



Zeolite-Y encapsulated ternary complexes of [Tyr-M(II)-Cys]: Synthesis and Characterization

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Abstract: The nanocavity Zeolite Y encapsulated M(II) (M= Co, Ni, Cu, Zn) ternary complexes of L-Tyrosine and L-Cysteine was synthesized in situ in Na-Y-Zeolites using ion exchange and flexible ligand techniques. The ternary encapsulated complexes, synthesized from the reaction of ion-exchanged with Na⁺ ions followed by diffusion of the amino acid ligands tyrosine and cysteine into the super cages of the zeolite, where coordination with the metal centers occurred to form encapsulated ternary complexes by the reaction of ion exchanged process and flexible ligand method. The geometry and binding modes were explained by using various characterization techniques such as TGA, XRD, ESR, SEM, EDX, UV and IR spectroscopy.

Key words: Zeolite-Y, L-Tyrosine, L-Cysteine, Flexible ligand synthesis, Encapsulation

1. INTRODUCTION

Metal-zeolite bifunctional catalysts are important in various processes, such as shape-selective catalytic reactions, because metals can change oxidation states, zeolites can be acidic, and micropores can only fit particular forms [1-3]. But zeolite-supported metal catalysts manufactured with typical methods often don't spread the metal evenly, which implies that the metal active sites and zeolite acid centers don't operate well together. Also, metals that are supported on zeolite are simple to clump together, sinter, and may be lost in solutions or at high temperatures. This makes the catalyst less active and stable, which makes the target product less selective [4-6].

The addition of metal complexes to zeolite micropores, super-cages or cavities can make a catalyst significantly more active, selective and stable. Because the zeolite structure is relatively stable, inserting metal nanoparticles inside zeolite crystals can keep the metal particles from melting together at high temperatures [7]. Second, zeolite micropores have a shape-selective action that can greatly improve the selectivity of the product you want. But this also makes it take longer for the target product to move, which has a huge effect on how fast the reaction happens.

There have been big steps forward in the design and production of zeolite-encapsulated complexes for use as catalysts [8,9]. Most of the catalysts that were made were based on ligand systems such bipyridine, phthalocyanines, ethylenediamine, and salen [10-13]. Subsequent studies on these encapsulated complexes have demonstrated their distinctive reactivity for numerous industrially significant processes. For instance, encapsulated salen complexes have been effectively utilized for phenol oxidation, p-xylene oxidation to terephthalic acid, epoxidation and direct methane oxidation to methanol. Encapsulated phthalocyanine complexes are also known to help hydrocarbons that act as metalloenzymes oxidize [14-16], make adipic acid directly from cyclohexene or cyclohexane [17, 18]. Recently, Y zeolite-encapsulated compounds of 3-formylsalicylic acid have been reported as catalysts for oxidation processes [19]. The recent surge of literature on encapsulated catalysts indicates a burgeoning interest in investigating zeolite complexes with novel ligand systems for structural and catalytic research. However, there has been inadequate investigation on the complexes of N, N-bis(salicylidene) propane-1,3-diamine regarding the decomposition of H₂O₂. The [Mn(salpn)] has been used without any coating to study its catalytic activity in the epoxidation of alkenes, whereas [Mn(salpn)] coated with Y-zeolite has been used as a catalyst for the oxidation of p-xylene [20].

In this research we have synthesized zeolite encapsulated [Tyr-M(II)-Cys] ternary complexes. In addition, the properties of the prepared metal complexes of amino acids with zeolite Y nano materials were investigated using various kinds of analytical technique such as UV, IR, XRD, ESR, SEM, EDX and TGA.

2. Experimental

2.1 Materials

M(II) nitrates (M=Cu, Co, Ni & Zn), tetrahydrofuran and DMF are obtained from Merck (GR grade). Na-Y-Zeolite with Si:Al ratio of 5:1 and hydrogen peroxide are purchased from Aldrich, while ethanol, methanol, N, N-Dimethyl formamide, Tyrosine and Cysteine are purchased from Sigma-Aldrich. All these commercially available reagents obtained were used without any further purification

2.2 Synthesis methods:

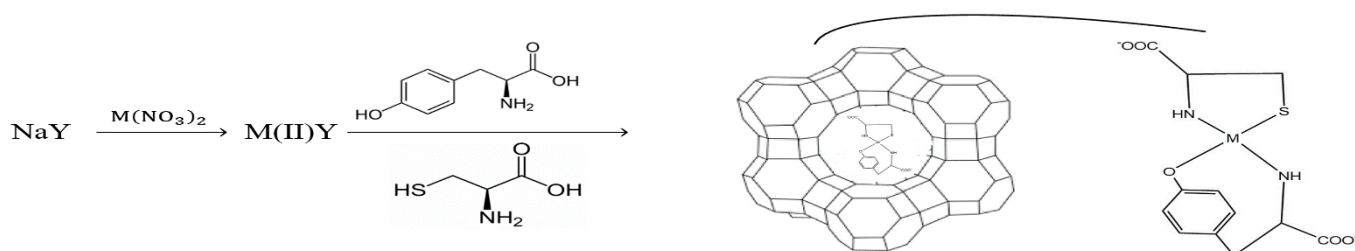
2.2.1 Synthesis of the encapsulated complex was carried out by employing two steps

Step 1: Preparation of metal exchanged Na-Y Zeolite: M(II)-Y

The ion exchange process was utilized to swap metal ions with Na ions in zeolite -Y. In 100 cm³ of deionized water, 2 g of Na-Y zeolite is added. Then, M(NO₃)₂ (0.025M) (M=Cu, Co, Ni & Zn), was added to this and the mixture is gently stirred at 90 °C for 24 hours. The precipitate is filtered and washed with sufficiently hot deionized water until the filtrate is free from Na ions. Then, the precipitate is dried in a hot-air oven at 100 °C for 10 hours.

Step 2: Synthesis of [Tyr-M(II)-His]-Zeolite Y Encapsulated Ternary Complexes

For the synthesis of Zeolite Y Encapsulated ternary complexes, flexible ligand synthesis method is used. The L-Cysteine (5.01 mmol) is added to a stirred solution of methanol and M(II) Zeolite Y. After 8 hours of refluxing, the solid was filtered, washed with ethanol, and dried in a hot air oven at 80 °C for 14 hours. After that, mix this binary complex (2 g) and L-Tyrosine (4.99 mmol) taken in 100 cm³ of methanol and reflux for 24 hrs at 90 °C. The precipitate is filtered and dried then extracted soxhlet with DMF and ethanol for 3 to 4 hours to remove the additional compounds that are adsorbed on the zeolite. After soxhlet extraction, the final product is dried in a hot air oven at 90 °C for 12 hours [21].



Scheme 1. Synthesis of encapsulated ternary metal complexes Tyr-M(II)-Cys.
[M(II) = Co, Cu, Ni & Zn]

2.2.3. Characterization

The Zeolite encapsulated [Tyr-M(II)-Cys] ternary complexes are characterized by UV-Vis spectrophotometer Shimadzu UV-1900i/1280 was used to study the concentration and assess purity of synthesized ternary metal complexes. The materials FT-IR spectra of the complexes using the KBr disc method on an FT-IR DIGILAB Biorad spectrometer. The powder X-ray diffraction (XRD) using Ni filtered CuK α radiation ($\lambda=1.5406$ Å) in the scan range of 10-80° on a Rigaku Miniflex (Rigaku Corporation, Japan) X-ray diffractometer. The FE-SEM images and EDX analysis of zeolite encapsulated [Tyr-M(II)-Cys] ternary complexes were captured using a JEOL FE-SEM-7610F microscope. In addition, the TGA analysis was carried out by using NETZSCH TG 309 Libra. The ESR analyser Ali Fax Roller 20 LC was used find the coordination geometry of [Tyr-M(II)-Cys]-Y ternary complexes.

3 Results and discussion

3.1 Characterization techniques

The optical properties of the synthesized Zeolite encapsulated [Tyr-M(II)-Cys]-Y ternary complexes were studied by UV-visible spectroscopy. An absorption peak could be found at 200 – 400 nm in the UV-Vis Diffuse reflectance Spectroscopy (UV-Vis DRS) for all [Tyr-M(II)-Cys] complexes. Which primarily indicates the presence of transitions within the peptide backbone and the aromatic side chain of tyrosine and typically indicate the presence of aromatic amino acid residues of cysteine and tyrosine and their interaction with the metal ion. Ligand-induced transitions were predominantly observed in the ultraviolet (UV) region, while d-d transitions were noted in the visible region. In the case of [Tyr-M(II)-Cys]-Y (M=Co, Ni, Cu and Zn) metal complexes clear absorption bands showed at 214 and 271 nm, these corresponding to $\pi \rightarrow \pi^*$ transition. The UV-vis spectrum also showed another low-intensity peak between 347 and 442 nm. This peak could be linked to the $n \rightarrow \pi^*$ ($4A_2F \rightarrow 4T_1F$) and $n \rightarrow \pi^*$ ($4A_2F \rightarrow 4T_1P$). The bands 500-600 nm region

indicates the d-d transition states, which suggests that the cobalt (II) ion has a square planar geometry structure. The magnetic moment of the Co (II) complex was computed to be 4.48 μ_B , which corresponds to the anticipated square planar geometry [22]. The d-d transition does not occur in the Zn [Tyr-Zn (II)-His-Y] complex, due to the absence of unpaired electrons (d^{10} configuration).

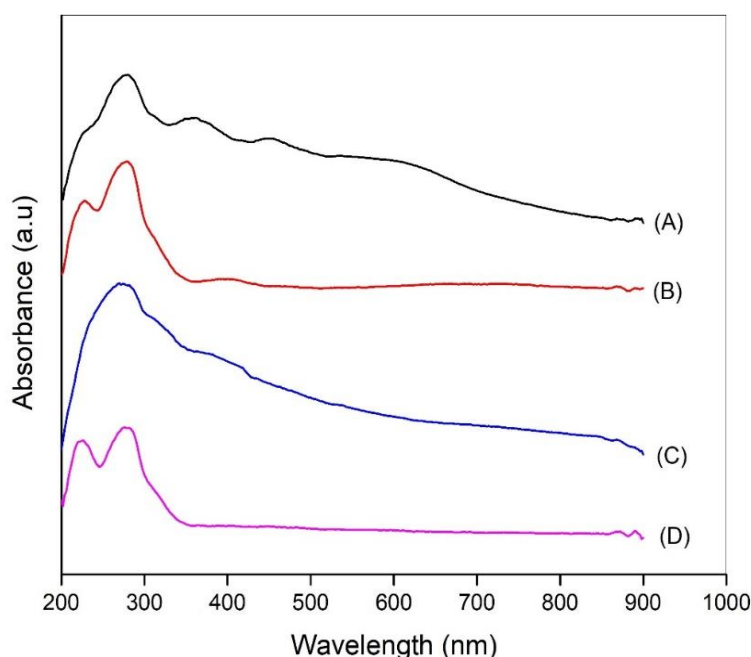


Figure 1: UV-Vis spectra of (A) [Tyr-Co (II)-Cys]-Y, (B) [Tyr-Ni (II)-Cys]-Y, (C) [Tyr-Cu (II)-Cys]-Y, (D) [Tyr-Zn (II)-Cys]-Y

FT-IR was utilized to find the functional groups in the synthesized Zeolite encapsulated [Tyr-M(II)-Cys] ternary complexes. The results are shown in Figure.2. The less strong IR peaks show that the complexes are trapped in the zeolite matrix. The FT-IR spectra of both metal-exchanged zeolite and parent zeolite exhibited pronounced bands within the range of 450-1200 cm^{-1} . There is a strong and wide band in the area of 1020 cm^{-1} that shows asymmetric stretching vibrations of $(\text{Si}/\text{Al})\text{O}_4$ units of zeolite. There are some wide bands close to 3428 cm^{-1} that are likely caused by phenolic -OH functional groups [23]. In addition, all the ternary metal complexes showed 2550 cm^{-1} ascribed to S-H functional groups of cysteine. The encapsulated ternary metal complexes FT- IR spectra could be found as no shift in the zeolite lattice bands (1017 cm^{-1}). This means that the zeolite's framework has not changed after it was encapsulated. The bands between 1200 – 1600 cm^{-1} show that there is coordination in the pores, where zeolite does not have any bands. But these bands aren't as strong because the encapsulated complexes aren't as concentrated in the lattice. The shift in the distinctive bands of carboxylic acids after coordination is also looked at. Amino acids in their free state exist as zwitterions, having two vibrations, one for vsCOO^- and one for vasCOO^- , that are about 1410 and 1647 cm^{-1} . When the carboxylate group binds to the metal ion, it loses its zwitterion form. This means that the bands will have no change in the shift with the frequency of (vsCOO^-) and (vasCOO^-) indicating that carboxylate group is not bonded in the metal complexes [24].

The Vs and Vas of COO^- (Fig. 2) in the encapsulated complexes do not show any shifts in the stretching frequency confirming that $-\text{COO}^-$ is not involved in metal coordination ($\text{M}=\text{Co}, \text{Ni}, \text{Cu}$ and Zn). The Phenolic -OH peak present in the free tyrosine does not appear in the metal complexes indicating that metal ion is binds to the phenolic -OH group of tyrosine.

The vNH_3^+ in an amino acid usually shows up between 3094 and 3078 cm^{-1} for tyrosine and histidine respectively. The bands of vNH_2 at 3128, 3147, 3128, and 3126 cm^{-1} confirmed the bonding with Co, Ni, Cu and Zn (II) metal ions, respectively. The free histidine contains imidazole peak at 1579 cm^{-1} , which is shifted to higher frequency (1589-1591 cm^{-1}) indicating that imidazole nitrogen binds to the metal ion. The IR data clearly indicates that the coordination number is four around the metal ion in the synthesized ternary complexes. Which concludes the synthesized ternary complexes might be square planer complexes.

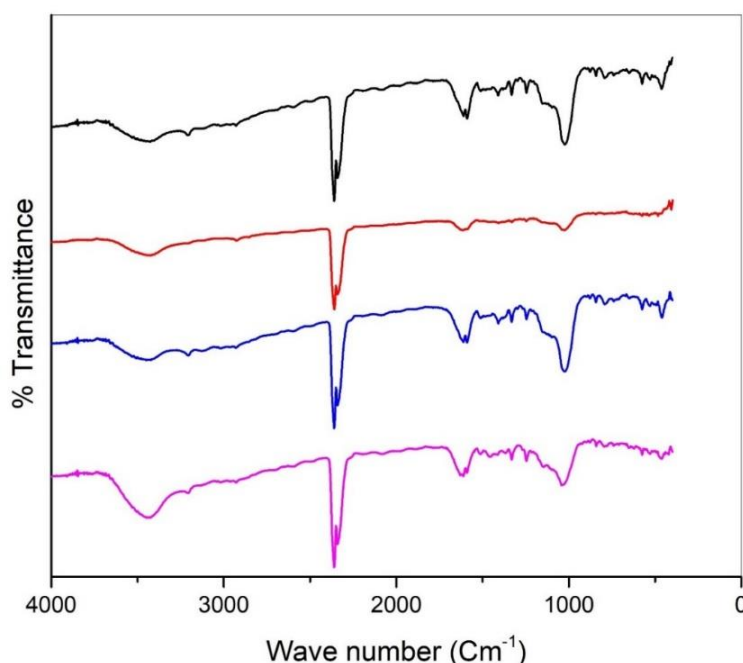


Figure 2: FTIR spectra of (A) [Tyr-Co (II)-Cys]-Y, (B) [Tyr-Ni (II)-Cys]-Y, (C) [Tyr-Cu (II)-Cys]-Y, (D) [Tyr-Zn (II)-Cys]-Y

Table 1. F T - I R Vibrational spectra of L-Tyrosine (Tyr), L-Cysteine and of the [Tyr-M(II)-Cys]-Y (M=Co, Ni, Cu, Zn) complexes

Assignment	Free L-Tyrosine	Free Cysteine	Try-M-Cys-Y (M=Co, Ni, Cu, Zn)			
	IR	IR	Co	Ni	Cu	Zn
$\nu_{as}(\text{NH}_2)$	3400-3500	3400-3500	3258	3243	3249	3241
$\nu_s(\text{NH}_2)$	3200-3400	3300-3400	3142	3149	3128	3140
$\nu_{as}(\text{NH}_3^+)$	3094 vs	3078	-	-	-	-
$\nu_{as}(\text{COO}^-)$	1589 vs	1606	1578	1575	1585	1578
$\delta(\text{NH}_2)$	1580-1650	1580-1650	1628	1627	1624	1620
$\nu(\text{C=O})$	1670-1780	1600-1700	1591	1585	1564	1545
$\delta(\text{NH}_3^+)$	1668	1670				
$\delta(\text{CH}_2)$	1459 s	1450	1458	1458	1431	1481
$\nu(\text{COO}^-)$	1412 vs	1412	1412	1411	1408	1411
$\nu(\text{S-H})$	2570	2550-2570	2558	2558	2558	2558
$\delta(\text{CH})$	1317 m	1350-1470	1315	1321	1324	1298
$\nu(\text{C-N})$ aliphatic	1097 s	1062	1085	1078	1087	1087
$\delta(\text{COO}^-)$	743 vs		730	728	720	723
$\nu(\text{OH})$ Tyrosine	3400-3500	-	-	-	-	-
$\nu(\text{M-N})$			465	457	456	467
Zeolite (Si-O-Al)	1020		1020	1020	1024	1024

The X-ray diffraction technique was employed to learn about the structure of the synthesised encapsulated ternary complexes. What we found is shown in Figure 3. At $2\theta = 10.3^\circ, 15.9^\circ, 18.6^\circ, 23.9^\circ, 27.4^\circ$, and 31.6° , all of the materials had a distinct peak in their XRD patterns. The (2 2 0), (3 3 1), (4 4 0), (5 5 3), (6 4 2), and (7 5 1) planes were found to reflect Na-Y zeolite [25]. There were no other peaks in the XRD patterns that were associated to metal ions. This means that the [Tyr-M(II)-Cys] ternary complexes that are inside the zeolite are well spread out in the zeolite cavities. So, the conditions around the zeolite host do not affect how well its crystallinity.

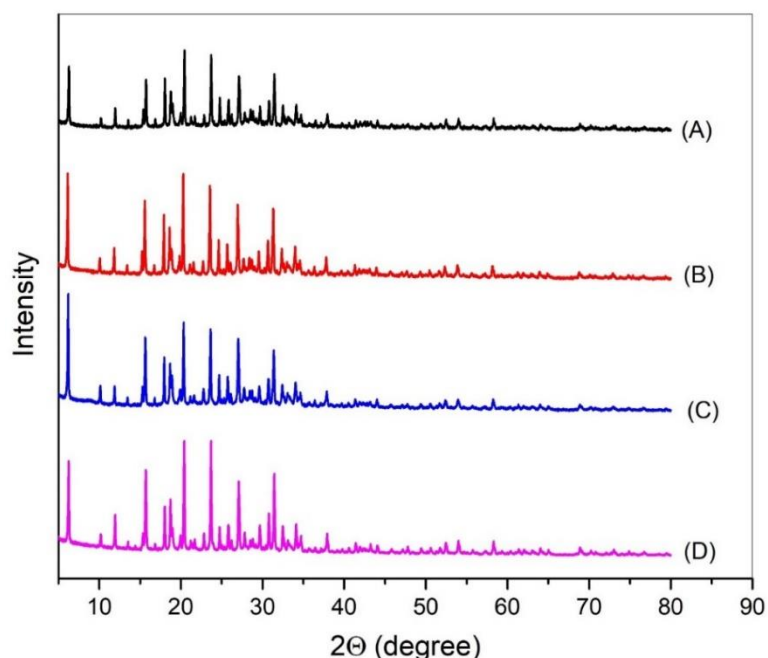


Figure 3: XRD Pattern of (A) [Tyr-Co (II)-Cys]-Y, (B) [Tyr-Ni (II)-Cys]-Y, (C) [Tyr-Cu (II)-Cys]-Y, (D) [Tyr-Zn (II)-Cys]-Y

The ESR spectra of encapsulated Co (II) and Cu (II) complexes were carried out to know bonding nature, geometry and structure at room temperature, and it can be seen in Fig. 4. The ESR spectrum indicates the encapsulation of copper and cobalt complexes. The spectra clearly indicated the hyperfine structure of the zeolite-encapsulated species, which is what you would expect from isolated monomeric Co (II) and Cu (II) complexes. The diamagnetic zeolite matrix keeps the encapsulated metal complex separate from other molecules, which lets us see resolved hyperfine structures.

The ESR spectrum structure of the solid copper (II) complex exhibits axial symmetry, and it can be seen Table 2. This was confirmed by the $g_{\parallel} > g_{\perp} > 2.0023$. This indicates that ternary complexes possess a square planar structure with the unpaired electron located in the $d(x^2-y^2)$ orbital. In square planar complexes with an electron in $d(x^2-y^2)$ orbital gives $2B_{1g}$ as the ground state [26]. The elevated covalence characteristic of the complex exhibiting distorted symmetry is indicated by the computed value of $= (g_{\parallel} + 2g_{\perp})/3 = 2.13$ [27]. The g -values are connected by the equation $G = (g_{\parallel} - 2.003)/(g_{\perp} - 2.003) = 4.0$ under axial symmetry; if G exceeds 4, there is minimal exchange contact between Cu (II) centers in the solid state, and vice versa. The G value of the copper complex is determined to be 11.54, ruled out the possibility of exchange interactions [24], so supporting the encapsulation and existence of isolated monomeric Cu (II) and Co (II) complexes within zeolite cavities. The stereochemistry of Cu (II) complexes can be demonstrated using the $(g_{\parallel}/A_{\parallel})$ values. The ranges $105-135 \text{ cm}^{-1} > 135-250 \text{ cm}^{-1}$ are documented for square planar and tetragonally deformed complexes, respectively. The copper complex has a g -value of 108 cm^{-1} , which falls within the range documented for square planar Cu (II) complexes [28]. The cobalt complex exhibits an isotropic g value of 4.20, indicating a deformed octahedral configuration. The results align with the magnetic moment values: the Cu complex exhibits 1.75 BM ($S=1/2$), while the Co complex shows 3.80 BM ($S=3/2$).

Table 2: The ESR spectra of [Tyr-Cu-Cys]-Y and [Tyr-Co-Cys]-Y ternary complexes

Complex	$g_{\parallel}$	$g_{\perp}$	g_{av}	$A_{\parallel} (\times 10 \text{ cm})$	$A_{\perp} (\times 10 \text{ cm})$	$g_{\parallel}/A_{\parallel} (\text{cm}^{-1})$
[Tyr-Cu-Cys]-Y	2.25	2.07	2.23	224	26	112
[Tyr-Co-Cys]-Y	4.19	2.05	2.72	213	23	208

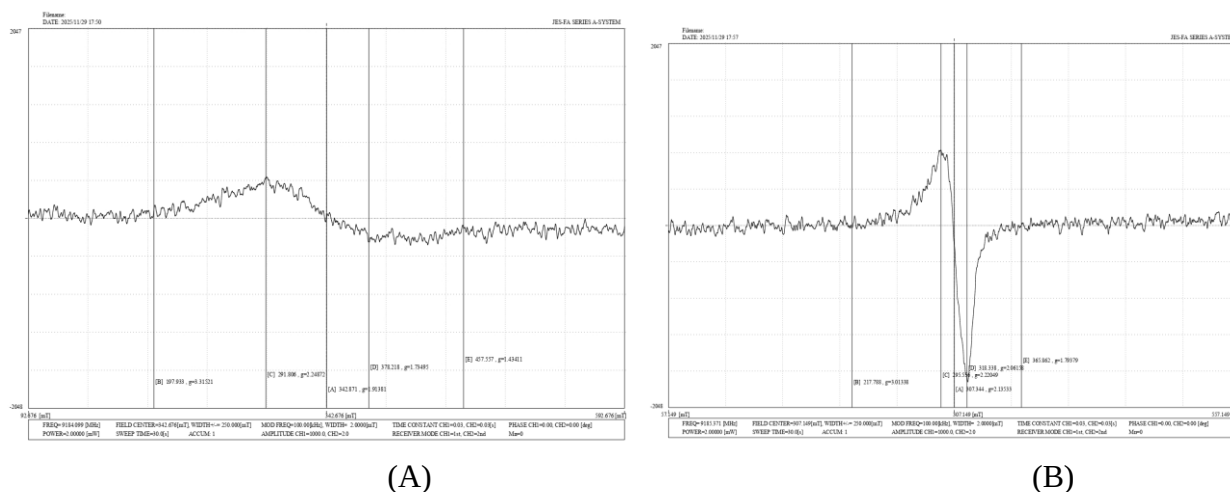


Figure 4: ESR spectra of (A) [Tyr-Co (II)-Cys]-Y, (B) [Tyr-Cu (II)-Cys]-Y

The ternary complexes, encapsulated in Zeolite and analysed using FE-SEM micrographs and EDX investigations, displayed a faujasite (FAU) framework structure typified by a cubic crystal system, as illustrated in Figures 5 and 6. It typically exhibits octahedral or tetrahedral crystals with acute edges that tend to aggregate when produced through conventional methods. The EDX experiments indicate that sodium ions are the primary constituents of the NaY zeolite. They are situated within the zeolite framework and on the surface to maintain the stability of the negative charges from the aluminium. Silicon and aluminium, which are also constituents, exhibit tetrahedral interactions with oxygen. The development of [Tyr-M(II)-Cys] ternary complexes modified the NaY zeolite. The carbon content of the metal complexes in organic molecules decreased from 45.2% to 9.19% upon decomposition. Table 3 presents the detailed EDX elemental composition of the ternary metal complexes of [Tyr-M(II)-Cys]. It encompasses the Si/Al ratio and the Na (wt %) concentration. The Si/Al ratios of [Tyr-M(II)-Cys] ternary complexes are generally lower than those of the original NaY zeolite. The results indicate that the surface deposits have been eradicated, and the scanning electron microscopy pictures obtained post-soxhlet extraction distinctly reveal the zeolite surface boundaries. This unequivocally demonstrates that complexes have been encapsulated [29].

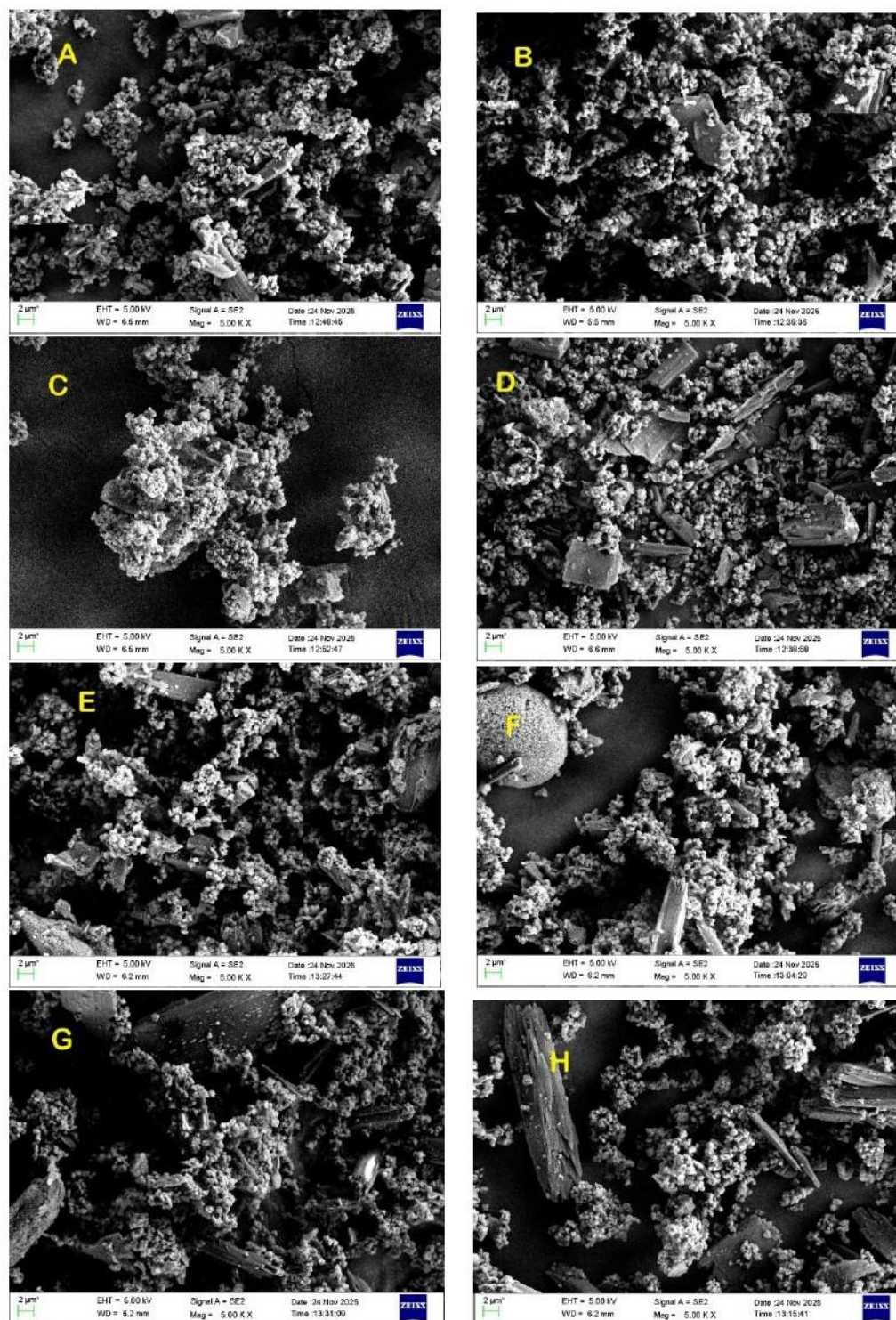


Figure 5: FE-SEM Images of (A) [Tyr-Co (II)-Cys]-Y BS, (B) [Tyr-Co (II)-Cys]-Y AS , (C) [Tyr-Ni (II)-Cys]-Y BS, (D) [Tyr-Ni(II)-Cys]-Y AS, (E) [Tyr-Cu(II)-Cys]-Y BS, (F) [Tyr-Cu (II)-Cys]-Y AS, (G) [Tyr-Zn(II)-Cys]-Y BS, (H) [Tyr-Zn(II)-Cys]-Y AS

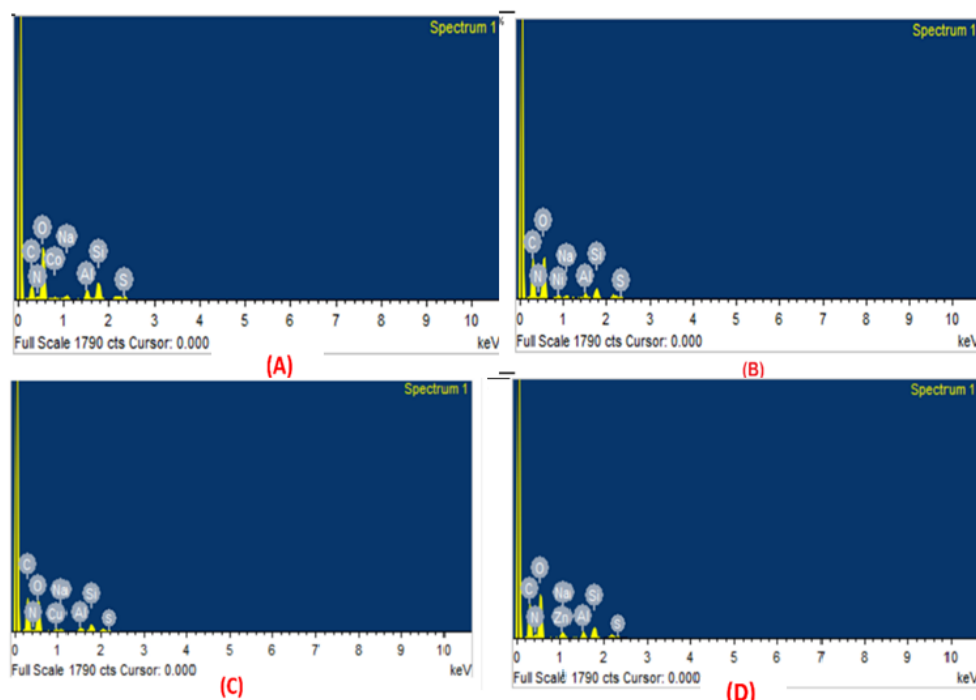


Figure. 6. EDX elemental analysis of (A) [Tyr-Co (II)-Cys]-Y (B) [Tyr-Ni (II)-Cys]-Y (C) [Tyr-Cu (II)-Cys]-Y (D) [Tyr-Zn (II)-Cys]-Y

Fig. 7 shows the results of thermogravimetric analysis (TGA) and DTA, which were conducted from room temperature to 1000 °C. Tyr-M(II)-His ternary complexes' TGA profile. The first weight loss below 210 °C is mainly caused by the evaporation of moisture and highly volatile compounds. The breakdown of Tyr anions and co-intercalated nitrate, as well as the dihydroxylation of the brucite-like layers, cause the second one (250–400 °C), which involves a progressive loss of weight. The third one, where the combustion of the carbonaceous residue causes a corresponding exothermic reaction and a sharp weight loss in the 400–800 °C temperature range [25].

The Tyr-M(II)-His ternary metal complexes of DTA curves along with TGA curves were depicted in Fig. 7. Four steps make up the thermal breakdown of Tyr-M(II)-His: the first occurs between 20 and 150 °C and is caused by the removal of surface and interlayer water; the second occurs between 150 and 250 °C and is related to the dihydroxylation of the host layers with a weak endothermic reaction. Tyr ion breakdown and brucite-like layer dihydroxylation are responsible for the third weight loss step (260–400 °C), while the carbonaceous residue burning is responsible for the final one (400–800 °C) [26].

Table 3. EDX elemental percentages of [Tyr-M(II)-Cys]-Y & Metal (II) -Y ternary metal complexes

Element	Zeolite	Tyr-Co-Cys-Y	Co-Y	Tyr-Ni-Cys-Y	Ni-Y	Tyr-Cu-Cys-Y	Cu-Y	Tyr-Zn-Cys-Y	Zn-Y
C	45.2	13.56	9.19	33.99	-	36.83	15.97	29.24	15.48
N	-	2.80	-	1.61	-	2.15	-	4.88	-
O	38.62	41.22	48.02	35.95	50.90	34.74	46.74	38.95	47.88
Na	3.11	2.19	3.28	1.52	3.15	1.30	2.59	2.35	3.68
Al	3.23	7.90	7.91	4.74	9.39	4.52	7.44	5.44	7.04
Si	9.85	22.65	23.72	14.04	28.42	13.45	20.91	14.37	21.35
S	-	4.72	-	3.58	-	2.40	-	2.51	-
Si/Al	3.04	2.86	2.99	2.96	3.02	2.97	2.81	2.64	3.03
Metal	-	4.96	7.89	4.58	8.14	4.60	6.34	3.27	4.58

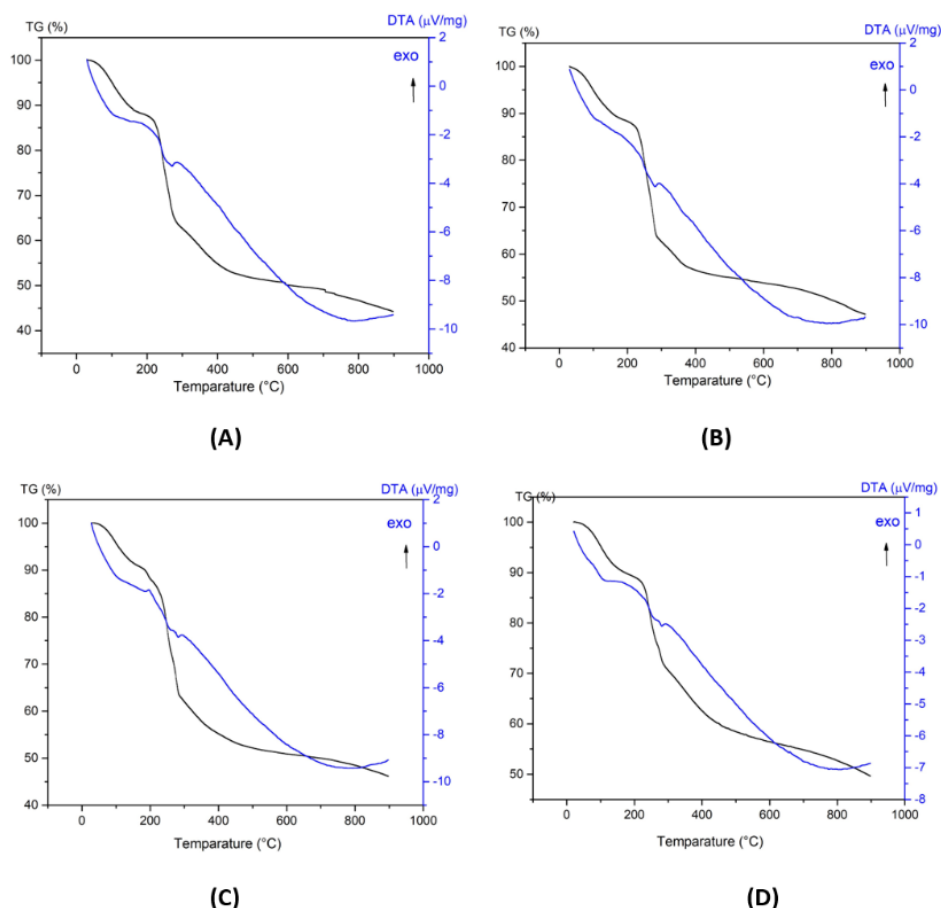


Figure 7: TG-DTA of (A) [Tyr-Co (II)-Cys]-Y, (B) [Tyr-Ni (II)-Cys]-Y, (C) [Tyr-Cu (II)-Cys]-Y, (D) [Tyr-Zn (II)-Cys]-Y

4. Conclusion

The Nanocavity Zeolite Y Encapsulated M(II) (M= Co, Ni, Cu, Zn) ternary complexes of Tyrosine and cysteine in situ in Na-Y-Zeolites were successfully synthesized using the ion exchange and flexible ligand method. Various characterization techniques indicating that the ternary complexes of amino acids are successfully encapsulated in zeolite-Y.

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Declaration of Interest

The authors declare no conflict of interest.

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