalline phase of free metal ions or encapsulation ligand complexes were not detected in any of the patterns as their fine dispersion in zeolite might have rendered them non-detectable by XRD (Figure 2).

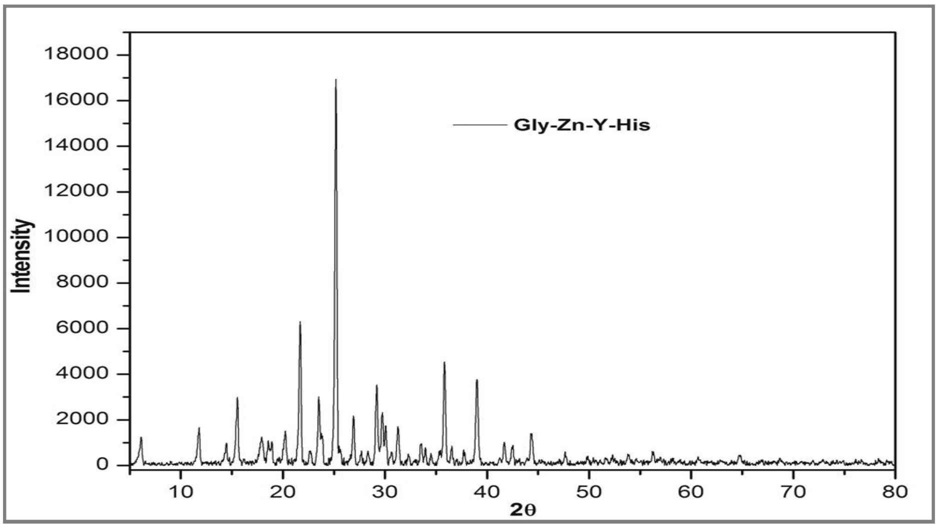


Figure 2. XRD of $(HIS\text{-}Zn\text{-}GLY)^{+2}Y$ Zeolite.

FTIR spectroscopy: IR spectra of Y-Na and metal-exchanged zeolites show strong zeolite lattice bands in the range 450-1200cm^{-1}. The strong and broad band at the region 1024 cm^{-1} could be attributed to the asymmetric stretching vibrations of (Si/Al) O_4 units. The broad bands at the region 1650 and 3500 cm^{-1} are due to lattice water molecules and surface hydroxylic groups (19). IR spectra of encapsulated complexes are presented in figure below. No shift of zeolite lattice bands is observed in the spectra of encapsulated complex, which further implies that the zeolite framework has remained unchanged upon the encapsulation of complexes. The coordination in the pores could be identified from the bands observed in the regions 1200-1600 cm^{-1}, where zeolite has no bands. However, the bands due to complex are weakly intense due to their low concentrations in the lattice. The vC=N observed at 1581 cm^{-1}, in the spectrum of free histidine has shifted to 1496, in the case of Y- His-Zn(II)-Gly. The lowering of stretching frequency suggests the coordination of imidazole nitrogen atom. The peaks at 1593, 1330 and 1128 cm^{-1} corresponds to vassy COO-, vsym COO- and vC-N stretching frequencies respectively, suggests the coordination of carboxylate and amino nitrogen group. Hence the encapsulation of His-Ni(II)-Gly complex is confirmed (Figure 3).

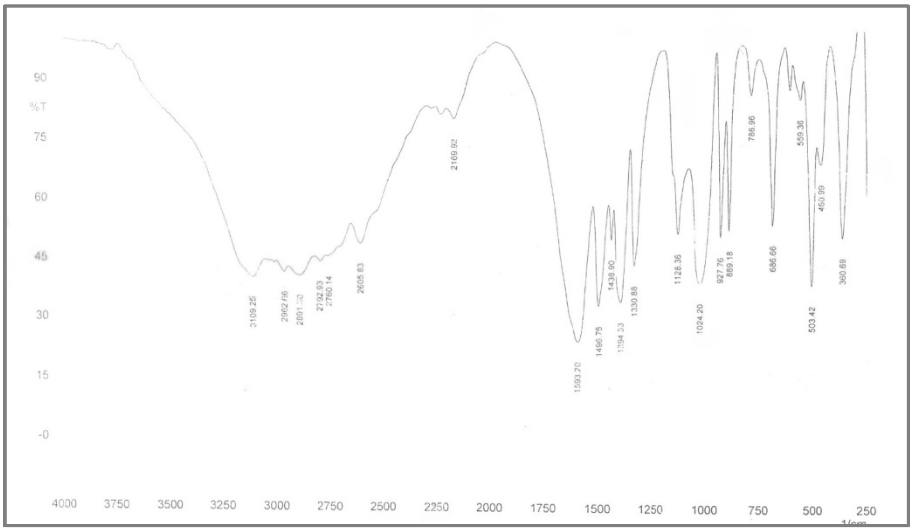


Figure 3. FTIR of (HIS-Zn-GLY)$^{+2}$Y Zeolite.

APPLICATION

Zeolite encapsulated complexes posses a number of structural similarities to metalloenzymes and therefore they are expected to mimic enzyme active sites for the catalytic reactions, they are oxidation, hydrogenation, dehalogenation, friedal-craft alkylation. In addition to these mimicking other catalytic reactions of zeolite encapsulated complexes include partial oxidation of benzyl alcohol and ethylbenzene with hydrogen peroxide. These catalysts are also active for oxidation at aerobic conditions. The catalytic behavior could be mainly attributed to the geometry of encapsulated complex. Encapsulated complexes can be recovered and reused without the loss of catalytic activity. To summarize, zeolite-encapsulated complexes have interesting catalytic potential particularly with respect to the activity for partial oxidation and stability, and offer further scope to design efficient catalyst systems by an appropriate choice of guest and host materials.

CONCLUSION

In summary, the results show that (HIS-Zn-GLY) complex can be encapsulated in the nanocavity of zeolite. Furthermore, the spectroscopic data suggest that the encapsulated complexes experience very little distortion in the super cage and that the chemical ligation to the zeolite surface is minimal. The zeolite framework keeps the guest complexes dispersed and prevent their dimerization leading to the retention of catalytic activity. Further studies include the design and synthesis of zeolite–encapsulated complexes for catalytic applications.

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