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Abstract. Copper (II) and Cobalt (II) metal complexes of phlantocyamine was effectively encapsulated into the super cages of Zeolite-Y using the flexible ligand method and H_2O_2 as the oxidant. The characterization of the synthesized encapsulated catalysts was carried out using the various physico-chemical and spectroscopic methods such as the Brunauer-Emmett-Teller (BET), Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES), Fourier Transform Infrared Spectroscopy (FT-IR), Thermogravimetric/ Differential Analysis (TGA/DTG), Scanning Electron Microscopy (SEM), X-ray powder Diffractometer (XRD) and CHNS Analyser. All the characterization techniques used suggest and confirm the existence of the metal complexes encapsulated inside the super cavities of the Zeolite-Y. The prepared catalyst was used in the oxidation of phenol and benzene which gave an excellent result. There was an increase in the catalytic activity and stability of the catalysts as a result of encapsulation. The prepared encapsulated metal complexes were recovered by vacuum filtration and was re-used three time with almost no change in its catalytic activity suggesting the eco-friendly nature of the prepared encapsulated metal complex catalysts.
Keywords: Zeolite, Catalysis, Encapsulation, Phenol, Benzene.

1. Introduction

The encapsulation of metal complexes into the cavities of zeolite and other allied materials has been one of the current researches in the area of catalysis as a result of their ability to act as biomimetic heterogeneous catalyst for various oxidation reactions [1-4]. The as synthesized hybrid organic-inorganic material not only possess the characteristics properties of a heterogeneous catalysts but also maintains the high catalytic properties of an homogenous catalysts as a result of the site isolated effect [5, 6]. In this regard, the encapsulation of metals complexes into the cavities of zeolite have been receiving tremendous attention in recent times [7-9]. So far, quite a number of methods have been suggested for the encapsulation of metal complexes into the zeolite cavities however, the choice of which method to use is determined by the size of the ligand with respect to the diameter of the zeolitic channels [10]. Among the several methods that has been suggested is the flexible ligand method which is the most widely used method as it is a straight forward method and it has a simple strategy [11]. The flexible ligand method is based on the assumption that the free ligand can enter with ease into the super cages of the zeolite structure because they are flexible enough to pass through the restricting walls into

the larger zeolitic cages. It is assumed that once the ligand move into the cages and chelate with the previously exchanged metal ions, the resulting complex formation is unable to leave the cages owing to its bigger size than that of the zeolite pore diameter [12]. The current curiosity in the oxidation of phenol to useful compounds has to a great percentage been driven by its usefulness in most sector of the chemical industry including pharmaceuticals, agro-chemicals, flavours, polymerization inhibitors, and anti-oxidants [13]. The production of catechol which is one of the major products of phenol oxidation takes place in two processes; (i) orthoformylation of phenol followed by oxidation and (ii) the oxidation of phenol to o-quinones and later reduction into catechol. These multiple stage pathways are most times prolonged, rigorous and generate so many oxidized, coupling and polymerized products [14]. So in other to meet the ever increasing demands for the products arising from the oxidation of phenols as well as satisfy the environmental regulations, encapsulation of metal complexes into the cages of zeolite have been utilized. The development of a clean oxidation process has been an important topic of relevance in present day chemistry. Several researchers have reported that mimicking the active site of enzymes is a fruitful approach to the development of catalyst which could operate under mild conditions and in a clean fashion. However, the accessibility of the catalysts in terms of their price and availability on a large scale also play a significant role of the economic viability of the processes. Therefore the metal complexes of pthaltocynamine used in this research present a unique attribute in the sense that pthaltocynamine is cheap and readily available. Also their macrocyclic structure looks like that of the porphyrin complexes which is used naturally in the active sites of oxygenase enzymes which means that it has a potential to be used as catalysts for oxidation. The use of pthaltocynamine complexed with metal have not used studied for catalytic oxidation reactions to the best of our understanding or not been studied in detail.

In this research work, Cu(II) and Co(II) ions were complexed with pthaltocynamine ligand using the flexible ligand method. The prepared catalyst was characterized and used for the oxidation of phenol and benzene. The rate of conversion was monitored and compared with the blank and ordinary metal exchange. The reusability studies of the prepared catalysts were also evaluated.

2. Materials and Methods

2.1. Materials

The chemical used for this research study are as follows; Zeolite NH$_4$-Y (received from the OCM laboratory Indian Institute of Petroleum, Dehradun, India), HPLC water (Fisher scientific) Copper (II) Chloride (Sigma Aldrich), Cobalt (II) Chloride (Sigma Aldrich), Phenol (Sigma Aldrich), Hydrogen Peroxide (Sigma Aldrich), Ethanol (Sigma Aldrich), Ethyl Acetate (Sigma Aldrich), Acetonitrile (Sigma Aldrich), n-Hexane (Sigma Aldrich), Dichloromethane (Sigma Aldrich), Benzene (Sigma Aldrich), phthalocyanine (Sigma Aldrich) .

2.2. Methods

2.2.1. Synthesis of Cobalt exchanged NH$_4$-Y zeolite (Co-Y). 10.0 g of NH$_4$-Y zeolite was weighed into a 1000 mL beaker containing 0.649 g of CoCl$_2$ in 500 mL in of HPLC water after which the mixture was stirred 70°C for 12 hrs. The solution was maintained between a pH of 4.0-4.5 was maintained during the stirring. The slurry formed was filtered using a vacuum pump and the residue was washed several times with deionized water to remove the excess chloride ions present. It was then dried at 100°C for 24 hrs before it was dehydrated at 300°C for 4 hrs in the oven. The catalyst formed was then characterized using the various characterization techniques.

2.2.2. Synthesis of Copper exchanged NH$_4$-Y zeolite (Cu-Y). 10.0g of NH$_4$-Y zeolite was weighed into a 1000 mL beaker containing 0.672 g of CuCl$_2$ in 500 mL of HPLC water after which the mixture was stirred 70°C for 12 hrs. The same procedure used for Co-Y was followed for the Cu-Y.

2.2.3. Synthesis of Co Ligand Y (Co-L$_2$-Y). 1.0 g of Co-Y was added to 3.0 g (dissolved 150 mL of methanol) Phlantocyamine (L$_2$). The mixture was refluxed for 8 hrs after which it was cooled and filtered

using a vacuum pump. The sample obtained was washed several times with absolute ethanol and dried at 110°C for 6 hrs in the oven. The unreacted ligand and metal complexes were washed away with methanol in soxhlet apparatus. The resulting compound was treated by using 0.1 M NaCl solution for 9 hrs at room temperature. The pure sample obtained was washed with water to remove the chloride ions present. Finally, the sample was dried at 110°C for 12 hrs to obtain the final catalyst. The same procedure was used in the preparation of the Cu-L_2-Y counterpart.

3. Results and Discussion.

3.1. Powder XRD Analysis
The results of the X-ray diffraction studies of the prepared catalysts is as displayed in Fig 1.
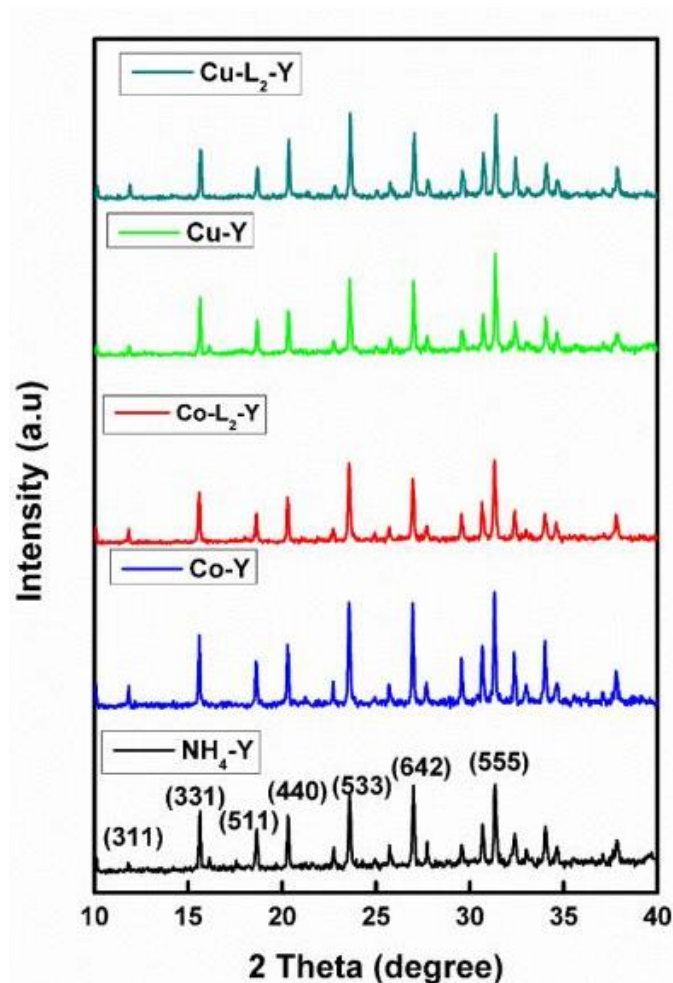

Figure 1. The XRD plots of the various synthesized catalysts.

The Fig 1 demonstrates the XRD configurations for NH_4-Y, Cu-Y, Cu-L_2-Y, Co-L_2-Y and Co-Y. The X-ray pattern of raw zeolite (NH_4-Y), metal exchanged and the encapsulated metal complexes appeared to be similar in their patterns. This suggests the formation of the similar crystalline phase as a result of the encapsulation of the metal complexes. The various peaks observed were indexed and these indexed peaks are in agreement with those found in literature corresponding to (JCPDS 43-0168) [15, 16]. The intensity of the peaks was observed to remain significant upon the introduction metal complexes into the super cages of the zeolite framework. This observation suggests that there is a good crystallinity of the encapsulated in the zeolite. Also, a small discrepancy was noticed in the intensity of

the encapsulated metal complexes when compared with that of the parent zeolite and the metal exchanged counterparts, this may be connected to the effect of coordination of the pthatocynamine to the metal ions which has already been exchanged inside the supper cages of the zeolite framework. Also, the X-ray diffraction (XRD) configurations of the prepared catalysts were recorded to propose that the encapsulation of metal complexes inside the super cages of zeolite-Y has happened (Fig 1). The zeolite encapsulated metal complexes displayed the same peaks in comparison to those of the parent NH_4 Y of cause with a minor discrepancy in the intensity of the peaks, no new crystalline configuration was noticed. These indications suggest that the zeolitic structural arrangement and crystallinity of the zeolite has been preserved all through the encapsulation process and that the complexes are well arranged in the cages as suggested by the Si/Al ratio in the ICPAES result.

Therefore, all the aforesaid justifications clearly point in the direction of the intact crystallinity of the Y zeolite framework in the course of the metal exchange and encapsulation procedure as well. These results also show that the cavities have the capability to accommodate these complexes without any change in crystalline framework of the parent zeolite. It was also observed that the intensity of the peaks shown by the zeolite encapsulated complexes appeared to be slightly lowered in compared to that of the parent zeolite, the reason for this maybe as because small amount of complexes formed in the super cavities of the zeolite as seen in the ICPAES result in Table 1

Table 1. Analytical Compositions of the various prepared catalyst.

No	Name of sample	% of metal present	Pore Volume (cm^3/g)	Micropores Volume(cm^3)	BET Surface area (m^2/g)	% of Si Present	% of C present	% of H present	% of N Present	% of Al Present	Si/Al ratio
1	NH$_4$-Y	Nil	0.343	0.3880	925.00	20.12	Nil	Nil	Nil	8.8	2.45
2	Co-Y	1.76	0.250	0.2687	697.26	19.83	Nil	Nil	Nil	8.88	2.23
3	Cu-Y	2.90	0.291	0.2826	799.91	19.78	Nil	Nil	Nil	8.88	2.40
4	Co-L-Y	1.14	0.210	0.1924	616.83	19.78	2.64	0.40	1.52	8.78	2.39
5	Cu-L-Y	1.85	0.205	0.1984	679.69	19.68	2.20	0.35	1.33	8.80	2.35

3.2. Elemental Analysis.

The analytical analysis was carried out to confirm the elemental composition of the parent zeolite, metal exchanged ones and their corresponding encapsulated counterparts. The (Table 1) displays the elemental analysis for the various synthesized catalysts. The result shows the percentages of Si, Al, Co, Cu, C, H and N. The ICP-AES result was used to confirm that the percentage of Al and Si is between 19.68- 20.12 % and 8.76-8.80 % correspondingly. The percentage of metal content that is present was also confirmed by the use of ICP-AES. It was discovered that the parent zeolite (NH$_4$-Y) has zero percentage metal present in it while Co-Y, Cu-Y, Co-L$_2$-Y and Cu-L$_2$-Y contain 1.76, 2.90, 1.14 and 1.85 % respectively. The analytical data of the synthesized catalysts as represented in (Table 1) below indicated that the percentage of Si and Al in the zeolite-Y encapsulated complexes, the zeolite metal exchange and zeolite-Y are almost in the same range of ratio. This same ratio suggested that there is an insignificant difference in the zeolite framework and this difference is not as a result of dealumination during encapsulation process and more so the difference is so small that it can be ignored. As a result of this we can say that the zeolitic framework of the catalysts are still together and have not been fragmented or destroyed throughout the encapsulation and metal exchange process [17-19]

Furthermore, it was observed that the percentage of metal ion in the zeolite encapsulated complexes was noticed to have decreased more than the one in metal exchanged zeolite Y, this can be credited to the fact that there may have been some leaching of the metal ion during the encapsulation process [20] and it can also be proposed that the reduction is as a result of the fact that the metals have been used in

the coordination with the ligand inside the cages of the zeolite Y [21]. Again with the suspected leaching of the metal ions, only small amount of complex could be present inside the cavities of zeolite-Y as confirmed by the small amount of metal detected by the ICPAES in the encapsulated complexes [22]. The percentages of the carbon, Hydrogen and Nitrogen (CHN) present in the prepared catalyst was done using the CHN analyser. It was observed that parent zeolite NH_4-Y, Co-Y and Cu-Y contains 0 % of CHN. However, Co-L_2-Y and Cu-L_2-Y possesses 2.20-2.60 % of C, 0.35-0.40 % of H and 1.33-1.52 % of N. The elemental composition obtained were found to be in agreement with the theoretical values. This is a suggestion that the compound synthesized formed in the estimated and anticipated ratio. The percentages of the CHN was observed to be low in the encapsulated samples and has been ascribed to the low concentration of the metal complexes formed in the zeolite super cages. This result is further supported by the result of the ICP-AES as discussed above. Furthermore, these organic compounds presence can be assigned to the formation of complexes as a result of coordination inside the nano cages of the zeolite. A colour change was observed during the metal exchange and encapsulation process which maybe be as a result of the coordination between the metal and the ligand inside the super cages of the parent zeolite Y. This also indicates that there might have been a complex formation in the inner cages of the parent zeolite Y.

Furthermore, taking into consideration the explanation given by [23], the flexible nature of the ligand enables it to move into the zeolite super cavity and reacts with the earlier exchanged metal ions in the process forming a coordination with the metal ions already present in the cavities. In addition, the purification of the catalyst by the soxhlet apparatus helps to remove the excess ligand that are free and are not complexed in the super cages of the zeolite as well as any complex that is formed on the zeolitic surface. The excess metal ions that are present in the cavities are been detached by the reaction with 0.01 M solution of NaCl as this help to ensure that what is left is the metal complex in the super cavities of the zeolite samples hence the reason for the small amount of the metal ions detected by the ICPAES.

3.3. Surface Area Analysis
The result of the surface analysis parameters is as shown in Table 1. The results obtained clearly shows that the surface area of the samples reduced steadily with that of the parent zeolite (NH_4-Y) remaining the highest. It was observed that as the metals were exchanged in the parent zeolite, the surface area decreased and also when the ligand was incorporated into the metal exchanged samples the surface area further decreased drastically. This has been said to be due to a large material fused into the supper cages of the zeolite structure suggesting that the metal complexes have been formed in the super cages of the zeolite [21]. Additionally, on careful observation of the pore volume, it was noticed that there was a reduction in the pore volume when we compare the metal exchanged samples and their corresponding encapsulated samples. The adsorption desorption isotherm displays a distinctive isotherm features of microporous materials for all the prepared catalyst with a medium type 1 and II of Brunauer classification and in accordance with what has been reported in literature [24] Fig. 2.
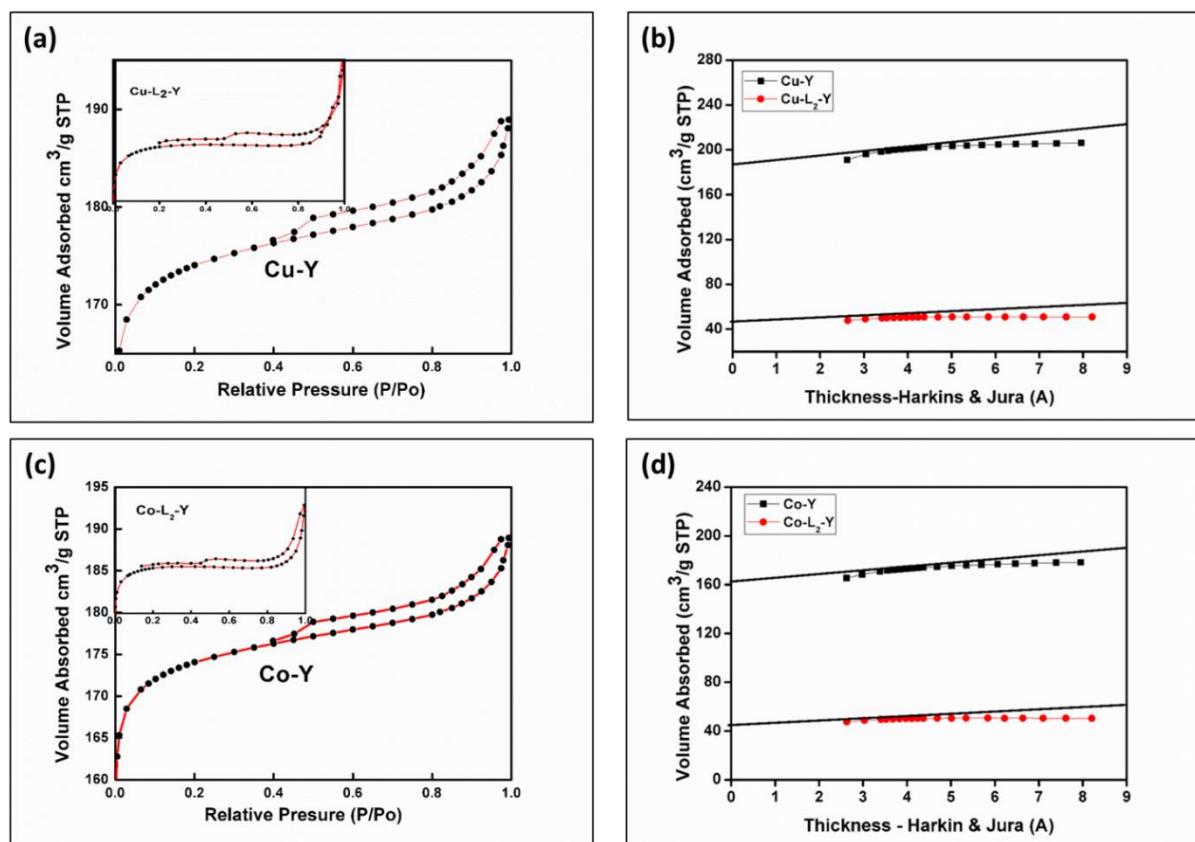
Figure 2. Absorption- Desorption Isotherms and t-plots of the prepared catalyst.

Also, a narrow hysteresis loop was detected in the case of the metal exchanged and encapsulated complex, which indicates the presence of small amount of mesopores but in the Cu-L_2-Y catalyst, the loops appeared to be filled up which might be as a result of the metal complexes filling up the pores of the zeolite framework. The different parameters gotten from the surface area analysis was recorded in Table 1. A drastic decrease was observed in the surface area and pore volume of the catalyst after encapsulation process. This drastic decrease in the surface area as well as the pore volume of the encapsulated catalyst obviously suggests that there is a formation of metal complexes inside the pores of the parent zeolite framework. It was also noticed that there is much decrease in the external surface area which could have been perhaps to the fact that the encapsulated complex is also encapsulated in Mesopores system of the parent zeolite.

The decrease in the micro pores volume and micro pore area in encapsulated metal complexes, gives an indication that a great percentage of the ligand are complexed in the micro cages of the parent Y zeolite. Similarly, the bending of the of the t plot curve was observed to point downwards indicating the presence of micropores confirming the microporous nature of the parent zeolite hence the microporous nature of the parent zeolite was not destroyed during the metal exchanged and encapsulation procedures as shown by the FT-IR and XRD. Furthermore, the decrease in the micropores area in the encapsulated catalyst were confirmed by the t plots where the encapsulated catalyst is showing less intercept. From the isotherm absorption- desorption plots the volume of nitrogen absorbed was found to decrease in the encapsulated catalyst when compared to the ordinary metal exchanged. This is also an evidence of the presence of metal complexes which has filled up the pore of the parent zeolites hence reducing the amount of nitrogen used.

The t-plots of the prepared samples are as shown in 2b and 2c. This shows the microporous nature of the prepared catalyst. It was observed that there is a reduction in the micropores volume from 0.2916 cm^3/g in the case of metal exchange (Cu-Y) to 0.2467 cm^3/g in the case of metal complex encapsulation

(Cu-L-Y). The Same thing was observed for cobalt hence Cu-Y and Cu-L-Y was taken as a representative catalyst. This reduction in the micropores volume can be attributed to the presence of the metal complexes being formed and well-arranged inside the pore of the zeolite catalyst. The small difference in the micropores volume maybe as a result of small amount of metal complexes formed inside the cages of the zeolite structures as suggested by the ICP-AES analysis result.

3.4. Infrared Analysis

The FT-IR spectral of the zeolite Y encapsulated metal complexes together with their respective metal exchange are represented in Fig..3. It was observed that the intensity of the bands associated with that of the encapsulated complexes appeared to be weak and this has been ascribed to the low concentration of metal complexes formed in the zeolite cavities as confirmed by the ICPAES and buttressed by [22]. In addition, the zeolitic framework [TiO_4 where Ti = Si or Al] signals remained dominant. The band at 570,720,780 and 1015 cm^{-1} can be attributed to the T-O (structure sensitive band) double ring, symmetric stretching and asymmetric stretching respectively [11]. The widening or shifting of these zeolite structure sensitive vibration upon the encapsulation of the metal complexes which further confirms which further confirms the xrd results which shows that the zeolite framework remains intact throughout the encapsulation period. Also, the ꝺ (O–H) of the coordinated water molecules which appeared in the spectra associated with the encapsulated complexes was recorded at 840 cm^{-1}and the Metal (O–H) was noticed as a broad band at 3440 cm^{-1}.
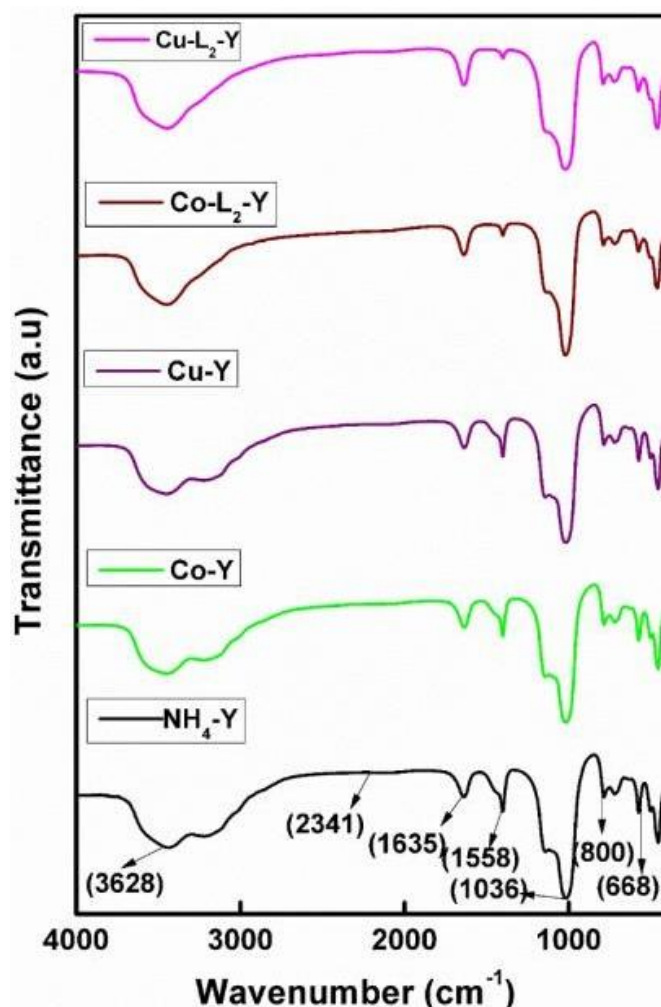

Figure 3. FT- IR plots of various prepared catalyst.

3.5. Thermogravimetric Analysis

The thermal activities of the zeolite entrapped catalysts were explored and their respective TGA/DTG curves were recorded at a heating rate of 10°C per minute up to l000°C in an atmosphere of nitrogen. The resultant changes in weight takes place as an effect of the destruction or formation of chemical bonds when there is a rise in temperature, or as a consequence of the elimination of volatile product present in the catalyst [25]. Literature has revealed that the thermal stability of heterogeneous complexes is most times greater than their analogous homogeneous ones [24]. The TGA curves of Cu-L_2-Y and Co-L_2-Y are given in Fig. 4. From the Fig. 4, it is clear that the change in weight losses appear slightly invisible and this has been attributed to the considerably small amount metal complexes encapsulated within the super cages of the zeolite. In addition, the TG/DTG data also makes available clear facts about the rate of decomposition with respect to temperature of the encapsulated catalysts under investigation.
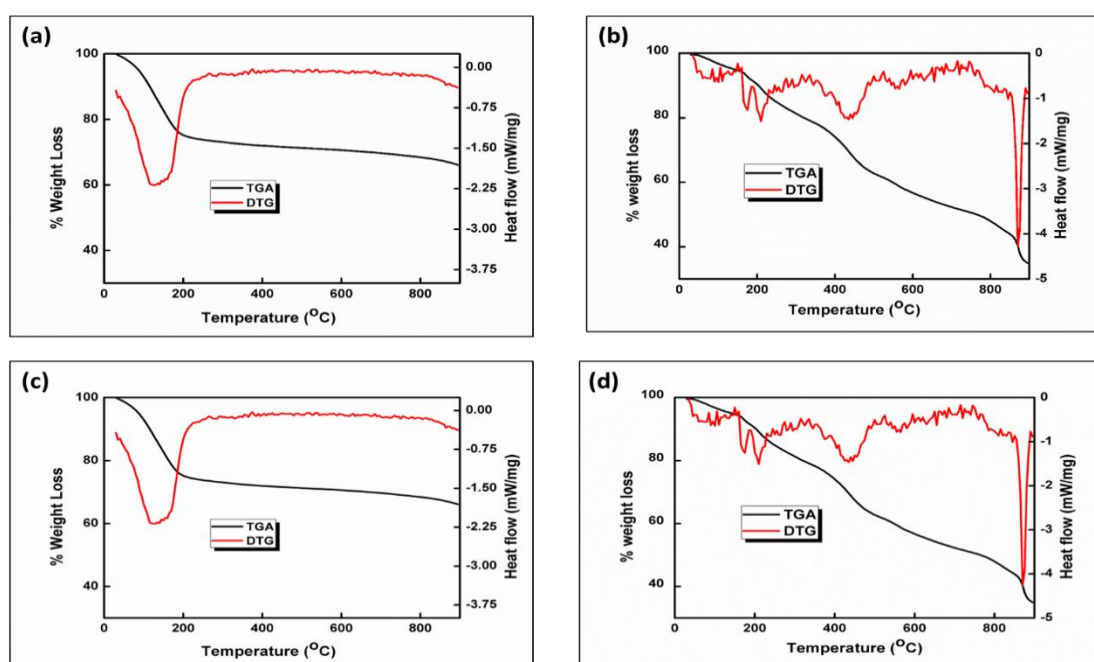

Figure 4. TGA/DTG plots of catalyst. (a) Cu-Y (b) Cu-L_2-Y (c) Co-Y (d) Co-L_2-Y.

Similarly, from the TGA/DTG plot shown above, it was observed that the catalyst Cu-L_2-Y and Co-L_2-Y were stable up to about 110°C. There are three major weight losses that was observed throughout the thermal degradation period. The first phase of decomposition started at about 110°C and remains stable up to 450°C. A loss in weight around the temperature range between 30- 110°C could be ascribed to the loss of water molecules from the catalyst. The weight loss taking place between 110°C and 450°C with peak temperature can be credited to the removal of entrapped water molecules in the parent zeolite inner structures [15]. Also, there is a significant weight loss around 450°C which can be attributed to the decomposition of the metal complex inside the inner cages of the zeolite samples further confirming the formation of the metal complex in the super cages of the zeolite [5, 8, 17]. However, further than 650°C there is no major weight loss up to 950°C. The destruction of the zeolite framework appears to have taken place at around 950°C which is accordance to what has been reported in literature [9]. Also, it can be proposed that the variation in the thermal decomposition pattern exhibited by the catalyst is a sign that there is the formation of the complex inside the cages of the zeolite material [18]. The percentage loss in weight gives a probable clue of the amount of intra-zeolite metal complex that is formed. The decomposition process is detailed in Table 2.

Table 2. Decomposition process of zeolite metal complex

Catalyst	Temperature range (°C)	Weight Loss (%)	Group Lost
NH$_4$-Y	0-300	20.34	nH$_2$O molecules
Cu-Y	0-300	18.34	nH$_2$O molecules
Co-Y	0-300	16.45	nH$_2$O molecules
Co-L$_2$-Y	0-150	15.65	Surface water molecules
	150-300	2.06	Inter zeolitic water molecules
	350-450	4.24	Possible encapsulated metal complex and uncomplexed ligand decomposition
	500-800	6.23	Structural OH group
Cu-L$_2$-Y	0-150	15.65	Surface water molecules
	150-300	3.06	Inter zeolitic water molecules
	350-450	3.24	Possible encapsulated metal complex and uncomplexed ligand decomposition
	500-800	5.23	Structural OH group

3.6. Scanning Electron Microscopy Analysis (SEM)
The morphological studies of the encapsulated metal complexes (Cu-L-Y and Co-L-Y) were studied to follow the structural changes as a result of presence of metal complexes. Fig. 5 shows the SEM images obtained for Co-Y, Cu-Y, Co-L-Y and Cu-L-Y. It was observed that Co-Y (a) displayed non symmetrical shapes like particles with nanoball shapes. The interchange of the metal ions is related to the presence of nano-rod particle in the structure. The nanoballs formed, coagulated together to give a scattered particle. However, upon the introduction of metal complexes into the zeolite structure Co-L-Y (b), there was a transformation of the shape into a crystalline particle with a mixture of non-uniform spherical and bigger rod shapes. Also the SEM image of Cu-Y (b) catalyst shows uniform spherical shapes while the encapsulated complex Cu-L-Y (d) shows a non-uniform square shape mixed with a rod like shape. The difference between the structures could be related to the effect caused by the introduction of the metal complex [26] . Also the elemental mapping of the representative Cu-L-Y is as shown in Fig. 6. The results show that all the elements are evenly distributed with the zeolitic framework of the catalyst. The cobalt counter parts gave a similar result hence Cu-L-Y was taken as a representative.
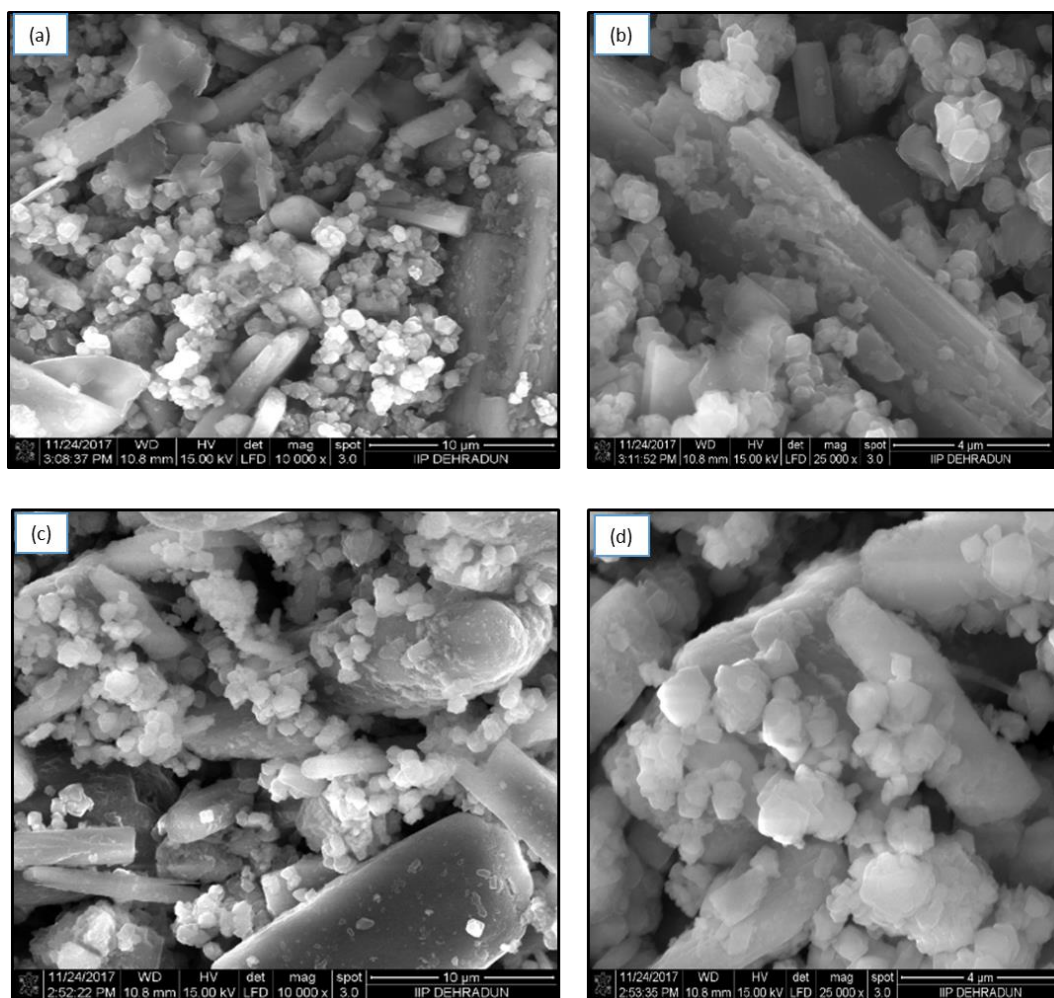
Figure 5. SEM images of some selected prepared catalysts. (a) Co-Y (b) Co-L$_2$-Y (c) Cu-Y) and (d) Co-L$_2$-Y.
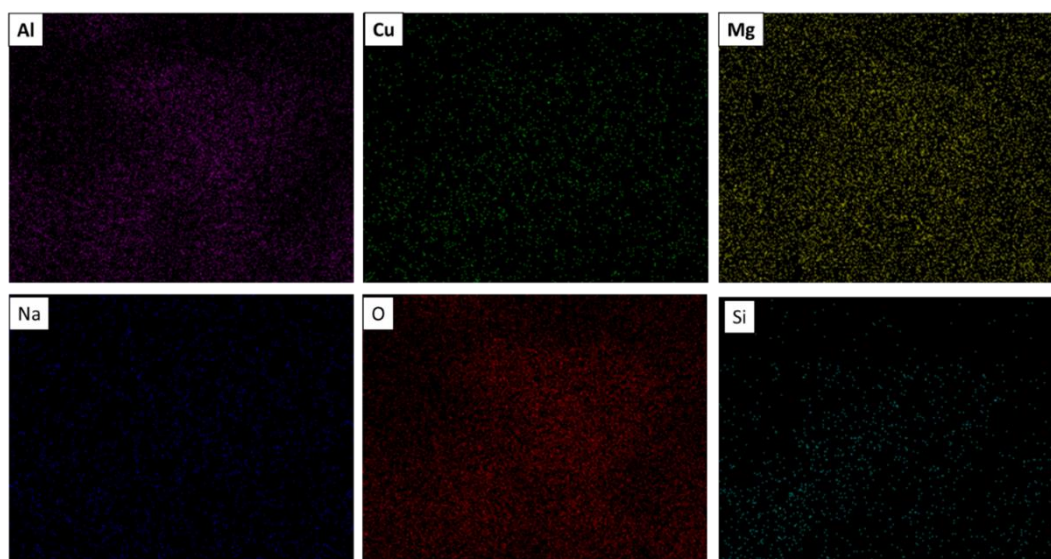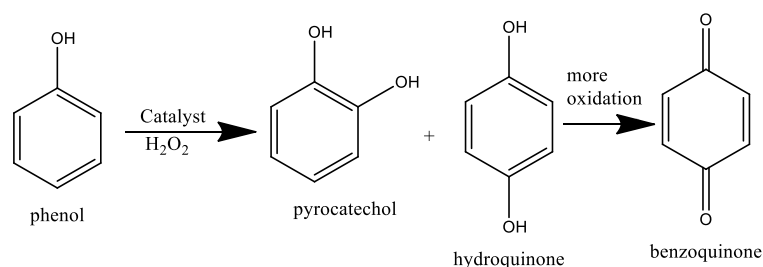

Figure 6. Elemental mapping of representative Cu-L$_2$-Y.

3.7. Oxidation of phenol catalytic activity.

The catalytic oxidation of phenol (PhOH) generally gives two main products which are Pyrocatechol (pCAT) and Hydroquinone (HQ). However, sometimes some more oxidation may possibly happen to give para-benzoquinone (P-BQ) as shown in scheme 1. Literature reveals that so many factors enhances the catalytic activity of the reaction hence, in this research study, the molar ratio of H_2O_2/phenol, temperature, amount of catalyst, type of solvent and volume of solvent parameters were investigated.

Scheme 1. Reaction pathway for Oxidized products of Phenol

3.8. Effect of oxidant substrate ratio

In order to determine the effect of H_2O_2: PhOH molar ratio on the oxidation of (Phenol), the molar ratios 1:1, 2:1 and 3:1 were considered, using Cu-L_2-Y as representative catalyst, and at the same time as keeping a stable amount PhOH (0.025 mol) and catalyst (0.40 g) in 3 mL acetonitrile at approximately 80°C and also keeping the reaction for 24 hrs. A small aliquot of the sample was taken using a laboratory syringe and the products were analysed and identified using an advanced GC-Ms with organic compounds database. The result of the analysis revealed that on increasing the concentration ratio of H_2O_2: PhOH from 1:1 to 2:1, a significant increase in the conversion was observed as shown in Fig. 7. This increase can be said to be about 4 times from 18.85 to 58.89 percent but a decrease in the selectivity of pCAT was noticed after 18hrs, giving 70 percent. However, the poor activity of the catalyst at lower molar ratio may perhaps be attributed to the insufficiency of the hydroxyl radicals that is been generated by the H_2O_2 [4] while the low activity at the higher molar ratio have been suggested to be as a result of significant consumption of the hydroxyl radicals during the reaction hence leading to a reduction in the hydroxyl radicals that is being created from H_2O_2 which are able to react with the extra phenol to generate the intermediate [18]. Moreover, it was again noticed that when the quantity of H_2O_2 was increased to thrice the amount, the percentage conversion reduced to 48.99 percent and also the percentage of catechol selectivity decreased but not much thereby increasing the selectivity to favour the formation of HQ. It can therefore be established that the effect of oxidant concentration has no much effect on product selectivity. For this reason, and also in order to optimize the amount of oxidant consumption and the amount of oxidizer-substrate used, it was suggested that the best ratio to work with was 2:1. Also, a high selectivity towards the production of catechol was obtained for all ratios used as shown in Table 3.
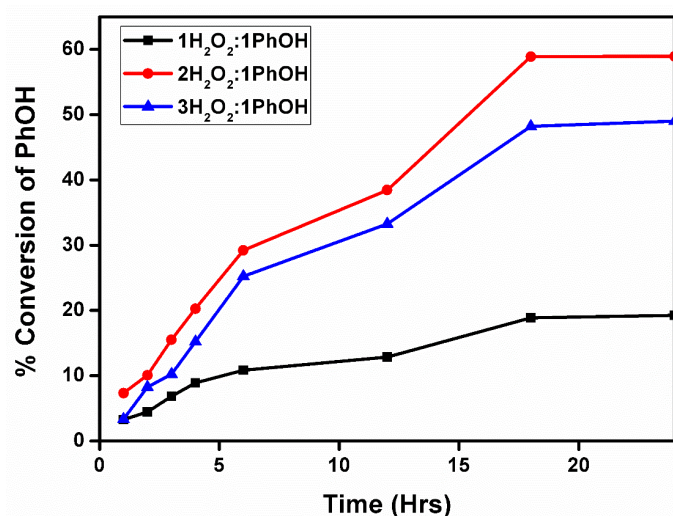
Figure 7. Percentage PhOH conversion using various H_2O_2: PhOH molar concentration

Table 3. Effect of molar concentration of the synthesized catalysts

H_2O_2:PhOH Molar ratio	% of PhOH Conversion	% Product Selectivity	
		pCAT	HQ
1:1	18.85	78.00	22.00
2:1	58.89	70.00	30.00
3:1	48.99	66.00	34.00

Reaction conditions: PhOH-0.025M, H_2O_2- 0.05M Cu-L_2-Y -0.40 g, Acetonitrile - 5 mL, 80°C, 18hrs

3.9. Effect of Temperature:

The catalytic activity of the catalysts was studied at 60, 80 and 100°C for a period of 24 h. An aliquot of the sample was taken using a laboratory syringe and was analysed using an advanced GC/MS. The Fig. 8 exhibits the effect that temperature has on the oxidation of PhOH. It was noticed that at temperature of 60°C the reaction exhibited low activity catalytically in terms of conversion which brought about a high selectivity towards pCAT formation and some HQ formation. However, when the temperature was raised to 80°C the percentage conversion improved considerably although leading to a decrease in pCAT (77.66%) selectivity and a considerable increase in HQ. However, when the temperature of the reaction was taken to 100°C there was a drop in the conversion rate which may perhaps be as a result of the decomposition of the PhOH reaching the maximum at the previous temperature and as a result lessening the amount of metal peroxo species therefore favouring the formation of HQ significantly at higher temperature [5]. Although, a decrease in the percentage selectivity of pCAT was observed, it still remains the most significant product formed. Consequently, it can be suggested that when the temperature is increased (higher temperature) the reaction reached a maximum conversion, but with a decrease in product selectivity of pCAT and increased HQ as shown in Table 3. Nevertheless, one main shortcoming of working at higher reaction temperatures is the likelihood of the oxidant degrading thermally (i.e. H_2O_2) [27]. This can be attributed to the H_2O_2 that is being used up in the parallel reaction of decomposition ($H_2O_2 \rightarrow H_2O + 1/2\ O_2$) [28]. As a result, and for the purpose of this research and in order to work at lower temperature and conserve energy, and to get both good selectivity of products in relation to conversion, it can be recommended that the optimum temperature to work with is 80°C.
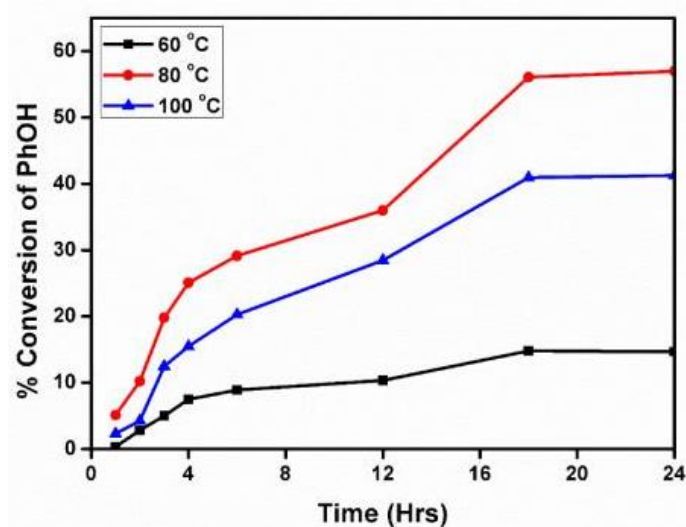
Figure 8. Effect of Temperature on the conversion of PhOH

Table 4. Effect of temperature on conversion and product selectivity

Temperature °C	% of PhOH Conversion	% Product Selectivity	
		pCAT	HQ
60	18.85	78.00	22.00
80	58.89	70.00	30.00
100	48.99	66.00	34.00

Reaction conditions: PhOH-0.025M, H_2O_2- 0.05M Cu-L_2-Y -0.40 g, Acetonitrile - 5mL, 80°C, 18hrs.

3.10.   Effect of various solvents:

It is a well acknowledged statement that the nature of the solvent employed in a particular reaction has a momentous influence on the kind of result the reaction produces, i.e. on the yields, the products formation and the reaction kinetics [18]. On the other hand, the influence of solvent on the catalytic action for the oxidation of phenol was studied engaging the use of five various solvents which covers both polar (Acetonitrile, ethanol and ethyl acetate) and non-polar (Dichloromethane and n-hexane) concurrently keeping all the other reaction factors fixed. It has been revealed in the Literature that Solvents impacts the rate of reaction by competitive sorption/adsorptions which occurs in the super cages of zeolite, polarity, solvation power and the size of the solvent molecule [10]. Thus, the effect of various solvents on the oxidation of the substrate (phenol) is demonstrated in Fig. 9. From Table 5 it can be seen that the nature of the solvent that is used has a key influence on the reaction rate as well as product selectivity. Relatively small conversions were recorded in n-hexane and ethyl acetate. Nevertheless, out of all the solvents considered, acetonitrile was the one which gave the highest PhOH conversion as it gave 51.29 percent conversion after 18hrs of reaction time. Again for all the solvents used it was noticed that there is a significant selectivity towards HQ. However, one clarification for this remains that acetonitrile has the capability to easily harmonize better to the encapsulated complex, therefore, forming a coordinated complex with acetonitrile in which the acetonitrile subjugates one site [29]. From these observations therefore, for optimum percentage PhOH conversion, the solvents can be reorganized as follows: acetonitrile >> Dichloromethane > ethanol > ethyl acetate > n-hexane. It can be suggested that acetonitrile was the best suitable solvent for maximum percentage PhOH conversion.
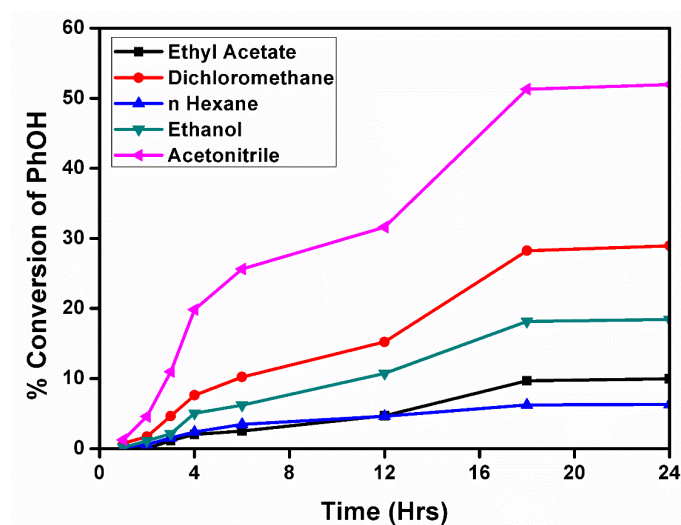
Figure 9. Effect of various solvents on percentage conversion of PhOH

Table 5. Effect of various solvents on conversion and product selectivity.

Solvent	% Conversion of PhOH	% Product Selectivity	
		pCAT	HQ
Acetonitrile	51.29	69.56	30.44
Ethyl acetate	9.68	78.92	21.08
n- hexane	6.24	80.56	19.44
Dichloromethane	28.26	75.78	24.22
Ethanol	18.14	81.67	18.33

Reaction conditions: PhOH-0.025M, H_2O_2- 0.05M, Cu-L-Y -0.40 g, Acetonitrile - 5 mL, 80°C, 18 h.

3.11.   Effect of mass loading.

The influence of the quantity of catalyst that is used, on the catalytic performance as regards the oxidation of PhOH is as shown graphically in Fig. 10 and Table 6. Three varying quantities of catalyst was studied, 0.020, 0.040 and 0.060 g, concurrently keeping the other reaction parameters constant (PhOH-0.025 mol) and (H_2O_2- 0.05 mol) in 5 mL Acetonitrile at 80°C. The results show that increasing the quantities of catalysts enhanced the effect of PhOH conversion. As expected, when the quantity of catalyst was increased from 0.020 g to 0.040 g, it increased the conversion from 12.05 percent to 52.95 percent after 18 h. An additional increase in the amount of catalyst to 0.060 g saw the percentage conversion decreased to 35.22 percent which means the percentage conversion decreased significantly. Nevertheless, the main reason for the significant increase in catalytic activity may be as a result of the accessibility of large surface area and the acid sites as established by the BET, which favours the even distribution of more active species. Therefore, the ease of access of large numbers of reactant molecules to the catalyst is favoured. Furthermore, the reduction in PhOH conversion as a result of catalyst addition can be said to be due to the increase rate at which H_2O_2 decomposes in the presence of increased catalysts therefore, increasing the activity of the organic substrates as expected. Also, the decrease in the catalytic activity at higher quantity of catalyst may possibly be as a result of adsorption or chemisorption of two reactants on different catalyst particles, thereby in so doing increasing the chance to interact and in the process increases the rate of H_2O_2 decomposition as revealed by [30]. In addition, it was observed that

increasing the amount of catalyst also increased the selectivity towards pCAT and some HQ formation was also noticed. The selectivity towards pCAT was noticed to be at the maximum when the catalyst quantity was 0.020 g which gives a yield of 87.23 percent, while the selectivity towards HQ was observed to be at the lowest of 12.77 percent. Nevertheless, on increasing the amount catalyst to 0.040 g a decrease in catechol selectivity was observed while this favoured the formation of more HQ. Upon additional increase of catalyst to 0.060 g a further decline in pCAT was equally observed while there is an increase in HQ selectivity but pCAT remains the dominant product. Therefore, in order to maximize the potential of the catalyst used in terms of conversion and selectivity of both products, it is recommended that 0.040 g catalyst is the appropriate amount for optimum conversion and selectivity.
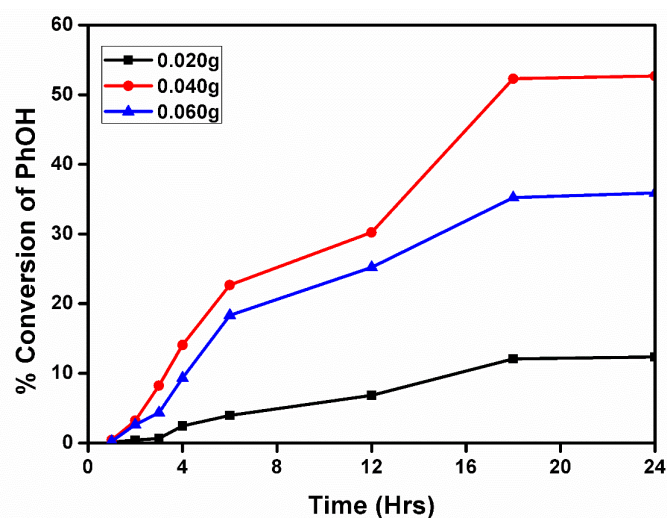

Figure 10. Effect of mass loading on percentage conversion of PhOH

Table 6. Effect of mass loading on PhOH oxidation and product selectivity.

Mass of Catalyst	% Conversion of PhOH	% Product Selectivity	
		pCAT	HQ
0.020g	12.35	87.23	12.77
0.040g	52.29	79.78	20.22
0.060g	35.22	68.45	31.55

Reaction conditions: PhOH-0.025M, Cu-L-Y -0.040 g, H_2O_2- 0.05M, Acetonitrile - 5 mL, 80°C, 18hrs.

3.12.   Comparative studies of Copper and Cobalt encapsulated complexes.
The relative investigation of the copper and cobalt catalyst was carried out under the optimized reaction circumstances (PhOH - 0.025 mol, 0.050 mol H_2O_2:H_2O_2/PhOH molar ratio is 2:1, catalyst- 0.040 g, Acetonitrile-5 mL and temperature- 80°C). The encapsulated copper and cobalt complexes, copper and cobalt ion exchanged zeolite, raw NH_4-Y exchanged zeolite and a blank was studied and their catalytic activities are as shown in Fig. 11 and Table 7. Also, it was observed that the reaction was a bit slow in the first few hours using the encapsulated Cu/Co catalysts and thereafter showed some improvements as the reaction time increased. However, it was noticed that the copper and cobalt encapsulated zeolite metal complexes showed a greater catalytic activity than their respective metal exchanged counterparts attaining maximum and greater percentage conversion in about 18 hours. From the Table 7, it was observed that both encapsulated copper and cobalt catalysts shows a higher percentage conversion for

PhOH in comparism to their metal exchanged counterparts. The encapsulated catalysts also showed a more selectivity behaviour towards pCAT and HQ than the corresponding metal exchange this can be said to be a confirmation that it is the metal complexes encapsulated inside the zeolite super cages that are responsible for the selectivity rather than the metal exchange counterparts [19]. Nevertheless, when the reaction time was increased from 18hrs to 24hrs, it was only an insignificant change in percentage PhOH conversion and product selectivity that was observed. The parent zeolite was also tested for the catalytic and it was discovered that it behaved poorly in oxidizing phenol. Also, a blank reaction was carried out under the same optimized conditions to serve as a control experiment and no catalytic activity was detected. Furthermore, there it was observed that the copper encapsulated metal complexes displayed a slightly more catalytic activity than the cobalt encapsulated ones. This can be attributed to the fact that maybe there are more active species in the copper system than the cobalt system and maybe it is because of the more surface area that copper as seen in both the BET and ICPAES results. It can thus be confirmed that the new encapsulated catalysts are more active and exhibit almost similar selectivity as compared to their individual ion-exchange catalyst. The activity of these copper and cobalt catalysts can be organised in the following order: $Cu-L_2-Y > Co-L_2-Y > Cu-Y > Co-Y > NH_4-Y >$ Blank
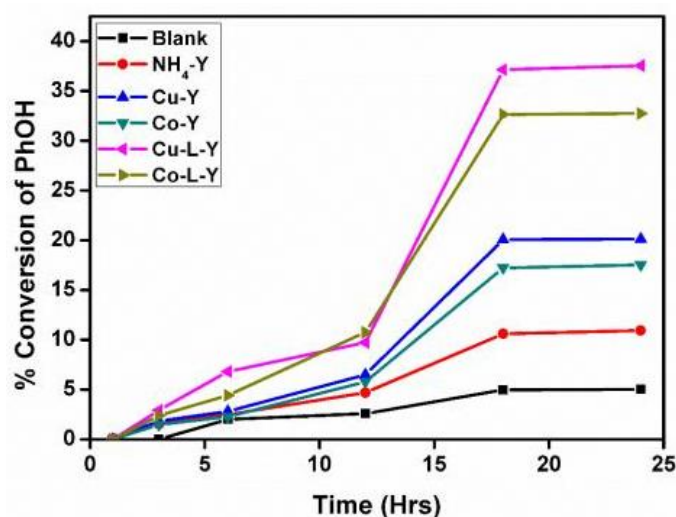

Figure 11. Comparative studies of various prepared catalysts on the phenol conversion.

Table 7. Comparative Catalyst table of conversion and selectivity.

Catalyst	% Conversion of PhOH	% Product Selectivity	
		pCAT	HQ
Co-L-Y	32.64	70.90	29.1
Cu-L-Y	37.13	75.50	24.50
Co-Y	17.22	64.20	35.80
Cu-Y	20.06	65.60	34.4
NH_4-Y	10.59	95.70	4.30
Blank	4.97	92.40	7.60

Reaction conditions: PhOH-0.025M, $Cu-L_2-Y$ -0.040 g, H_2O_2- 0.05M, Acetonitrile - 5 mL, 80°C, 18hrs.

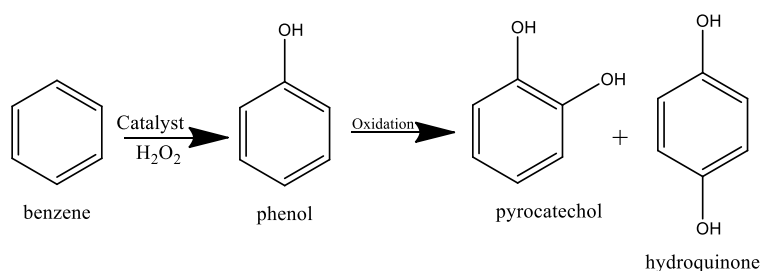*3.13.   Reusability Studies for Phenol Oxidation*

The representative catalyst (Cu-L$_2$-Y) was used to test the recyclability and stability of the catalyst for the oxidation of phenol using the optimized condition stated above. The catalyst was used for the re-run reaction three times in order to be sure of its recyclability and stability. The conversion of the first re-run was about 37.00 percent while the second re-run gave about 36.26 percent and the third re-run gave 35.92 percent respectively as shown in Table 8. When we observe the second and third re-run of the catalyst it was noticed that there was no significant difference in the conversions with minor differences in the selectivities. Thus, from these results obtained after the re-run, it can be suggested that the catalyst retained its catalytic properties even after three re-runs and thus can be reused for the oxidation of phenol without much loss in its catalytic activity. Besides, the recyclability of the catalyst also gives credence to the absence of any irreversible deactivation of the encapsulated metal complexes, which is one of the main disadvantages homogenous catalyst in homogenous catalytic reactions as revealed by [31].

Table 8. Reusability of the prepared catalyst under optimised conditions.

Number of Re-runs	% Conversion of Phenol	% Product Selectivity	
		pCAT	HQ
1	34.23	75.50	29.10
2	33.78	74.90	25.10
3	32.10	72.30	27.70

3.14.   Catalytic Oxidation of benzene

The oxidation of benzene was investigated using the same maximized parameters as used for the oxidation of phenol. The products of the oxidation with respect to the reaction are represented in Scheme 2. The Table 9 reveals that under these reaction conditions, the encapsulated complexes Cu-L$_2$-Y and Co-L$_2$-Y recorded a low conversion (16.58% and 13.29% respectively) after the reaction time of 18hrs and in each case resulting into phenol as the major product except for Cu-L$_2$-Y where a little bit of further oxidation took place. The catalytic activity of the metal exchanged compounds, Cu-Y and Co-Y was also investigated using the same reaction parameters as that of the encapsulated complexes. It was discovered that the metal exchanged Cu-Y and Co-Y exhibited a lower catalytic activity when compared to their encapsulated counterparts suggesting that the encapsulation helped in promoting the rate of conversion of benzene.

Scheme 2. Products of oxidation of benzene.

Fig. 12 demonstrates the catalytic comparison of the encapsulated and the metal exchanged compounds as a function time. It was observed that there was increase in the conversion rate as the time was being increased but at 18hrs no more conversion occurred as the graph remains steady. The Table 9 presents the percentage of benzene conversion and product selectivity when the various prepared catalyst was used. It was discovered that for the encapsulated catalyst, they exhibited an advance oxidation of phenol leading to the formation of catechol and hydroquinone. One reason for this is that

the selectivity of the product (phenol) is more reactive than benzene [32]. It was also observed that the one-step oxidation conversion of benzene was low. This establishes the difficulty of C-H bond activation as a result of the resonance stability possessed by benzene [33]. Also, the oxidation of benzene using NH_4-Y and blank (no catalyst) exhibited very low conversion.
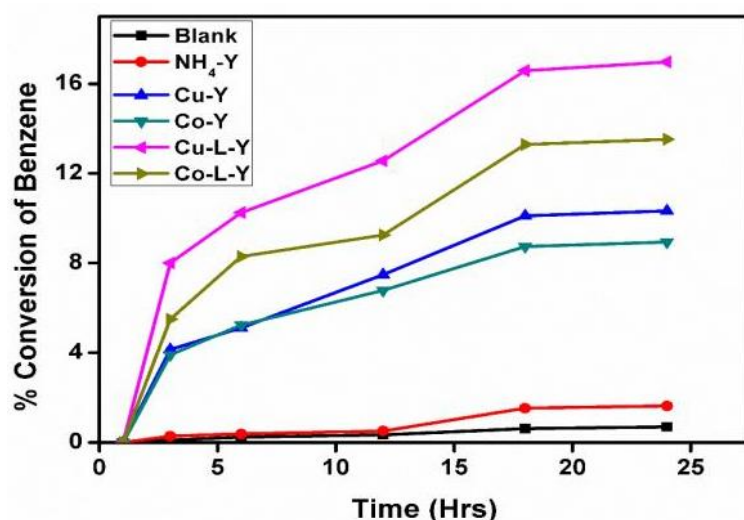

Figure 12. Percentage conversion of Benzene as a function of time using various catalyst.

Table 9. Percentage conversion of Benzene and product selectivity.

Catalyst	% Conversion of Benzene	% Product Selectivity		
		PhOH	pCAT	HQ
Blank	0.62	100	-	-
NH_4-Y	1.52	100	-	-
Co-Y	8.74	100	-	-
Cu-Y	10.11	100	-	-
Co-L-Y	13.29	97.23	1.56	1.21
Cu-L-Y	16.97	94.74	4.48	0.78

Reaction conditions: PhOH-0.025M, Cu-L-Y -0.040 g, H_2O_2-0.05M, Acetonitrile - 5 mL, 80°C, 18hrs

4. Conclusion

Cobalt (II) and Copper (II) complexes of pthatocynamine were prepared and encapsulated in zeolite-Y super cages. The various characterization techniques established the encapsulation of the metal complex inside the super-cage of zeolite-Y. The encapsulated complexes catalyse the oxidation of phenol and Cyclohexene effectively using H_2O_2 as oxidant. The major products were catechol and hydroquinone for Phenol as well as cyclohexene oxide, cyclohex-2- enol, cyclohex-2-eone, cyclohexane-1, 2-diol for Cyclohexene. The effects of different factors such as the effect of oxidant ratio, mass, temperature etc. were also investigated. The results show that encapsulated complexes are active catalysts for the oxidation of phenol and cyclohexene with high selectivity towards there major products. It was also

noticed that the cobalt encapsulated metal complex gave the best catalytic activity while there was no catalytic activity when no catalyst was used.

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