



Synthesis and Characterization of Zeolite-Encapsulated Copper(II) Complexes with Isomeric Benzoylpyridines

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An attempt has been made to encapsulate copper(II) complexes of 2-, 3- and 4- benzoylpyridines in the cages of zeolite Y by flexible ligand method. These complexes are characterized by infrared, electronic and X-ray diffraction techniques. The data revealed that Cu²⁺ ion is in a pseudo tetrahedral environment in the cages of zeolite without any modification of the morphology and structure of zeolite.

Key Words: Copper(II) complexes, Zeolite, Encapsulation.

INTRODUCTION

Synthesis and designing of materials with desired novel properties by controlled manipulation of their structure on the atomic level is a vibrant area of research today because of the potential of these materials in many modern technologies including catalysis. These materials are assembled from nanometer sized-building blocks consisting of the crystalline and large volume fraction of intercrystalline components. These materials possess a considerably higher surface areas. Zeolites (aluminosilicates) are one of the brilliant examples belonging to this group of materials, which are crystalline porous nano structures with long range crystalline order and pore size varied from about 4 Å to 15 Å. Their uniform intracrystalline micro porosity with channels and cages provide access to very large and well defined surfaces and their strong acidity promised unique opportunities for their wide range applications in catalysis¹.

Although catalysis by zeolites has developed to a certain maturity, a special category of catalyst with uniform catalytic sites is represented by zeolites containing catalytic species encapsulated inside its cages². The ordered structure of zeolites provide an ideal environment to encapsulate active metal complexes or metal clusters providing a new kind of catalysis which combines advantages of both homogeneous and heterogeneous catalytic system. General benefits of these systems, are their ruggedness and easy separation of catalyst from the reaction medium along with the possibility of using a large variety of different solvents and reaction conditions³⁻⁸. In these systems, the topology and dimensions of the zeolite cages are likely to have a profound influence on the geometry that the

encapsulated complex adopts, leading in-turn to appreciable changes in the electronic and magnetic properties. Furthermore, the encapsulated complex would be free to move within the confines of the cage and thereby retain some of the homogeneous properties. The reactivity of such complexes may be modified by the properties of zeolites⁹⁻¹⁴.

Until now, a variety of transition metal complexes consisting of porphyrins, phthalocyanines, amines and Schiff bases have been successfully encapsulated in zeolites, especially zeolite Y and which have shown improved catalytic properties in the oxidation of different types of organic substrates⁹⁻¹⁸. However, little attention has been paid to complexes based on pyridines and their derivatives. In the present work we report the encapsulation of copper(II) complexes with 2-, 3- and 4-benzoylpyridines (2-BOP, 3-BOP and 4-BOP) in the cages of zeolite Y. These isomeric benzoylpyridine possesses two potential sites (i) pyridine ring nitrogen and (ii) oxygen of the carbonyl group. These isomeric ligands have been chosen to check, if the steric position of carbonyl group affect the encapsulation process inside the zeolite pores. The physico-chemical properties of the resulting encapsulated complex is studied and compared with their neat complexes to describe the structural and textural properties of encapsulated species.

EXPERIMENTAL

Preparation of neat complexes: In the preparation of Cu (2-BOP), Cu (3-BOP) and Cu (4-BOP), the hot solutions of ligand (40 mmol in 10 mL methanol) were mixed with the hot solutions of the copper(II) sulphate (10 mmol in 20 mL methanol). The complexes which crystallized out or

precipitated immediately were suction filtered, washed with methanol and dried in an air oven at ~60 °C. (Yield *ca.* 80-85 % but in case of 2-BOP complex the yield was 10 %).

Preparation of Cu²⁺ exchanged zeolite Y [Cu(II)Y]: An amount of *ca.* 5 g NaY zeolite was suspended in *ca.* 500 mL distilled water containing CuSO₄ (50 mmol). Mixture was heated with continuous stirring at 90 °C for 24 h. After the exchange was completed, the solid was filtered, washed with hot distilled water to remove the excess of unreacted ions till the filtrate was free from any copper ions and then dried for 12 h at 120 °C in air.

Preparation of zeolite encapsulated Cu(II) complexes: Zeolite Y- encapsulated copper(II) complexes with isomeric benzoylpyridines were prepared by flexible ligand method^{19,20}. First Cu(II)Y was mixed thoroughly with excessive amounts of ligands in the ratio of 1:3 in a round bottom flask. The reaction mixture was heated at *ca.* 110 °C for 15 h in an oil bath with stirring, where ligand slowly diffused through the zeolite pores and formed complex with Cu²⁺ ions. The resulting solid was taken out and extracted with methanol till it becomes free from any unreacted ligand. Uncomplexed Cu²⁺ ions in the zeolite were then removed by exchanging with aqueous 0.01 M NaCl solutions. The resulting solid was further washed with hot distilled water until it is free from Cl⁻ ions. It was then dried at *ca.* 120 °C to constant weight.

Physico-chemical characterization: The percentage of copper(II) content in the neat and encapsulated complex was determined gravimetrically as oxinate after destroying the organic moiety first with concentrated nitric acid and then with concentrated sulphuric acid. Sulphate in the neat complex was estimated as BaSO₄ gravimetrically.

IR spectra were recorded as KBr pellet on a Perkin-Elmer spectrophotometer model 983. Electronic spectra were recorded in Nujol mull on a Shimadzu 1601 UV-VIS spectrophotometer. X- ray diffractograms were recorded using Philips PW 1140/90 X-ray powder diffractometer with CuK_α (λ = 1.5 Å) as the X-ray source with Ni filters.

RESULTS AND DISCUSSION

All the copper(II) complexes with 2-, 3- and 4- benzoylpyridines were encapsulated in the cages of zeolite Y by the flexible ligand method²⁰. First the preparation of Cu²⁺ exchanged zeolite was carried out by exchanging Na⁺ ions of NaY with 0.01 M solution of CuSO₄ in aqueous solution and then the heating of Cu(II)Y zeolite was done in excess of ligands at *ca.* 110 °C for 15 h. All the ligands 2-, 3- and 4-BOP are able to diffuse easily through the zeolite pores due to their flexible nature and get complexed with Cu²⁺ already embedded in the skeleton of zeolite matrix. The resulting complex inside the matrix cages of zeolite is now too large to come out of the pores. Neat complexes formed and excess of the ligands inside the pores as well as located on the surface of zeolite were removed by Soxhlet extraction in methanol. The percentage of Cu²⁺ ions were estimated gravimetrically and which suggest the encapsulation of metal complexes inside the cages of zeolite Y. All the complexes, neat as well as encapsulated inside the cages of zeolite Y were characterized by various physico-chemical techniques such as IR, electronic

absorption spectroscopy and X-ray diffraction. Analytical data of all the complexes are presented in Table-1.

TABLE-1
ANALYTICAL DATA OF NEAT AND ENCAPSULATED COMPLEXES

Complex	Colour	Cu (wt %)	m.p. (°C)	μ _{eff} (B.M.)
Cu (2-BOP) SO ₄	Green	17.6	194	1.48
Cu (3-BOP) ₂ SO ₄	Blue	11.3	212	0.99
Cu (4-BOP) SO ₄	Green	17.6	190	1.48
NaY	White	-	> 300	Diamagnetic
Cu(II)Y	Pale Blue	6.90	> 300	0.98
Cu(II)Y(2-BOP)	Light Blue	0.35	> 300	0.62
Cu(II)Y(3-BOP)	Pale Green	0.16	> 300	0.36
Cu(II)Y(4-BOP)	Light Blue	0.27	> 300	0.55

TABLE-2
INFRARED SPECTRAL DATA (cm⁻¹) OF LIGAND, NEAT AND ZEOLITE ENCAPSULATED COMPLEXES

Complex	ν(CO)	ν(C≡C) ν(C≡N)	Ring vibrations
2-BOP	1655	1570	998
		1555	600
			405
3-BOP	1657	1590	999
		1563	601
			402
4-BOP	1655	1570	998
		1557	601
			405
Cu(2-BOP)SO ₄	1656	1620	1027
		1590	630
			425
Cu(3-BOP) ₂ SO ₄	1657	1618	1025
		1585	635
			428
Cu(4-BOP)SO ₄	1652	1620	1020
		1598	618
			420
Cu(II)Y(2-BOP)	1656	1620	1025
		1588	630
			428
Cu(II)Y(3-BOP)	1657	1620	1025
		1585	635
			428
Cu(II)Y(4-BOP)	1654	1620	1022
		1592	614
			418

Each of the benzoylpyridine used here possesses two potential donor sites- (i) pyridine ring nitrogen and (ii) carbonyl oxygen. Significant absorption bands due to their carbonyl group remain either unperturbed or undergo slight positive shifts in the IR spectra of copper(II) sulphate complexes, thereby, indicating that these donor sites remain inert towards coordination. On the other hand, all the spectra exhibit appreciable perturbations in the fundamental frequencies of the pyridine part of the ligand molecules (Table-2). Absorption bands at *ca.* 1600 and 1550 cm⁻¹ due to ν(C≡C) and ν(C≡N) modes, respectively and the pyridine ring vibrations at *ca.* 990, 605 and 405 cm⁻¹ in the uncoordinated ligands undergo significant shifts to higher frequencies in the copper(II) complexes. These shifts indicate conclusively that coordination of 2-, 3- and 4- BOP take place *via* their pyridine ring nitrogen only^{21,22}.

Comparison of the infrared spectra of neat complexes with those of the corresponding encapsulated complexes facilitated the assignment of bands. It is interesting to observe that the spectra of all the encapsulated complexes showed essentially the similar bands, though weak in intensity. This weakness is due to their low concentration in zeolite matrix.

Moreover, the spectra of all the encapsulated complexes are dominated by the bands assignable to surface hydroxyl groups, internal and external vibrations of tetrahedral geometry of the type (Si, Al) O_4 ^{23,24}. Infrared spectral data, thus, support the encapsulation of the complexes in the cages of zeolite matrix.

Fig. 1 represents the electronic spectra of encapsulated complexes along with that of Cu(II)Y. The spectrum of Cu(II)Y showed a broad band centered at 670 nm assigned to ${}^2E_g \rightarrow {}^2T_{2g}$ transition in a tetragonal distorted octahedral environment around the Cu(II) ion^{24,25}. No band was observed above 300 nm in the spectrum of Cu(II)Y, however, spectra of encapsulated complexes in nujol displays two absorption bands at ca. 530 and 828 nm in the visible region. The former band is due to the symmetry forbidden ligand to metal charge-transfer transition while the later one is due to $d-d$ transition of the complex. These studies suggest that the complexes are encapsulated in the zeolite matrix in a pseudo-tetrahedral configuration²⁵. Moreover, low values of magnetic moments (Table-1) also indicates that the Cu(II) ions are very close to each other.

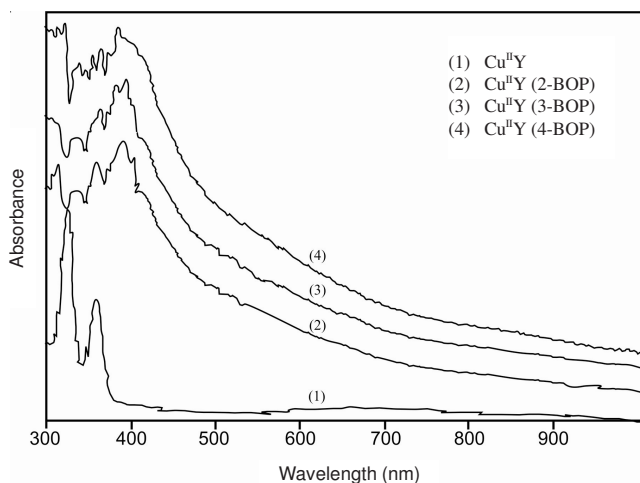


Fig. 1. Electronic spectra of Cu(II)Y, Cu(II)(2-BOP)Y, Cu(II)(3-BOP)Y and Cu(II)(4-BOP)Y

The X-ray diffraction patterns of NaY, Cu(II)Y and encapsulated copper(II) complexes were recorded at 2θ values between 5° and 70° to study the crystallinity and to ensure the process of encapsulation. The XRD patterns of Cu(II)Y and their encapsulated complexes are found to be almost similar to that of NaY sample, though slight change in the intensity of the bands has been observed. These observations indicate that the framework of zeolite matrix has not undergone and significant structural changes during encapsulation. This means that the zeolite lattice retained its original Na^+ distribution even after the encapsulation process²⁴. The representative XRD patterns of NaY, Cu(II)Y and Cu(II)(2-BOP) are displayed in Fig. 2. These clearly suggest of the presence of metal complexes in zeolite matrix.

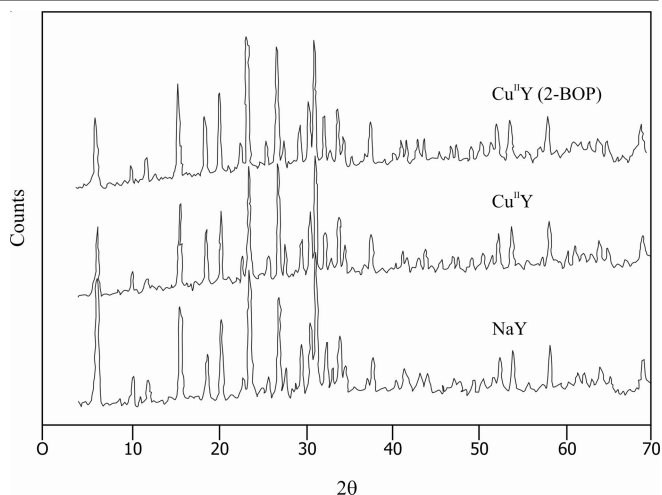


Fig. 2. XRD pattern of NaY, Cu(II)Y and Cu(II)(2-BOP)Y

In conclusion, complexes of Cu(II) with 2-, 3- and 4- BOP have been successfully encapsulated inside the cages of zeolite Y by flexible ligand method. Magnetic and spectral studies along with XRD patterns clearly indicate the encapsulation of complex in the zeolite Y with a probable structure as depicted in Fig. 3.

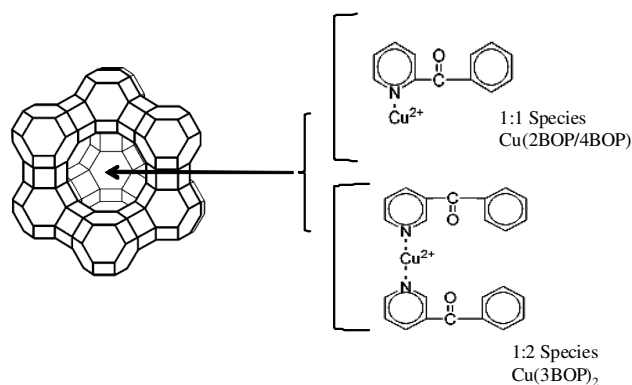


Fig. 3. Proposed structure of Cu(II)Y (2/3/4-BOP) complex (Structure of zeolite frame work has been adopted from zeolite atlas)

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