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Zeolite Incorporated Copper-Schiff Base Complex: Synthesis, Characterization and Heterogeneous Catalytic Oxidation

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A zeolite immobilized hybrid catalyst Cu(MeO-salpn)-NaY has been synthesized by incorporating Cu(II) Schiff base [where MeO-salpnH_2 is *N,N′*-(propane-1,3)-*bis*-(3-methoxysalicylaldiimine)] complex in the porous matrix of zeolite NaY. The prepared hybrid material has been characterized by infrared, UV-visible spectra, powder X-ray diffraction (XRD) and thermogravimetric (TG-DTA) analyses. The X-ray powder diffraction analysis showed that the crystalline integrity of the pristine NaY zeolite remained intact upon immobilization of the complex. Spectroscopic study indicates that CuN_2O_2 basal plane of neat complex undergoes distortion upon immobilization of the complex in zeolite cavity. The hybrid catalyst was employed in the oxidation reactions of phenol and 1-naphthol and found to be catalytically active with impressive selectivity. At the same time, free complex [Cu(MeO-salpn)(H_2O)] and hybrid material Cu-NaY were prepared and applied for the same reactions, but the catalytic activity of these species were found to be very poor. This study shows that there occurs a distortion of the coordination environment around copper(II) upon immobilization which is a major reason behind the different catalytic activity of these copper-Schiff base systems.

Keywords: Copper(II) Schiff base, Heterogeneous catalyst, NaY zeolite, Catalytic oxidation.

INTRODUCTION

Natural zeolites are crystalline hydrated aluminosilicates of group IA and group IIA elements such as Na^+, K^+, Mg^{2+} and Ca^{2+}. Chemically, they are represented by the empirical formula $M_{2/n}O\cdot Al_2O_3\cdot ySiO_2\cdot wH_2O$, where y is 2 or more, n is the cation valence and w represents the water contained in the voids of the zeolite [1]. An empirical rule, Loewenstein rule [2] suggests that in zeolites, only Si-O-Si and Si-O-Al linkages be allowed. In other words, the Al-O-Al linkage does not occur in zeolites [3] and the Si/Al molar ratio is ≥ 1. These types of solids contain internal networks of linked channels, which open on larger cages or pores. For example, zeolite NaY has a supercage dimension of ~ 13 Å. This zeolite also has a sodalite cage (~7 Å). These materials are found be some of the best agents for preparation of functional materials [1,4,5]. These types of materials have been found to be effective in catalysis, photocatalysis, photoredox applications.

Some sensors have also been prepared by incorporating organic dye molecules in zeolitic cavities. These types of functional materials have been found to be excellent agents in the field of industrial separation and catalysis [6]. In one of the pioneering works, Sykora & Kincaid [4] reported the $[Ru(bpy)_n(bpz)_{3-n}]^{2+}$ complexes (bpz = 2,2′-bipyrazine and bpy = 2,2′-bipyridine) upon immobilization in zeolites could be used for the photochemical storage of light energy. In terms of catalysis, preparation of well defined, solid supported, single site catalysts by immobilizing transition metal complexes in a porous matrix would be a major advancement as regards the industrial implementation of catalytic technologies [7].

In the natural life processes also, nature has designed mechanisms to produce only the products required for its sustainability, thereby not producing undesired or waste materials. Enzymes are one of the best examples of these types. These enzymes usually contain an active metal center like copper or manganese [8] and many others. Reproducing these type of naturally specific life process reactions in laboratory may be extremely difficult, but mimicking them can improve the chemical reactions that we follow today. In enzymes, the active centres are actually encapsulated in protein cavities to prevent them from degradation. So, to mimic the activity of enzymes, the metal complexes are attempted to be encapsulated in some porous matrices. Metal complexes using ligands like phthalocyanines, porphyrenes or Schiff bases can mimic the active centres of enzymes. The commonly used porous matrices are zeolites or molecular sieves, which can structurally resemble enzymes [9,10]. So, these type of porous matrix can be used for directing a chemical reaction, by immobilizing metal complexes as active centres [11]. Due to their porous nature, they can also show shape selectivity to a great extent. One example of mononuclear copper complex as an active centre in enzyme is galactose oxidase [12], which stereospecifically oxidizes the phenolic compounds. Schiff base complex of copper has a comparable environment around the central metal ion comparable to the active sites of galactose oxidase. The oxidative reactions in homogeneous medium which are catalyzed by metal complexes have been frequently found to be impeded due to the degradation of the complexes and or formation of μ-oxo dimers. But, recently, it was shown that immobilization of metal complexes within porous matrices increases the catalytic efficacy in compared to their homogeneous counterparts [13]. Schiff base complexes have been immobilized in zeolite matrices and catalytic efficacy of these complexes have been tested in oxidation reactions both under homogeneous and heterogeneous conditions [13-17] and many other types of catalytic reactions like epoxidation [18], coupling reactions [19], Baeyer-Villiger oxidation [20], *etc.* Kundu *et al.* [21] recently synthesized and characterized zeolite encapsulated host-guest copper Schiff base complexes and studied their catalytic efficacies in a number of different types of reactions. All these reactions have proved that the zeolite incorporated complexes have shown better catalytic efficacies than their homogeneous counterparts. Applications of zeolites and immobilized materials have recently been well reviewed by Li *et al.* [22] suggesting their growing importance in chemical and industrial fields. Due to their easy separation, recovery and recyclability, these types of zeolite immobilized biomimetic heterogeneous catalysts are gaining huge importance in environmental and sustainable chemistry nowadays, because these will limit the waste generation by decreasing the number of undesired chemicals [7,8,10].

Hydrogen peroxide (H_2O_2) has fascinated the scientists for a long time due to its environmentally friendly reduction products, water and oxygen. That is why various types of oxidation reactions by H_2O_2 have been undertaken by many groups in last few years, many of them trying to mimic the natural metalloenzymes [23]. Synthetic iron and manganese complexes have been employed in different biomimetic reactions containing heme or non-heme environments for the catalytic oxidation by hydrogen peroxide [24-26]. These types of oxidation reactions are gaining importance due to their environmental benign nature.

Herein, the synthesis of a copper Schiff base complex [CuMeO-salpn)(H_2O)] [where MeO-salpnH_2 = N,N′-(propane-1,3)-*bis*-(3-methoxysalicylaldiimine)], incorporation of the complex in zeolite NaY matrix, characterization and catalytic efficacy of hybrid material using environmentally benign oxidizing agent H_2O_2 in the oxidation reaction of phenol and 1-naphthol is reported. The recyclability and heterogeneity of the catalyst have also been studied.

EXPERIMENTAL

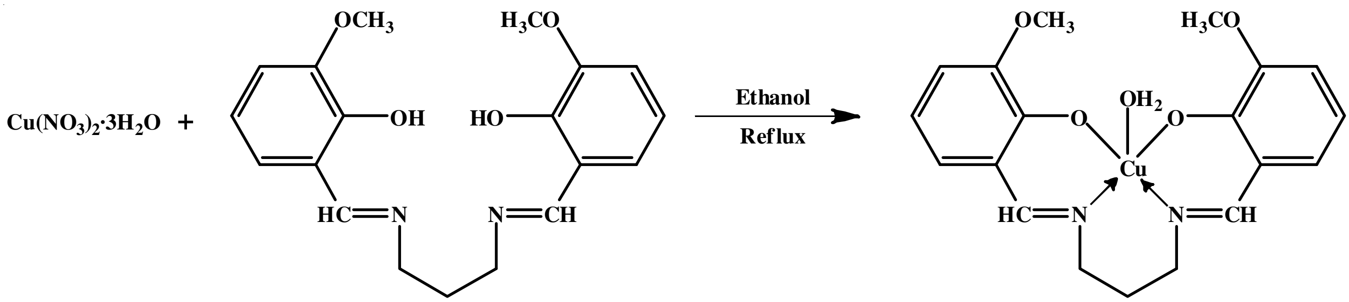
The NaY zeolite was obtained from Tosoh Corporation, Japan. 3-Methoxysalicylaldehyde, propane 1,3-diamine and copper nitrate trihydrate $Cu(NO_3)_2{\cdot}3H_2O$ (E. Merck, India) were of AR grade and used without further purification.

Characterization: Infrared and electronic spectra were measured on Perkin-Elmer 783 and Hitachi U 3400 spectrophotometer, respectively. The X-ray powder diffraction studies were performed on Rigaku miniflex X-ray diffractometer. The catalytic reaction products were analyzed in Hewlett-Packard 5880A gas chromatograph equipped with flame ionization detector.

Synthesis of ligand MeO-salpnH_2: Ligand MeO-salpnH_2 was synthesized by condensation of 3-methoxy salicylaldehyde with propane 1,3-diamine using standard condensation procedure [27,28]. 3-Methoxy salicylaldehyde (0.304 g, 2 mmol) was dissolved in 10 mL of ethanol and this solution was added to an ethanolic solution of 1,3-diaminopropane (0.074 g, 1 mmol). The mixture was refluxed for 1 h and the collected the obtained yellow solid by filtration.

Synthesis of Cu(MeO-salpn)(H_2O): Ethanolic solution (20 mL) of $Cu(NO_3)_2{\cdot}3H_2O$ (0.489 g, 2 mmol) was added slowly to an ethanolic solution of MeO-salpnH_2 (0.444 g, 2 mmol) with continuous stirring. The reaction mixture was turned deep green and then refluxed for 1 h, filtered and the filtrate was kept for slow evaporation. The green product obtained was recrystallized from ethanol (**Scheme-I**).

Incorporation of Cu(II) in NaY zeolite: Copper(II) was incorporated in NaY zeolite matrix by the ion exchange process [13]. NaY zeolite (1.0 g) was added to $Cu(NO_3)_2{\cdot}3H_2O$ (1 g was dissolved in 50 mL of water) solution. The resulting slurry



Scheme-I

was stirred continuously for 10 h at room temperature. The white zeolite turned blue during the stirring. The resulting mass was filtered and washed with ample amount of distilled water and finally dried under vacuum. Calcination was not performed to avoid the migration of Cu(II) ion from the vicinity of the supercage of the zeolite. The light blue powder thus obtained will be designated hereinafter as Cu-NaY.

Immobilization of Cu(MeO-salpn) in NaY: Cu-NaY (1 g) was mixed thoroughly with excess MeO-salpnH_2 in a round bottom flask, then N_2 was purged to maintain inert atmosphere. The flask was heated at 130 ºC with occasional stirring for 4 h, whereby the whole mass turned green. The reaction mixture was cooled, filtered and then finely pulverized. The product was subjected to Soxhlet washing using ethanol and acetonitrile as solvents. The final product obtained was light green powder. and designated as Cu(MeO-salpn)-NaY (**Scheme-II**).

Catalytic reactions: The efficacy of the prepared hybrid material as heterogeneous catalyst was tested in the oxidation reactions of phenol and 1-naphthol. The catalytic reactions were performed in a glass batch reactor. In a representative reaction, 1 g of substrate in 10 mL of solvent was added to 50 mg catalyst and then the reaction mixture was equilibrated in an oil bath to 50 ºC. The H_2O_2 solution (2 mL, 30%) was added with continuous stirring (**Scheme-III**). The products were collected at different time intervals and identified by GC.

In order to determine the efficacy of catalyst as heterogeneous catalyst, the reaction of 1-naphthol was stopped in middle, the catalyst was filtered off and then the reaction was continued without catalyst. It was observed that the reaction did not proceed further. In another test, the reaction mixture, after the separation of catalyst was subjected to AAS analysis to determine the metal ion in solution. The copper ion was not found in the reaction medium.

RESULTS AND DISCUSSION

A 'ship-in-a-bottle' method was employed for the incorporation of the metal complex within the zeolite pore [29]. Cu-NaY was reacted with the molten Schiff base ligand having flexible backbone. It is obvious that Cu(MeO-salpn) complex will be formed both on the surface and within the pores of the NaY zeolite matrix. Since this copper Schiff base complex is neutral, there will be only weak van der Waals type of force operative to hold the complex on the surface. The prepared material was Soxhlet washed with C_2H_5OH and CH_3CN to remove the complexes that have been adhering on the surface of the zeolite matrix. However, the complexes formed inside the zeolite supercage will not be washed away as the complex formed within the supercage is large in size with respect to the channels and could not get out, due to their actual physical entrapment within the pores. The final product was pale green in colour. The total copper content in Cu(MeO-salpn)-NaY is given in Table-1. The copper content agrees well with the carbon and nitrogen analyses value.

TABLE-1
ELEMENTAL ANALYSES FOR COMPLEX
Cu(MeO-salpn)(H_2O), Cu-(MeO-salpn)-NaY

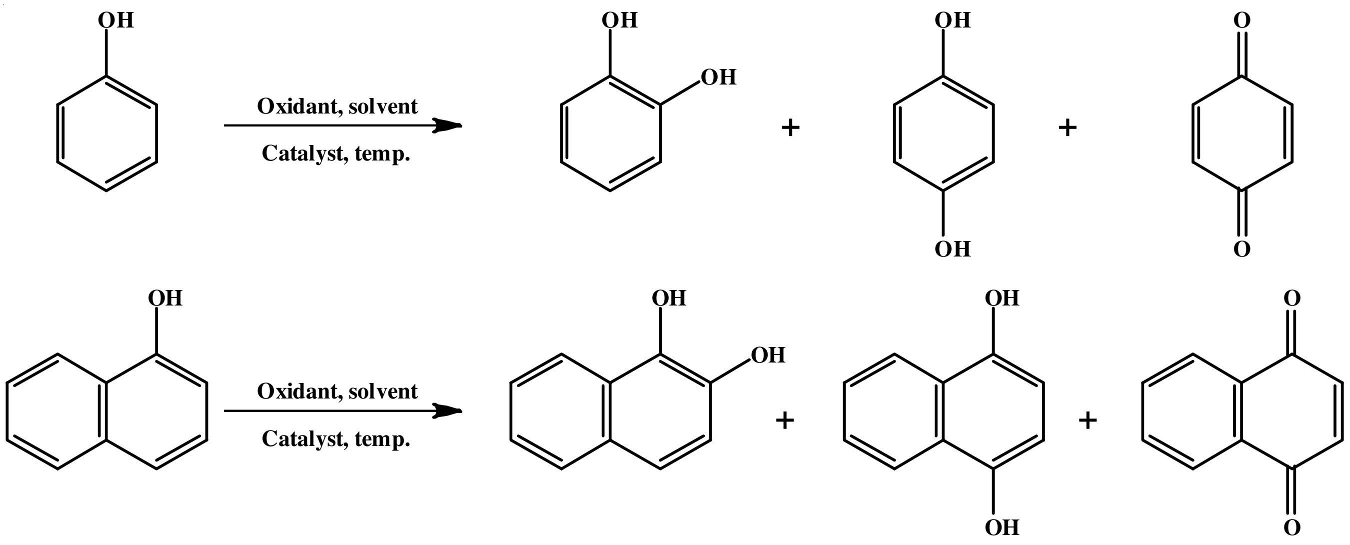
Species	Copper(II) content (wt.%)	Cu-Schiff base concentration (mol/g)
[Cu(MeO-salpn)(H_2O)]	15.1 (15.06)[a]	–
Cu(MeO-salpn)-NaY	2.74	4.31×10^{-4}

[a](Calculated)

IR studies: The IR of the free complex (Fig. 1) shows a sharp band at 1650-1630 cm^{-1}, which can be attributable to the azomethine group of the Schiff base ligand. This band occurs at ~10 cm^{-1} higher frequency in case of free ligand [29-31].

$$Cu(NO_3)_2{\cdot}3H_2O + NaY \xrightarrow[\text{Ion-exchange}]{\text{Water}} Cu\text{-}NaY \xrightarrow[\text{or in soluion}]{\text{Ligand in molten state}} CuL\text{-}NaY$$

Scheme-II



Scheme-III

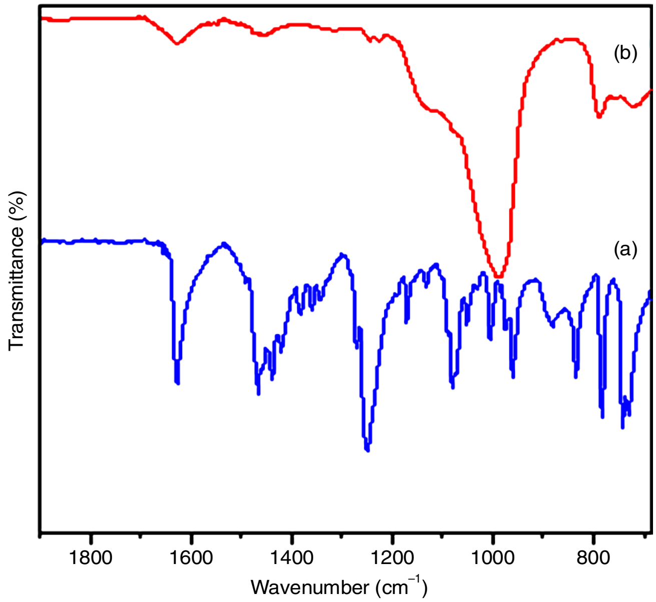


Fig. 1. IR spectra of Cu(MeO-salpn)(H_2O) (a) and Cu(MeO-salpn)-NaY (b)

The bands at 1400-1300 cm^{-1} can be attributed to the C-O stretching frequency [31]. In case of Cu(MeO-salpn)-NaY, the bands have become very feeble, which is obvious from the fact that the weight% of complex within the zeolite is very small. But, still, the bands in the range 1650-1300 cm^{-1} are present in the immobilized complex. As no zeolitic band appears in this range, except the band for HOH bending vibration of H_2O, which disappears upon careful drying of the zeolite, it can be inferred that the complex has been formed inside the zeolite matrix. The vibration bands of the host zeolite matrix actually obscures the bands of the copper complex in the other regions. The IR bands of Cu(MeO-salpn)-NaY shows a strong peak at *ca.* 1031 cm^{-1}, it is attributable to the asymmetric stretching of Al-O-Si band of the zeolite. The symmetric stretching and bending bands of Al-O-Si appear at 732 and 454 cm^{-1}, respectively [30,31].

Thermal analysis: The TG-DTA profile of free Cu(MeO-salpn)(H_2O) complex and immobilized species Cu(MeO-salpn)-NaY are shown in Fig. 2. It is clearly observed that the free complex starts losing solvent molecule in the temperature range a little above ambient temperature and the corresponding DTA shows small endothermic peak (Fig. 2a). A very strong exothermic peak is observed in the temperature range 220 ºC to 260 ºC corresponding to the decomposition of the complex. The corresponding TGA curve shows corresponding weight loss in this temperature range. For the immobilized species (Fig. 2b), the zeolite moiety starts losing water molecules above ambient temperature and continues to lose weight up to approx. 500 ºC as huge amount of loosely bound water molecules are present in the zeolite matrix. Also, there occurs a small peak at around 250 ºC corresponding well to the decomposition of the copper Schiff base complex within zeolite cavity. In total, a broad peak is observed in the thermogram of the hybrid material.

UV-vis studies: The electronic spectra of the complex [Cu(MeO-salpn)(H_2O)] and catalyst Cu(MeO-salpn)-NaY were measured in solid state (Fig. 3). The bands appearing at 598 and 373 nm for the free complex [Cu(MeO-salpn)(H_2O)] are assigned to *d-d* transition band and ligand charge transfer bands, respectively [29]. These bands have been found to be shifted to 540 nm and 361 nm, respectively for the immobilized species *i.e.* Cu(MeO-salpn)-NaY (Table-2). This blue shifting (shifting to higher energy) of UV-Visible bands implies that the in-plane ligand field around the metal ion of the complex becomes stronger upon immobilization of complex in zeolite cavity [17,29].

TABLE-2
UV-VISIBLE SPECTRAL PARAMETER

Species	*d-d* Transition band	Ligand charge transfer band
[Cu(MeO-salpn)(H_2O)]	598 nm	373 nm
Cu(MeO-salpn)-NaY	540 nm	368 nm

XRD studies: The powder X-ray diffraction pattern of free NaY zeolite and the prepared catalyst is shown in Fig. 4. It can be clearly observed upon comparison of the XRD spectral patterns of Cu(MeO-salpn)-NaY with the standard patterns of NaY zeolite that the crystallinity of the mother zeolite matrix remains unchanged upon immobilization of copper Schiff base complex [18-20]. As the weight % of copper complex in this hybrid material is very low, the peaks are in general obscured by the zeolite crystalline peaks [18-20].

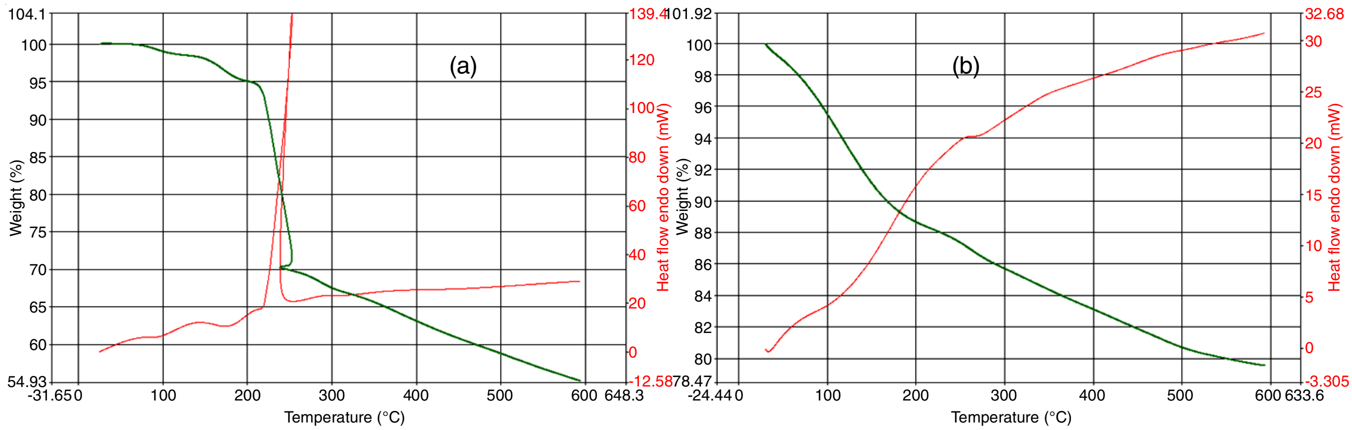


Fig. 2. Thermogravimetric analyses of Cu(MeO-salpn)(H_2O) (a) and Cu(MeO-salpn)-NaY (b). Rate of heating 10 °C/min, standard α-Al_2O_3

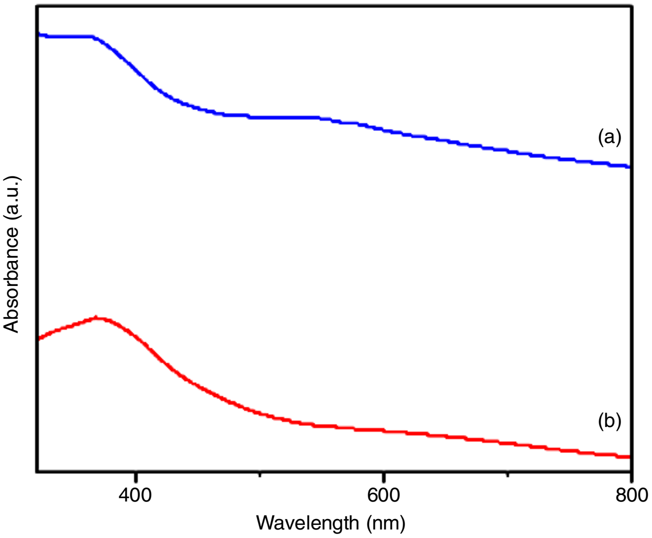


Fig. 3. UV-visible spectra of Cu(MeO-salpn)-NaY (a) and Cu(MeO-salpn)(H_2O) (b)

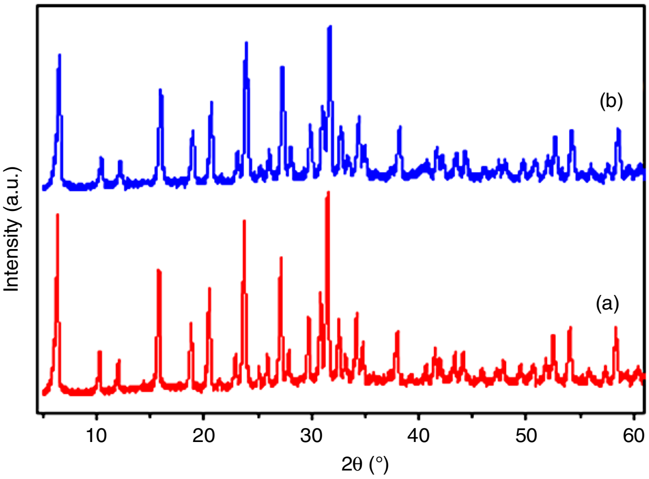


Fig. 4. Powder X-ray diffraction patterns of NaY (a) and Cu(MeO-salpn)-NaY (b)

Catalytic reactions: The oxidation of phenol and 1-naphthol were carried out to test the catalytic efficiency of the prepared catalyst. In these reactions, the hybrid catalyst has shown some commendable catalytic activity (Table-3). It is interesting to mention that pristine free complex Cu(MeO-salpn)(H_2O) has little catalytic activity, so also the Cu-NaY. Hydroxylation of phenol selectively yields two products, catechol and quinone, though three products are possible in this reaction like catechol, hydroquinone and benzoquinone. In case of 1-naphthol, there has been only one product 1,4-naphthaquinone, instead of three possible products namely 1,2-dihydroxybenzene, 1,4-naptha-quinone and 1,4-dihydroxynaphthalene. The reaction profiles of the catalytic performance of the hybrid material are shown in Fig. 5. There has been some tar formation in the reaction phase for phenol oxidation which may block the reaction, but for 1-naphthol oxidation, the catalyst could be recycled for at least two cycles without much drop of activity. It can be seen that 1-naphthol was oxidized to a greater extent than phenol itself. In case of phenol oxidation, there has been some tar formation during the course of the reaction which may have blocked the zeolite pores structure, thereby decreasing the contact of the metal ions with the reactants or the oxidant. The recyclability test shows that for the first two reaction cycles there is not much change in the substrate conversion. The third cycle shows a little drop in catalytic activity of Cu(MeO-salpn)-NaY, where 1-naphthol conversion was observed to decrease to 68% (Fig. 6).

Heterogeneity test: To ascertain that the reaction was following truly heterogeneous catalytic pathway, the metal leaching was tested in the reactions. The reaction was stopped in the middle, the catalyst was filtered off and the reaction was continued without catalyst. The reaction did not proceed further. Also, in another way, the reaction mixture was subjected to Atomic Absorption spectroscopic study to test for copper in the solution, but no metal was observed in the reaction phase. This indicates that the catalyst was behaving as a heterogeneous catalyst.

Conclusion

In summary, zeolite immobilized hybrid catalyst Cu(MeO-salpn)-NaY has been synthesized by incorporating Cu(II) Schiff base, which has a square pyramidal geometry [17], undergoes the distortion of the basal plane upon immobilization in zeolite cavity. The shifting of spectral band to lower wavelength region (blue shifting) indicates the axial ligand field has become weaker in the immobilized species. This may be due to the loss of axial ligands of the complex during immobilization, which will result in a tetracoordinated species. Evidently, a copper Schiff base moiety becomes catalytically more active when the distortion around the central metal ion is greater [29]. This

TABLE-3
COMPARISON OF CATALYTIC PERFORMANCE OF Cu(MeO-salpn)-NaY, [Cu(MeO-salpn)(H_2O)] AND Cu-NaY IN THE OXIDATION REACTION OF PHENOL AND 1-NAPHTHOL[a]

Catalyst	Time (h)	Phenol					1-Naphthol			
		Overall conversion (%)	TON[b]	Product selectivity (%)			Overall conversion (%)	TON[b]	Product selectivity (%)	
				BQ[c]	CAT[c]	HQ[c]			1,4-NQ[c]	1,4-DHN[c] /1,2-DHN[c]
Cu(MeO-salpn)-NaY	3	14	–	–	–	–	49	–	–	–
	6	20	98.6	–	65	35	76	244.5	100	–
[Cu(MeOsalpn)(H_2O)]	6	< 5%								
Cu-NaY	6	< 5%								

[a]Reaction condition: 1 g substrate, 10 mL solvent, 2 mL oxidant, 50 mg catalyst, temperature; [b]TON = Turn Over Number = (moles of substrate converted)/Active sites; [c]BQ = Benzoquinone, CAT = Catechol, HQ = Hydroquinone, 1,4- NQ = 1,4-Naphthaquinone, 1,4-DHN = 1,4-Dihydroxy naphthalene, 1,2-DHN = 1,2-Dihydroxynaphthalene.

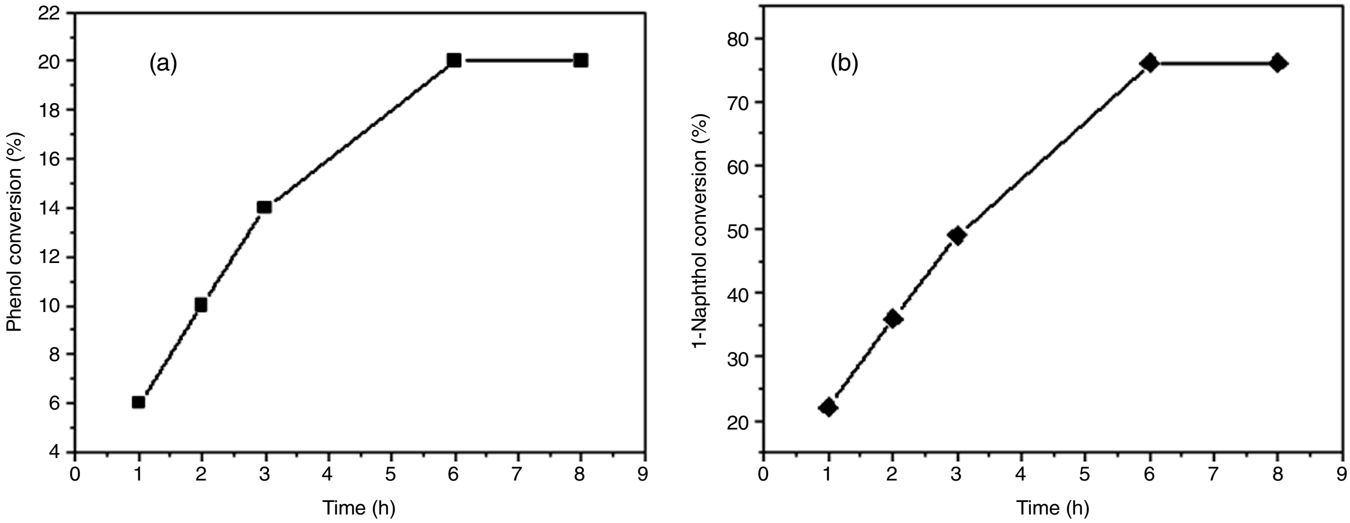


Fig. 5. Reaction profile diagrams of phenol (a) and 1-naphthol (b) by Cu(MeO-salpn)-NaY as catalyst

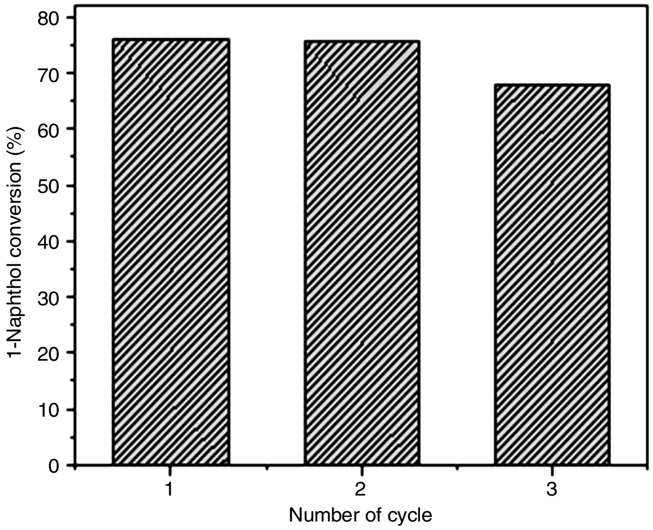


Fig. 6. Recyclability test of the catalyst Cu(MeO-salpn)-NaY

is clearly reflected in the catalytic activity, as can be seen that the free complex is almost catalytically inactive, but the hybrid material shows strong catalytic activity. This can originate from the weakening of axial ligand field, facilitating the nucleophilic attack by the oxidant, thereby promoting the catalytic efficacy. It is pertinent to mention that though in metalloproteins more complex situations were observed, in blue copper proteins, the activity of the metal centre is maximum where the coordination environment around the metal centre is intermediate between tetrahedral and square planar. Flexibility of the diamine back bone of the ligand is crucial for the immobilization of complex.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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