**Zeolite Encapsulated Ni(II) and Cu(II) Complexes with Tetradentate N2O2 Schiff Base Ligand: Catalytic Activity Towards Oxidation of Benzhydrol and Degradation of Rhodamine-B**

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Zeolite Encapsulated Ni(II) and Cu(II) Complexes with Tetradentate N₂O₂ Schiff Base Ligand: Catalytic Activity Towards Oxidation of Benzhydrol and Degradation of Rhodamine-B

G. Ramanjaneya Reddy, S. Balasubramanian, K. Chennakesavulu

Abstract
The nickel (II) and copper (II) complexes of the Schiff base ligand O, O'-trimethyl bis(salicylidene isonicotinylhydrazone)(H₂L) were synthesized and characterized. The encapsulation of these complexes in the cavities of zeolite was achieved by a fixed ligand method (FLM). The free complexes (FC) and the retention of zeolite encapsulated metal complexes (i.e Ni(II)L-Y, Cu(II)L-Y) (ZEMC) were studied by several spectroscopic, thermal analysis, sorption and microscopic techniques (FTIR, NMR, ESI-mass, Conductivity, DRS/UV-Vis, EPR, XPS, AAS, TGA, XRD, Nitrogen isotherm, Magnetic and (SEM/TEM)EDX). This studies reveals the formation and stability of the metal complexes in the cavities of zeolite. The catalytic activity of free complexes and encapsulated complexes was studied in liquid phase oxidation of the benzhydrol/H₂O₂ and photo degradation of rhodamine-B (RhB) under UV/Visible(H₂O₂) irradiations. The catalytic activity of benzhydrol (BH) oxidation and RhB degradation was higher with free complexes and encapsulated complexes respectively. In most of the cases the copper (II) (Cu(II)L₂ClO₄,Cu(II)L-Y) complexes was shown better activity of than nickel (II) complexes (Ni(II)L₂ClO₄,Ni(II)L-Y) in both BH and RhB degradation reactions. The enhancement of the Cu(II)L-Y activity mainly due to the metal percentage was present in cavities and surface area. Hence in the case of FC the copper (II) complexes rate of the reaction (% of conversion) is more than nickel (II) in BH.
oxidation but in the case of ZEMC the photocatalytic activity and rate of the reaction (% of conversion) more for Cu(II)L-Y than Ni(II)L-Y. These results show the both oxidation reactions follow the pseudo first order kinetics. The catalytic activity of the recovered and purified ZEMC checked with the fresh catalyst.

**Keywords**: N$_2$O$_2$ Schiff base, Nickel (II), Copper (II), Fixed ligand method, Benzhydrol oxidation, Rhodamine-B.

1. Introduction

Transition metal complexes play a vital role in the field of catalysis and photocatalysis i.e. liquid phase oxidation, reduction and polymerization etc.$^{1-3}$ The recovery and separation of transition metals from the products in homogeneous medium (e.g. hydrocarbons, aliphatic alcohols, alkyl benzenes, amides, amines, aliphatic carboxylic acids, thioethers and xanthenes class of dyes, etc) are challenging tasks. In order to overcome this difficulty, the research interest in the heterogeniation of homogenous catalyst was raised.$^{4,5}$ However the enhancement of catalyst activity with the nickel (II) and copper (II) based systems was alternative to the highly expensive metals like ruthenium, palladium. Hence, the impregnation of homogeneous transition metal complexes into solid support such as polymer, zeolite and MCM41 was attempted.$^6$ The zeolites are made up of the aluminosilicates named as "solid acid" and it is further alternative to commercially available toxic acids such as sulphuric acid, potassium dichromate, nitric acid. The zeolite Na-Y is an exchange bowl and interesting material due to its low cost and an intra crystalline cavity which was suitable the transition metal ions exchange. The exchange and encapsulation ability of the metal complexes within the cavities of supercages depends on the Na$^+$ ion and size of the zeolite host.$^7$ Hence the encapsulation (heterogeniation) of the metal complexes (homogeneous) within the supercages can used for the effectively in the photo (chemical) oxidation reactions. The modified catalyst has more
advantages than those homogeneous counter points. This can be act as effective ecofriendly catalyst to convert high toxic pollutants to the very less toxic minerals.

The modified zeolite can delocalise the band gap excited electrons of HOMO and LUMO levels of metal complexes. Hence they minimize the electron-hole recombination besides a relative number of active sites present on the high surface area based solid supports. In addition, ability of the modified zeolite favours photo induced electron-transfer reactions and generate the photo active powerful oxidative ion-radical species like \(^{\cdot}\text{OH}, \^{\cdot}\text{O}_2, \^{\cdot}\text{O}_2\text{H}\). The modified zeolite with green oxidant 30% \(\text{H}_2\text{O}_2\) can enhance the photo catalytic performance of various dyes (RhB, methyl orange, cango red) by generation of a most power full oxidant\((E_0=\^{\cdot}\text{OH} (E^\circ =2.8 \text{ V})\) than other oxidants.\(^8\) These supported systems improves the rate of the reaction and catalytic activity towards the decolourisation of the carcinogenic xanthenes (azo) class of dyes and oxidation of the aryl alchohols.\(^9\) Since, the photo degradation of dyes is an important and also very few reports are available to removes the xanthene class of dyes by using the pure and supported Schiff base hydrazones complexes.\(^10\)

The metal complexes of aryl hydrazones have good biological and catalytic significances, because of the tetradentate (dioxia diaza) moiety owing their chelating ability with the metal ions. In the liquid phase oxidation reactions, whose type of metal hydrazone analogues with the nickel (II) and copper (II) exchange zeolite was rarely reported.\(^11\) The synthesis and extensive studies of the acyclic tetradentate \(\text{N}_2\text{O}_2\) Schiff base ligand O, \(\text{O'}\)-trimethyl bis (salicylidene isonicotinoyl hydrazone) with Ni(II), Cu(II) and its corresponding encapsulated complexes by FLM in the cavities of zeolite and its usage in BH oxidation and degradation of RhB dyes were not established.\(^12\)

In the present study, an attempt was made on the synthesis of the Schiff base ligand O, \(\text{O'}\)-trimethyl bis(salicylidene isonicotinoyl hydrazone) (H\(_2\)L) by the condensation between 1, 3-

Bis(2-carboxyaldehydepbenoxy)propane(SAL) and isonicotinyl hydrazine (INH) in presence of
the perchlorates of the Ni(II) and Cu(II). The metal complexes are encapsulated in the cavities of zeolite by FLM.¹² The catalytic activity of the synthesised materials were tested in the liquid phase oxidation of BH and the photo degradation of RhB. The spectrophotometric technique was used for determination of the products and catalytic activity of the composite materials.

2. Experimental

2.1 Materials

The chemicals salicylaldehyde, 1, 3 dibromo propane, Isonicotinylhydrazide, Zeolite-Y (Si/Al = 2.7, Na₃₅₂[AlO₂]₅₂(SiO₂)₁₄₀], Benzhydrol, Hydrogen peroxide (30 %), Rhodamine-B were obtained from Sigma Aldrich. The Milli-Q water was used during the experimental work.

2.2 Physicochemical measurements and characterization

The NMR spectra were recorded on Bruker Avance 400MHz NMR spectrometer, the ESI mass spectral data were obtained using ESI-MS Thermo Finnigan LCQ model advantage MAX 6000ESI spectrometer, the FTIR spectra were recorded on a FTIR Perkin-Elmer 8300 spectrometer with the KBr disk and the UV-Visible Diffuse Reflectance Spectral (UV-Vis DRS) analyses were carried on a Perkin-Elmer lambda-650 DRS UV-visible spectrophotometer. The UV–Vis absorption spectra using a Perkin Elmer Lambda-35 spectrophotometer operating in the range 200-800 nm for liquid samples. Conductivity measurements were carried out in mmol solutions of the metal complexes in DMSO. The EPR spectrum of the copper (II) complex was recorded at LNT on a Varian E-4 X-band spectrometer using TCNE as the g-marker (2.0023). XPS analyses were carried out on XM1000 Omicron nanotechnology XPS system with Al-Kα monochromatic wavelength. The FC and ZEMC samples were made into pellets and were used as such for X-ray Photoelectron Spectroscopic (XPS) analysis. The high resolution XPS traces were deconvoluted using the Gaussian and Lorentzian statistical analysis by using origin-7 software. The crystalline nature of the FC and ZEMC was ascertained by the powder X-ray diffraction using Bruker D8
advance diffractometer with monochromatic Cu-Kα radiation (λ=1.5418 Å). After completely
destroying the zeolitic frame work with hot HCl, the nickel and copper percentage were
analyzed by atomic absorption spectrophotometer (AAS, Perkin-Elmer 4100-1319) and SiO₂
was determined by gravimetric analysis. TGA experiments were performed with Versa Therm
Cahn thermo balance TG-151 with a sensitivity of 10 µg. TGA experiments were conducted in
the temperature range of 300-1200 K with 20 ± 0.01 mg of the samples and the analyses were
carried out at a heating rate of 10 K/min under static air atmosphere. The N₂ adsorption,
desorption isotherms and Brunauer-Emmett-Teller (BET) specific surface area measurements
at 77K were carried out on Micrometrics ASAP (Model 2020) surface area analyzer with the
nitrogen and helium gases with a purity of 99.99%. The scanning electron micrograph (SEM)
was obtained using HITACHI-S3690 scanning electron microscope. HRTEM analysis was
carried out by using a FEI TECNAI G2 (T-30) transmission electron microscope with an
accelerating voltage of 250 KV. The average particle size was measured by the Image-J soft
ware tool. The products in one the BH oxidation were analyzed by LC-MS technique using
Agilent 6110 LC-MS ESI mode with carvacrol use as internal standard.

2.3 Preparation of the 1, 3-Bis (2-carboxyaldehydethenoxy) propane (SAL)
Salicyladehyde (0.61g, 5 mmol) was dissolved in 20 mL DMF and potassium
carbonate (1.73 g, 12.5 mmol) was added and mixture was stirred at room temperature and 1,3
dibromopropane (0.51g, 2.5 mmol) was added drop wise and then the reaction mixture was
stirred under reflux for 6 h. The resulted mixture was partitioned between water and
ethylacetate, the ethyl acetate layer was collected and concentrated under reduced pressure and
then subjected to silica gel 100-200 mesh column chromatography using 1:9 hexane-
ethylacetate as eluent to afford compounds(1.07g 75%) in pure form. the purified SAL was
characterized and the results are well matched with earlier reported method.¹³. (ESI: S35) ¹H
NMR (CDCl₃, 500 MHz): δ: 2.43 (2H, p, OCH₂CH₂CH₂O), 4.33 (4H, t, J = 7.6 Hz,
OCH$_2$CH2CH$_2$O), 7.03 (4H, m, Ar-H), 7.55 (2H, t, $J = 7.7$ Hz, Ar-H), 7.83 (2H, d, $J = 7.7$ Hz, Ar-H), 10.49 (2H, s, Aldehyde-H); $^{13}$C NMR (CDCl$_3$, 125 MHz) (ESI: S36): $\delta$ 29.2, 64.7, 112.5, 121.0, 124.9, 128.8, 136.2, 161.0, 189.6.

2.4 Preparation of the O, O'-trimethyl bis (salicylidene isonicotinoyl hydrazine (H$_2$L))

The O, O’-trimethyl bis (salicylidene isonicotinyl hydrazone) was prepared by refluxing the aliquot of the SAL (1.12 g, 2 mmol), isonicotinyl hydrazide (1.8 g, 4 mmol), two drops of the glacial acetic acid in absolute ethanol (40 mL) for 2 h, the resulting white solid was washed with the water, ethanol, chloroform, diethyl ether and dried under vacuum Yield:0.68 g (80%).

M.p. 521-523 K. ESI-mass: m/z 545.27 (M+Na).$^1$HNMR (DMSO-d6,400MHz) ppm: 12.02 (s, 2H, amide NH), 9.01-8.42 (m, 6H, Ar+H and imine CH), 8.07-7.53 (m, 6H, Ar+H), 7.37 (s, 2H, Ar+H), 7.11 (s, 2H, Ar-H), 6.98 (s, 2H, Ar-H), 4.27 (s, 4H, OCH$_2$) and 2.26 (s, 2H, OCH$_2$CH$_2$O); $^{13}$C NMR (DMSO-d6, 80 MHz) ppm: 162.08, 157.57, 150.77, 149.99, 144.91, 141.02, 132.37, 126.27, 123.60, 122.68, 122.03, 121.41, 113.26, 65.30 and 29.26.

UV/Vis (DMSO): $\lambda_{max}$ (ε:cm$^{-1}$ mol$^{-1}$ L$^{-1}$) =272 (56600), 288 (58577) and 332(6658).

2.5 Preparation of Ni(II)L. 2ClO$_4$

To the DMF solution (5 mL) of (H$_2$L) (0.52 g, 1 mmol), the 30 mL ethanolic solution of nickel perchlorate hexahydrate (0.38 g, 0.5 mmol) were added and then heated at 353 K for 3 h. The resulting lemon yellow solid was washed with the hot water, methanol, diethyl ether and dried under vacuum.Yield:0.6g (72%), M.p. and decomposition > 543 K; ESI-mass m/z 579.2.

$\lambda_{max}$ = 260 nm ($\varepsilon$ =14050 cm$^{-1}$ mol$^{-1}$ L$^{-1}$), 368 nm ($\varepsilon$ =18990 cm$^{-1}$ mol$^{-1}$ L$^{-1}$), 670 nm ($\varepsilon$ = 68 cm$^{-1}$ mol$^{-1}$ L$^{-1}$). Molar conductivity ($\Lambda$) =14.5 mho cm$^{-2}$ mol$^{-1}$.

2.6 Preparation of Cu(II)L. 2ClO$_4$

To the DMF solution (5 mL) of H$_2$L (1.1 g, 0.5 mmol), 30 mL ethanolic solution of copper perchlorate hexahydrate (0.36 g, 0.5 mmol) were added and heated at 353 K for 3 h. The resulting olive green solid was washed with the hot water, methanol, and diethyl ether and...
dried under vacuum. Yield: 0.7g (80 %) M.p. and decomposition > 513 K; MS: m/z 585. \( \lambda_{\text{max}} = 270 (\varepsilon =14829 \text{ cm}^{-1} \text{ mol}^{-1}\text{L}), 368 \text{ nm (}\varepsilon =19300 \text{ cm}^{-1} \text{ mol}^{-1}\text{L}), 685 \text{ nm (}\varepsilon =33 \text{ cm}^{-1} \text{ mol}^{-1}\text{L}). \) Molar conductivity (\( \Lambda \)) = 11.8 mho cm\(^2\) mol\(^{-1}\).

2.7 Preparation of metal exchanged zeolite, (M(II)-Y [M=Ni(II) and Cu(II)])

The metal perchlorate (M(ClO\(_4\)).6H\(_2\)O, 0.1 mmol) was added to the 50 mL aqueous solution of 1 g of Na-Y zeolite and it was stirred for 8 h at 368 K. The obtained solids were filtered, washed with 100 mL of hot distilled water and dried under vacuum for 10 h at 353 K.

2.8 Preparation of the metal hydrazone Schiff base complexes in the zeolite (M(II)L-Y) via FLM.

Preparation of the Schiff base aryl hydrazone metal complexes in the cavities of the zeolite was achieved by heating at 333 K in DMF/methanolic solution of H\(_2\)L with the M(II)-Y for 8 h. The resulting solids were washed with the hot DMSO (10 mL), water and dried for 12 h. The solids were soxhlet extracted with the ethanol and acetonitrile/DMF 6 and 24 h respectively to remove excess unreacted starting materials adsorbed onto the external surface of the zeolite crystalline. The resulting solids were dried at 253 K under vacuum for 24 h. Yield: 0.3-0.34 g. Colour: [Ni(II)L-Y] (pale yellow), [Cu(II)L-Y] (pale green).

2.9. Oxidation of the BH by the FC and ZEMC composite materials

A mixture of the M(II)L.2ClO\(_4\) (0.5 mg 0.01 mmol) (100 mg in case of ZEMC), 30% hydrogen peroxide (0.34 g, 1mmol) and BH (0.0184 g, 0.1 mmol) was added to a flask containing dry acetonitrile (10 mL) and reaction mixture was stirred for 7 h at 333 K and final products was analysed by the UV spectra and one of the reaction product benzophenone is confirmed by LC-MS analysis.

2.9.1 Photocatalytic degradation of the RhB under the UV and visible light irradiations.

The photo catalytic activities of the FC and ZEMC were evaluated in degradation of the RhB under UV as well as visible/ H\(_2\)O\(_2\) (1mmol) in a cylindrical glass reactor diameter 66 X 98
mm with contains a water jacket at room temperature. The mercury (Hg) (100W, 365 nm) was used as UV light source and a 250 W tungsten lamp (Philips) used as a visible light source equipped with UV cut-off filter were used to trigger the photo decomposition reactions. The catalysts 0.06 mmol M(II)\textsubscript{L}.2ClO\textsubscript{4} (0.05 g in case of ZEMC) was added to 0.01 mmol of 100 mL RhB aqueous solution and the above catalysts were added separately for the both UV(visible/H\textsubscript{2}O\textsubscript{2}) irradiations. After optimising the reaction conditions in dark at room temperature the suspension was irradiated by light sources. The 3 mL of the solution was collected for each predetermined time intervals (30 min) and consequence spectral changes were monitored by UV–Vis spectra using a Perkin Elmer Lambda 35 spectrophotometer operating in the range 200-800 nm at 554 (± 1) nm for 3 h. The percentage of the conversion and reaction rates in photo degradation process was formulated by the Lambert-beers correlation formulae

\[ A = \varepsilon \cdot c \cdot l \]  

(1)

Here \( \varepsilon \) =molar extinction coefficient \([M^{-1} \text{ cm}^{-1}]\), \( c = \) sample concentration =path length of cuvette (1 cm).

### 3.0 Results and discussion

#### 3.1 Chemical and magnetic studies

The chemical analysis (AAS) results are given in the Table: A (ESI †). The parent zeolite unit cell formula \( \text{Na}_{52}\left[(\text{AlO}_2)_{52}(\text{SiO}_2)_{140}\right] \) and \( \text{Si/Al} = \sim 2.7 \). The Silica aluminium ratio (SAR) quite same in all exchange process. The consistency of the SAR suggesting the no leaching of the aluminium during exchange processes and incomplete exchange of the sodium metal ion with both copper (II) and nickel (II) also found. The gradually decrease in percentage of the metal from free exchange metal to and metal ligand exchanged zeolite (ZEMC). shows the formation and presence of the Schiff base metal hydrazone complexes in the cavity of zeolite. The AAS analysis, SEM/TEM(EDAX) and XPS analysis confirms the presence of
the, nickel (II), copper (II), Si and Al. The simple gouy balance technique was used for the magnetic susceptibility studies. This reveals the magnetic moment value at 1.78 BM for the Cu(II)L.2ClO$_4$ this value slightly change to 1.92 BM for Cu(II)L-Y. The nickel (II) complex has shown the diamagnetic nature. These values well matched with the earlier reports for the mono nuclear complexes.$^{14}$

3.2 Infrared Spectroscopy (FTIR)

The FTIR spectra of H$_2$L, NaY, Ni(II)L.2ClO$_4$, Cu(II).2ClO$_4$, Ni(II)-Y and Cu(II)-Y are provided in ESI† (Fig. S7 - S12). The shifts in bands, their peak assignments in wavenumber are listed in the Table 1. The Fig. S7 shows the disappearance of the aldehyde carbonyl band. The bands in the FTIR spectra of ligand H$_2$L and the appearance of three new bands at 1618 cm$^{-1}$, 1603 cm$^{-1}$ and 1660 cm$^{-1}$ due to the stretching frequency of -C=N, C=N (π) and -C=O groups, respectively.$^{15,16}$ This clearly indicates that the primary amino group of the isoniazid was involved in the formation of azomethine group in the Schiff base ligand. The FTIR spectra of the Ni(II)L.2ClO$_4$ and Cu(II)L.2ClO$_4$ (ESI† (Fig. S7& S8) appear a band in the region of 1505-1520 cm$^{-1}$ assigned to valence vibrations of v(O-C=N) due to the enolization of H$_2$L during complexation.$^{17}$ The vibrations of the C=O group at 1660 cm$^{-1}$ is disappeared for the complexes and also a new broadband appears at 1135-1150 cm$^{-1}$ assigned to enol form of deprotonated hydrazone (v$_{C-O}$).$^{18}$ The azomethine (N=C) group frequencies appeared at the lower region (1594-1585 cm$^{-1}$) when compared with the ligand frequency 1618 cm$^{-1}$ due to the metal ion coordination.$^{19}$ This observation indicates the M(II) ion coordinate with the dianionic tetradentate N$_2$O$_2$ chelating ligand of the azomethine nitrogens and enolic oxygens. Moreover bands corresponding to one of the N-H groups also disappear and new medium bands appear around 1020 cm$^{-1}$ which corresponding to the N-N frequency. The pyridine (N=C) group stretching frequency around 1603 cm$^{-1}$ remains same in all complexes which shows metal ions do not involve in the coordination with pyridine nitrogen. The bands around 1378 and 767 cm$^{-1}$
are due to the bending vibrations of C-H of the aromatic ring. At lower frequency region the complexes exhibit medium intensity bands around 414-490 cm\(^{-1}\) and 518-580 cm\(^{-1}\) corresponding to M-N and M-O vibration modes respectively. From the ESI† (Fig. S8 & S9) a broad signal was appeared in the region of 1114 and 1084 cm\(^{-1}\) due to the antisymmetric stretching vibration of the perchlorate ions in complexes and a medium band at about 628 cm\(^{-1}\) and 1000 cm\(^{-1}\) due to the antisymmetric bending and stretching vibrations of the metal coordinated perchlorate moiety are confirmed.\(^{20}\). The FTIR spectral data can give the information of crystallinity of zeolite and encapsulation of complexes. The FTIR studies of NaY ESI† (Fig. S10) and ZEMC (Fig. S11 & S12) show that the peak intensities are weak due to the low concentration of the complexes in the cavity of zeolite. The NaY bands in the range 3600-3200 cm\(^{-1}\) due to the adsorbing tendency of the surface hydroxyl groups and the bands at 1200-450 cm\(^{-1}\) are due to the lattice (Si/Al)O\(_4\) vibrations.\(^{21}\) The bands of ZEMC and FC are exhibit bands in this region of 1615-1200 cm\(^{-1}\) which was absent in the NaY. The azomethine -C=N group stretching frequency is observed around 1595 cm\(^{-1}\) and the pyridine -N=C group stretching frequency is observed as broad band around 1616 cm\(^{-1}\) due to bending frequency of -OH groups the ZEMC. The C-O and N-N stretching frequencies were merged with the O-Si-O and O-Al-O lattice vibrations and all other peaks which were corresponding to C-H, C-C, C=C band vibrations of ZEMC are almost similar to FC. This observation confirms not only presence of metal complex in zeolite, but also no change in the lattice nature of zeolite. All ZEMC was shown peaks around 1121, 1020, 790 and 710 cm\(^{-1}\) because of the zeolite,\(^{22}\) indicating not only no consequent changes in the zeolite cavities but also no de-alumination during the encapsulation process. The new fairly less intense bands appearing at the lower frequency region around 550 cm\(^{-1}\) and 430 cm\(^{-1}\) in the encapsulated complexes originate from M-O and M-N vibrations.\(^{23}\) These observations suggest that very weak involvement in the metal ion in coordination in the zeolite. The FTIR spectral
analysis provided the evidence for the encapsulation of metal complexes in the zeolite matrix and crystallinity of the host zeolite.

Table 1: FTIR spectral values in cm\(^{-1}\) for the FC and ZEMC.

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<th>(\nu(_{\text{C=O}}))</th>
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<th>(\nu(_{\text{C=N-N-C}}))</th>
<th>(\nu(_{\text{C=NGN=C}}))</th>
<th>(\nu(_{\text{CGG}}))</th>
<th>(\nu(_{\text{CGGC}}))</th>
<th>(\nu(_{\text{NGN}}))</th>
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3.3 Optical absorption spectra /DRS studies

The UV-visible spectra were recorded for H\(_2\)L, FC and ZEMC and the corresponding spectra are given in the Fig.1 (a-e). The absorption spectrum of the H\(_2\)L in UV region exhibits three absorption bands at 272 nm (\(\pi\rightarrow\pi^*\)), 288 nm (\(\pi\rightarrow\pi^*\)), and 332 nm (\(n\rightarrow\pi^*\)). Ni(II)L.2ClO\(_4\) exhibit absorption bands at 258 nm and 352 nm due to the intra ligand \(\pi\rightarrow\pi^*\) transitions and \(n\rightarrow\pi^*\) transitions of azomethine(C=N) groups respectively. It shows a broad visible band centred at 650 nm assigned to \(^1A_{1g}\) to \(^1B_{1g}\) transitions.\(^{24}\) In addition the electronic spectral values in this region might be suggested slight distortion of the square planar geometry. The Ni(II) might have surrounded with the two imino nitrogen and two enolic form oxygen atoms.\(^{25}\) The Cu(II)L.2ClO\(_4\) in DMSO & methanol also exhibits the bands at 268 nm and 348 nm due to \(\pi\rightarrow\pi^*\) and \(n\rightarrow\pi^*\) transitions respectively. The square-planar Cu(II) complex gives a broad absorption band between 600 to 700 nm by Jahn-Teller distortion. Due to the \(\text{N}_2\text{O}_2\) moiety, the geometry of the copper complex might be distorted from octahedral to tetragonal or planar geometry.\(^{26}\)
The DRS spectra of the ZEMC are shown in Fig.1 (d&e). Ni(II)L-Y shows three characteristic bands at 223-269 and 334 nm due to the $\pi\rightarrow\pi^*$ and $n\rightarrow\pi^*$ transitions, respectively and a broad band centred at 608 nm for the d-d transitions. Cu(II)L-Y also shows the corresponding peak values at 222-266 nm and 325 nm are assigned to $\pi\rightarrow\pi^*$ and $n\rightarrow\pi^*$ transitions respectively. The Cu(II)L-Y shows a broad peak at 650 nm due to d-d transition.\textsuperscript{27,28}

The comparison of the ZEMC with FC the peaks shift was indicates the electronic transitions associated influence of the zeolite matrix and elongated axial coordination of the complexes. This further gives an idea about all complexes do not undergo a similar kind of structural change in zeolite-Y and (Si/Al)O\textsubscript{4} groups might be influence a peak shift. However, the presence of the similarly electronic transitions in the ZEMC in comparison to the neat complex (FC) in solution gives one of the probability to formation of geometry and stability of the complexes inside cavites of the zeolite-Y.

Fig.1: UV-VIS/DRS of the (a)H\textsubscript{2}L, (b) Ni(II)L.2ClO\textsubscript{4} (c) Cu(II)L.2ClO\textsubscript{4} (d)Ni(II)L-Y and (e) Cu(II)L-Y
3.4 EPR spectral studies

The EPR spectra of Cu(II)L.2ClO₄ and Cu(II)L-Y in liquid nitrogen temperature were recorded and presented in Fig.2 (a & b). The g values are calculated relative to tetracyanoethylene g-marker (TCNE, g=2.0023). The copper (II) (I=3/2) complex is typically anisotropic in nature at LNT. Nitrogen hyperfine splitting can be clearly seen in the spectrum. The Cu(II)L.2ClO₄ shows values of $g_{||}$, $g_{\perp}$ and $g_{av}$ at 2.34, 2.079 and 2.16 respectively. The $g_{||}$ > $g_{\perp}$ > 2.0023 indicates the covalent environment of the metal ion with the Schiff base and also the $A_\parallel$ value at 148 T indicates the coordinating metal environment might have a square planar geometry and unpaired electron in the $dx^2-y^2$ orbital. Further, Cu(II)L.2ClO₄ exhibit the G value $[G=(g_{||} - 2.0023)/(g_{\perp} - 2.0023)] = 4.56$ is slightly greater than 4, which indicates that the no exchange interaction in the (mono nuclear) copper(II) complex. It is evidenced that twist in the geometry may have octahedrally distorted square planar geometry or metal with incipient axial coordination.²⁹,³⁰ The Cu(II)L-Y also exhibit the g tensor values at $g_{||}$ (2.29) > $g_{\perp}$ (2.09) > $g_{av}$ (2.0023) this might be due to the hyper fine coupling of copper (II) with the tetradentate N₂O₂ with axial planar symmetry and the peaks are well isolated with less intensity. The hyper fine splitting factor ($A_\parallel$) at 160 T indicates presence of unpaired electron in the $dx^2-y^2$ orbital with axial interaction leads to elongated tetragonal distorted octahedral geometry with the square planar moiety.³¹ The Cu(II)L-Y exhibits G value $[G=(g_{||} - 2.0023)/(g_{\perp} - 2.0023)]$ are slightly greater than 4 its indicates that no copper(II) ion exchange interaction. It has been reported that high $g_{||}$ values are common to the six coordinate Cu(II) complexes with ligand containing hard donors such as nitrogen and oxygen. The $A_\parallel$ value of the Cu(II) L-Y is larger than Cu(II)L.2ClO₄, this might be either electrostatic interaction of the sodium ion or due to the silica skeleton. These observations conclude that geometry of the mono nuclear copper
complex in the free state and encapsulated state almost same and electronic studies also supports the EPR observation.\textsuperscript{32}

Fig.2: Experimental (thick) line stemming (dash) line spectra X-band epr spectra of the (a) Cu(II)L.2ClO\textsubscript{4} (b) Cu(II)L-Y at LNT (the spectrometer settings microwave power frequency 9.43GHz: microwave power 13mW: modulation frequency KHz; modulation amplitude 2G)

3.5 X-ray Photoelectron Spectroscopy analysis

The XPS spectra of ZEMC and FC are given in the ESI† (Fig:S 13a-d) it reveals the presence of the C, N, O, Na, Si, Al, Ni(II) and Cu(II) and which confirms respective surface chemical state of the elements.\textsuperscript{33} The peaks are related to carbon in free and encapsulated complexes show highly intense broad bands. The C 1S, N 1S, O 1S and Cl 2P appear at 285.1, 400.0, 531.2 and 207 eV respectively.\textsuperscript{34} From Fig.3(a-e) the C 1s XPS traces can be deconvoluted into five peaks corresponding values 284.6 eV, 285.1 eV, 286.4eV and 288.8 eV are attributed to the carbon sp\textsuperscript{2} (C=C), carbon sp\textsuperscript{3} (C-C), imine C=N, aryl ether (C-O-C) and carbonyl (C=O), respectively. The C=O group binding energy 288.9 eV disappears for the complexes and also a new broad peak appears at 286.9 eV assigned to enol form of deprotonated hydrazone (C-O') during complexation.\textsuperscript{35}

The XPS studies of FC reveal the multiplicity of electron, valence state, magnetic states of metal ions and stereochemical configurations. The phenomenon of shake-up satellite peaks in
the X-ray photoelectron spectra of 2p level spectra of the nickel(II) and copper(II) complexes are well documented.\textsuperscript{36} The appearance of shake-up satellite lines behind the M(II) 2p core lines of the Ni(II) and Cu(II) was shown covalency, magnetic and geometric properties of the compound. These XPS results are matched with an earlier investigation.\textsuperscript{37} From Fig.4 and Table 2 the traces of Ni(II)\textsubscript{L.2ClO\textsubscript{4}} indicate that no shake-up satellite peaks are observed behind the region of 878 eV for the Ni(II)(2p) and hence it confirms the planar form and diamagnetic nature of Ni(II).\textsuperscript{38,39} In 2p level spectra of Ni(II)L-Y, the \(\Delta 2P\) (ca.1.73 eV) more when compared to Ni(II)L.2ClO\textsubscript{4}. This may be due to existence of intracrystalline hydroxyl groups and electrostatic interaction with (Si/Al)O\textsubscript{4} lattice.

From ESI† (Fig S 14c&d) The copper (II) complexes was shown shake up satellites where as the diamagnetic Cu(I)(3d\textsuperscript{10}) never give any satellite peaks. Hence the Cu(II)L.2ClO\textsubscript{4} and Cu(II)L-Y shows the paramagnetic nature(3d\textsuperscript{0}). This observations confirms the presence of unpaired electron in dx\textsuperscript{2}−dy\textsuperscript{2} orbital and EPR spectral data also supports the same.\textsuperscript{40} The broadening of Cu 2p\textsubscript{3/2} satellite peak was observed. It may be due to distortion of octahedral to planar geometry. The Cu 2P peaks of Cu(II)L.2ClO\textsubscript{4} appears at the binding energy values at 934.12 eV and 953.87 eV as well as but the Cu(II)L-Y exhibits values at 934.90 eV, 954.30 eV for 2p\textsubscript{3/2} and 2P \textsubscript{1/2} respectively. The Cu(II)L-Y also exhibits the same peak position similar to Cu(II)L.2CLO\textsubscript{4} with the binding energy difference 0.41 eV. From FIG 4 the peak at 931.8 eV represents the reduction of Cu(II) to Cu(I) this was caused by the X-ray irradiation during acquisition time of the XPS analysis. But for nickel proximity the reduction is less, here xps spectra observes the broadening of the 2p level peak observed.\textsuperscript{41} The deconvoluted N1\textsubscript{S} and O1\textsubscript{S} (ESI† Fig.S15 & 16) XPS traces shown the binding energy values also suggest that the M(II) ion are coordinated with azomethine nitrogen and enol form of deprotonated oxygens in both FC and ZEMC.
The NMR, ESI-mass and the above spectral studies confirm the possible proposed structure of the complexes in the free and encapsulated systems as given in the Scheme (A&B).

<table>
<thead>
<tr>
<th>Compound</th>
<th>Si(2P)</th>
<th>Al(2P)</th>
<th>C(1S)</th>
<th>O(1S)</th>
<th>N(1S)</th>
<th>M(II) (2P)</th>
<th>Δ2P</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni(II)L.2ClO₄⁺</td>
<td>-</td>
<td>-</td>
<td>284.45</td>
<td>531.5</td>
<td>399.51</td>
<td>855.20, 873.13</td>
<td>17.45</td>
</tr>
<tr>
<td>Cu(II)L.2ClO₄⁺</td>
<td>-</td>
<td>-</td>
<td>285.05</td>
<td>532.03</td>
<td>399.60</td>
<td>934.12, 953.87</td>
<td>19.03</td>
</tr>
<tr>
<td>Ni(II)L-Y</td>
<td>102.5</td>
<td>74.6</td>
<td>284.85</td>
<td>532.03</td>
<td>400.12</td>
<td>855.97, 875.10</td>
<td>19.02</td>
</tr>
<tr>
<td>Cu(II)L-Y</td>
<td>102.6</td>
<td>75.8</td>
<td>284.75</td>
<td>532.4</td>
<td>400.80</td>
<td>934.90, 954.30</td>
<td>19.35</td>
</tr>
</tbody>
</table>

Fig. 3: Deconvoluted XPS of the C1s region for (a) H2L, (b) Ni(II)L.2ClO₄, (d) Cu(II)L.2ClO₄, (c) Ni(II) L-Y and (e) Cu(II) L-Y.
Fig. 4: M(II)p₃/₂ XPS patterns of the (a) Ni(II)L₂ClO₄ (b) Ni(II)L-Y (c) Cu(II)L₂ClO₄ and (d) Cu(II)L-Y.

3.6 Powder X-ray diffraction

The XRD of the NaY, Ni(II)L-Y, Cu(II)L-Y, Ni(II)L₂ClO₄, and Cu(II)L₂ClO₄ were recorded at room temperature shown in Fig. 5(a-c). The XRD patterns of the Ni(II)L-Y, Cu(II)L-Y are compared with the of Na-Y, though minute change in the peak intensity was observed. The relative peak intensities of the 220, 311, and 331 reflections for ZEMC slightly decreased when compared with the parent zeolite reflections, it can be attributed to change in sodium ion exchanged by metal moieties. The NaY has shown peak intensity I₃₃₁>I₂₂₀>I₃₁₁, but in case of the Ni(II)L-Y and Cu(II)L-Y the corresponding peak intensities I₃₃₁>I₃₁₁=I₂₂₀ and I₃₃₁>>I₃₁₁>I₂₂₀ are observed. The Ni(II)L-Y shows three new peaks at 2θ values 12.9°, 27.1°...
and 40.37° and Cu(II)L-Y also shows new peaks at 18.2°, and 42.6°. The new peak suggest allocation and formation of the metal complexes in the cavity of zeolite. In another way FC makes surface reduction of Na-Y during encapsulation process, hence peak intensity was observed to low. (Asterisks fig 5). The NaY crystalline nature does not change during the impregnation.

Fig.5: XRD spectra of (a)NaY, (b)Ni(II)L-Y and (c) Cu(II)L-Y (stick diagram shows XRD patterns of the (b) Ni(II)L.2ClO₄ and (c) Cu(II)L.2ClO₄). (Asterisks indexes the presence of the metal complexes on the cavity of the zeolite)

3.7 BET analysis

The Brunauer-Emmett-Teller (BET), N₂ adsorption/desorption isotherms, surface area and the pore volume studies for the NaY, Ni(II)L-Y and Cu(II)L-Y was shown in the (ESI† Fig S17a-c). The pore size distribution curves of samples was evaluated from adsorption branches of the isotherms (stick diagrams) using the BJH method these composites had type IV isotherms initially upto at p/p₀ =0.35 with a step increased at p/p₀ =0.35-0.7, reflecting their narrow pore size distribution due to the capillary condensation of the pores i.e. presence of the guest molecules in the pores of zeolite. The surface area of zeolite was observed to be 600 m²/g. But in case of ZEMC surface area was drastically reduced to 305 m²/g and 230 m²/g
respectively. The average pore size of free zeolite was 0.62 nm and it was reduced to 0.26, 0.17
nm on Ni(II), Cu(II) it may due to presence metal complexes in pores of zeolite. This clearly
suggesting the FC was encapsulated in the cavities of zeolite. The surface analysis revels the
ZEMC based on the metal loading, hence the copper (II) complexes was shown more reactive
sites than nickel (II).

3.8 Thermal analysis

The TG/DTG curves of FC and ZEMC were performed in static air atmosphere and
were shown in Fig 6(a-e). In the case of ZEMC the TG curve show a residual mass of around
85% clearly suggesting and shows thermal stability of composites. The DTG curves of FC and
ZEMC clearly shows the multi step decomposition. In case of Ni(II)L.2ClO$_4$, the first step
between 303- 423 K corresponds to the loss of coordinated counter ions with a mass loss of
8%. In the second step, the continuous loss of ligand molecules of the complex was observed in
the temperature range upto 731 K with a mass loss of 79%. The residual mass 12% corresponds
to the formation of nickel oxide. In the case of Cu(II)L.2ClO$_4$, the mass loss of (17%) lattice
water and perchlorate molecules occurs below 513 K. A further step corresponds to the
degradation of Cu(II)-ligand moiety between 523-773 K with a mass loss of 70%. The residual
mass 11% indicates the formation of CuO. From the Fig (6 c&d) DTG analysis the peak
temperature of ZEMC was higher when compared with peak temperatures of the FC. This
clearly suggests the metal free complexes were strongly inclusion in the cavities of zeolite
From Fig(7e) the NaY weight loss(15%) take place sharply in one step due to the presence of
water molecules, when comparison of these observations also suggesting the presence of the
metal complexes in the zeolite cavities.
Fig. 6: TG-DTG curves of the (a) Ni(II)L.2ClO₄ (b) Cu(II)L.2ClO₄ (c)Ni(II)L-Y, (d) Cu(II)L-Y and (e) Na-Y.
3.9: FESEM/HRTEM Analysis.

Typical scanning electron micrographs obtained for the parent NaY and the ZEMC are shown in Fig.7 (a-c). The, Na-Y possess shape of the particle is cubic angular. The SEM analysis of the ZEMC shows crystal nature the Na-Y was remains almost same even after complexation occurs in the cavities of the zeolite. From the (ESI† Fig: S18-21) EDAX spectra of the ZEMC conclude the each elements present in the cavity of zeolite. SEM image elemental mapping indicates that uniform distribution of elements in the cavities of zeolite. The elemental mapping clearly suggests that the particle surface boundaries do not have surface complexes. From image-J analysis software the histogram was plotted of the ZEMC. The average size of the ZEMC particles is calculated by the based on the Gaussian fit of the size distribution histogram NaY(ESI Fig: 25), Ni(II)L-Y and Cu(II)L-Y 98 nm corresponding average size are around 145 nm, 165 nm and 180 nm respectively.\(^4\),\(^7\),\(^8\)

Fig.7: The SEM image of the (a) NaY, (b) Ni(II)L-Y and (c) Ni(II)L-Y.
The TEM photographs of the parent NaY and ZEMC are shown in Fig.8 (a-c). This reveals that structure of the solid supports was rectangular spheroid (tablet shape) and its channels were well ordered. The encapsulated complexes Ni(II)L+Y and Cu(II)L+Y also show opaque nature and well ordered shape but slight change in the surface edges and the negligible agglomeration is observed when compared to parent zeolite. The morphology and the SAED patterns of the Ni(II)L-Y and Cu(II)L-Y shows crystalline nature even after encapsulation of the complex moiety in the cavities of zeolite. The black dot present in the zeolite micrograph itself hence if not indicating the surface present metal traces.

Fig.8: The HRTEM images of the (a) NaY, (b) Ni(II)L-Y and (c) Cu(II)L-Y and corresponding SAED pattern (d) NaY, (e) Ni(II)L-Y and (f) Cu(II)L-Y
4 Catalytic studies

4.1 Interaction of the Ni(II)L2ClO4 and Cu(II)L2ClO4 with the hydrogen peroxide

The effect of hydrogen peroxide in the presence of the Ni(II)L2ClO4 and Cu(II)L2ClO4 was recorded with UV-VIS spectra shown in the (ESI † Fig: S 25a&b) with the 2:1 molar ratio of the H2O2 and metal complexes. The decrement optical density for the d-d transition peak value was observed and new peaks around 450 and 470 nm may indicate the existence of either metal activated oxygen radicals or the formation of the superoxo and oxodimer species during the homogeneous conditions at last it result a colour less solid particles. Same phenomenon may be expected for the ZEMC in the formation of the new intermediates adduct and it can improve the substrates rate of the reaction rate and selectivity. It was observed that the copper has higher tendency in formation of the reactive intermediates than nickel. ZEMC less probability to formation of the polymeric and dimerised oxo species along with metal (II) centres where as the free complexes shows this phenomenon. This assets may show and leads to improving the product formation in the liquid phase oxidation reactions.49

4.2 Catalytic activity and kinetic parameters of ZEMC and FC in BH oxidation.

The catalytic activity of the FC and ZEMC was studied in the liquid phase (mild) oxidation reaction of the BH, while using H2O2 is an oxidant. Generally the metal complexes oxidation reaction depends on formation of the perhydroxy and hydroxyl radicals in presence of the oxidants. The polymeric nature of the free complexes might show less activity even at H2O2. In absence of H2O2 BH oxidation was not occurred, so metal active center play crucial role in the BH oxidation. In presence of the FC the optimum conversion was observed with H2O2 due to formation the [M(II)(L)].H2O2 adduct as an intermediate. The adduct can be generate the perhydroxy•OOH •OH intermediates with Nickel (II) and copper (II). From section 4.1 the decrease in the peak intensity of charge transfer and d-d transitions of FC and
simultaneously formation of the radical intermediates was observed around 450 and 470 nm.\(^{50}\) The BH oxidation the spectral change and consequences of the absorption spectra recorded at 223 and 259 nm. The aliquot samples were collected from reaction mixture for every 60 min and absorbance values were recorded at 223(±2) nm. From (ESI† Fig: S26a-e) the progressive decrement of absorption bands for every 60 min and those corresponding product benzophenone peaks also been absorbed at 250 and 340 nm.\(^{51}\) From the Fig. 9 (a) the percentage of conversion for NaY, Ni(II)L.2ClO\(_4\), Cu(II)L.2ClO\(_4\), Ni(II)L-Y and Cu(II)L-Y are 18%, 56%, 96%, 65% and 85% respectively (no significance conversion was observed even at 12 h). The copper complex was shown the higher conversion of percentage than nickel in both FC and ZEMC. The copper has more tendencies in the formation of the hydroperoxy intermediates with H\(_2\)O\(_2\) in acetonitrile medium than nickel. The Cu(II) is 15-electron species and participate actively in this electron back-donation process, hence it show higher catalytic activity in comparison to the corresponding 16-electron Ni(II) complex. The kinetic parameters in BH oxidation also follow the pattern of conversion percentage. From the Fig. 9 (b) The kinetic plot between ln(C\(_t\)/C\(_0\)) Vs time and plots shown the negative slope and the reaction follows the pseudo first order kinetics. All kinetic reactions show the same phenomenon. It may be due to the usage of H\(_2\)O\(_2\) and at constant BH concentration. The rate of the reaction follows the first order rate equation
\[
\ln \left( \frac{C_t}{C_0} \right) = -kt \tag{2}
\]
Here C\(_t\) is the concentration of the BH at different time, C\(_0\) is the initial concentration, t is the time and k is the reaction rate constant in min\(^{-1}\). From the figure 9 (b) The values of the rate constant for NaY, Ni(II)L.2ClO\(_4\), Cu(II)L.2ClO\(_4\), Ni(II)L-Y and Cu(II)L-Y catalysts are 0.000375 min\(^{-1}\), 0.00202 min\(^{-1}\), 0.00491 min\(^{-1}\), 0.00181 min\(^{-1}\) and 0.00468 min\(^{-1}\) respectively. The Cu(II)L-Y shows higher rate than Ni(II)L-Y this maybe formation adduct of the per hydroxyl ion with copper (II) centres is more than nickel. The surface area of the
Cu(II)L-Y less with more active species even than large surface area catalysts.\textsuperscript{52} Hence the copper, nickel enhance the host-guest interaction, which leads to avoid the formation of polymeric metal species and enhance the catalytic activity of the reaction.\textsuperscript{53}

**Fig 9:** The graph (a) & (b) Time Vs % Conversion, (c) & (d) kinetic plots for the both FC and ZEMC.

### 4.3 Mechanistic issues for photochemical performance

The photo catalytic degradation of the RhB with NaY, Ni(II)L-Y, Cu(II)L-Y, Ni(II)L.2ClO\textsubscript{4} and Cu(II)L.2ClO\textsubscript{4} under UV/Visible irradiation has been studied. The percentage of degradation and kinetic parameter calculated based Lambert-Beer's law

\[
\varepsilon = 103930 \text{ mol}^{-1} \text{ cm}^{-1} \text{ L} \]  

The degradation efficiency was calculated by the optical absorption spectral analysis. The aliquot samples of reaction medium were collected and the consequence absorption changes were recorded at 554±1nm. The spectral changes were given in the ESI†. Fig S27 &
The ZEMC has more degradation performance when compared to FC and NaY zeolite. In both probe reactions the removal percentages are 15%, 88%, 100%, 55% and 50% (26%, 73%, 78%, 44% and 63% in case of visible light) for the NaY, Ni(II)L-Y, Cu(II)L-Y, Ni(II)L.2ClO₄ and Cu(II)L.2ClO₄ respectively. The metal enhance the acidity of zeolite during exchange process, due to this photo catalytic performance, rate of reaction and removal efficiency of the RhB also increases. ZEMC could decrease the recombination of electron-hole pair and enhance the photo catalytic performance. The apparent rate constant (k_{app}) and fixed concentration of the H₂O₂ may leads to be concludes first order reaction. Fig. 9. reveals the negative slope in the both cases. The rate constants for the both irradiations was NaY, Ni(II)L-Y, Cu(II)L-Y, Ni(II)L.2ClO₄ and Cu(II)L.2ClO₄ (0.00128 min⁻¹, 0.375 min⁻¹, 0.0279 min⁻¹, 0.0115 min⁻¹ and 0.0285 min⁻¹( 0.0018, 0.00653, 0.00704, 0.00274, 0.00866 min⁻¹ in case visible light). The ZEMC show higher activity because of it metal loading efficiency (from tableA) which enhances the photo generated electron pairs (e⁻ and h⁺). Photo generated holes and electrons may react with surface hydroxyl groups are adsorbed water or O₂ to generate the active oxidative ionic radical (O₂⁻, OOH and •OH) from reaction medium. The O₂⁻ and •OH radicals are very reactive and quickly oxidise organic species at the surface of the zeolite. Hydroxyl radicals (•OH) is considered the most powerful oxidant (E° = 2.8 V) amongst other oxidants. Even the acidic nature can enhance in the formation of the active radical limits the degradation time. During the metal reduction from M(II) to M(I) the generation of the •OH radical is more in presence of the H₂O₂. Even the uniform distribution of metal in zeolite cavity leads to fast photo generation of hydroxyl radical (equation 3). So the catalytic activity depends on the percentage of metal, which results in more unsaturated surface coordination sites.
From the ESI† Fig :S28 lower in the wavelength around 5 nm due to either the electrostatic interactions with hydroxyl groups or formation de-ethylated spices of the dye molecule during the degradation.\textsuperscript{57} The photo generated electrons give more efficiency towards the hole formation and minimize the band gap energy, mean while the formation of the °OH, °°O₂H, °O₂ radical is a powerful oxidant and starts a cascade of oxidation reactions that can convert the organic matter in solution completely into water, carbon dioxide and inorganic compounds.\textsuperscript{58, 59} From (ESI† Figs:S38) the change in hypsochromic shift was around 25 nm, this cause the detachments of chromophoric group present in the dye molecule and formation de-ethylated intermediates of RhB molecules.\textsuperscript{60}

4.4 Recycle tests and metal leaching tests and catalytic activity

The stable (Si/Al)O₄ moiety of zeolite does not allows the metal ion leaching. Due to the higher cross sectional area of RhB, it is not possible to enter into the cavities of zeolite. While using H₂O₂ the negligible metal leaching was observed. The approximate cross sectional area the metal hydrazones complexes is 162 Å\textsuperscript{2} & 164 Å\textsuperscript{2} (measured by the chem sketch software tool). It can be fit for the zeolite unit cell dimensions and in liquid phase encapsulation the free complexes formation. Hence FC can be impregnates in the cavity of zeolite and stabilised by
Fig 10: The recovered ZEMC overall percentage of conversion of BH oxidation (bar diagram) and dye degradation (line diagram) in the three cycles.

(Si/Al)O\textsubscript{4} moieties. So, the metal ion leaching is very difficult after impregnation TBALE A..

After completing the reaction, ZEMC was recovered by nano-filtration and washed with water, dilute HCl, acetonitrile and methanol mixture. The resulted colour solid was dried at 353 K for 6 h and each composite catalytic activity checked and the overall percentage provided in the Fig. 10.

5. Conclusion

The Ni(II) and Cu(II) complexes of the H\textsubscript{2}L and their complexes encapsulated in the cavities of zeolite-Y were synthesized by FLM. The synthesized composite materials formation and geometry within the zeolite matrix have been studied along with their free complexes by several spectroscopic, thermal analysis, sorption and microscopic techniques. In both probe reactions the FC( ZEMC0 mild oxidation of the BH and photo catalytic degradation performance of were studied. From these studies the catalytic performance depends on the not
only surface area but also percentage of the metal present in cavities of the zeolite. The
generation of the perhydroxyl and hydroxy radical intermediates adduct(M- OOOH) teh
influence rate of conversion percentage. The optical spectral data and LC-MS data has shown
the benzophenone fragments in the BH oxidation. Photocatalytic reaction the removal
percentage of the dye also depends 'OH, °°'O₂H, °O₂ radical is a powerful oxidant and starts a
cascade of oxidation reactions that can convert the organic matter in solution completely into
water, carbon dioxide, and inorganic compounds. In the dye removal and BH oxidation the
apparent rate conatant(k.app) if representation the pseudo first order reaction in all cases. here the
percentage of the conversion if more for the copper complexes than nickel. Hence the surface
active species accelerate the rate of the reaction in both cases. The surface area and percentage
of the copper (Table:A ESI†) might influence the rate of the reaction rather than average
particle size and crystalline nature.

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Appendix A. Supplementary data†

1H and 13C-NMR spectra, ESI-mass, FTIR, N1s, and O1s deconvoluted XPS spectral
trace with survey graph and M(II) 2p spectrum. N2 isotherms, UV-VIS Spectral change,
microscopic analysis, percentage of the nickel, copper, silica and aluminium, The recovered
catalysts DRS/ UV-VIS spectra, PXRD and LC-MS are given in the electronic supplementary
data.
References


Scheme (A): The proposed reaction mechanism of Ni(II) and Cu(II) complexes with tetradentate N\textsubscript{2}O\textsubscript{2} Schiff base moiety.

Scheme (B): The proposed reaction mechanism and framework structure of zeolite with encapsulated metal aryl hydrazone complexes of nickel (II) and copper(II).