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Highlights

- > Copper containing macromolecules, viz., (CuTCPP) and (CuTPP) were synthesized.
- The ¹H NMR, mass spectral and elemental (CHN) analyses confirmed the structure of CuTCPP and CuTPP.
- > CuTCPP and CuTPP were grafted on the amino functionalized SBA-15.
- > The catalysts used for the hydroxylation of phenolic compounds.
- \triangleright CuTCPP showed comparable conversion of phenol (72 %) with an activation energy of

26.03 KJ/mol.

Copper based macromolecular catalysts for the hydroxylation of phenols

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Abstract

Copper containing macromolecules, viz., Copper-*meso*-tetrakis-(4-carboxyphenyl)porphyrin (CuTCPP) and Copper-*meso*-tetra-phenylporphyrin (CuTPP) complexes were synthesized and heterogenized on the surface of aminated SBA-15 molecular sieves. The ¹H NMR, mass spectral and elemental (CHN) analyses were performed to confirm the formation of these copper complexes (CuTCPP and CuTPP). The absence of ¹H NMR signal, characteristic of N-H bond (-2.79 *ppm* in TCPP and -2.74 *ppm* in TPP) in CuTCPP and CuTPP clearly confirms the

incorporation of copper ion in to the cavities of the TCPP and TPP ligands. In addition, the decreased intensity of the soret band and the reduction of the number of Q bands also supports the formation of copper complexes. Further the homogeneous CuTCPP and CuTPP were grafted on the amino functionalized SBA-15. The grafting of copper complexes on amino functionalised SBA-15 was evident from the surface area analysis, powder XRD and N₂ sorption isotherm. In the powder XRD, the shift in 20 value compared to parent SBA-15 materials, and the broadening of the signal supports the grafting of copper complexes in to the amino functionalized SBA-15. Both homogeneous and heterogeneous copper macromolecular complexes were used as catalysts for the hydroxylation of phenolic compounds. The catalysts showed comparable conversion (72 %) with the formation of *ortho-* and *para-* substituted products which have industrial importance. The hydroxylation reaction using the copper based macromolecular catalyst was found to be first order with an activation energy of 26.03 KJ/mol. Subsequently various substituted phenolic compounds, anisole and benzene also yielded the corresponding hydroxylated product with comparable conversion.

Keywords: Copper-*meso*-tetrakis-(4-carboxyphenyl)porphyrin (CuTCPP), Copper-meso-tetraphenylporphyrin (CuTPP), amino functionalized SBA-15, Phenol hydroxylation.

1. Introduction

Phenolic derivatives, such as catechol and hydroquinone are highly value-added chemicals having huge industrial applications for the manufacturing of pesticides, flavors, and fragrances. In addition, these compounds are widely used in the synthesis of pharmaceuticals, medicinal drugs, dyes, polymers, agrochemicals etc.1-5 Typical phenol hydroxylation processes in industries are catalysed by various metal ions, their complexes, sulphuric acid and various mineral acids.⁶⁻⁸ Traditional industrial processes for the synthesis of phenolic chemicals, catechol and hydroquinone, involve the oxidation of alkyl-benzene derivatives and aniline hydroxylation.9, 10 However, these methods have lost their market value because of the low yields, long synthetic routes, formation of numerous bi-products and its adverse effects to the environment.¹⁰ Recent years, numerous homogeneous and heterogeneous catalysts have been developed for phenol hydroxylation. Among homogeneous catalytic processes, the well-known Brichima process is based on Fe^{2+} and Co^{2+} complexes such as ferrocene and cobalt containing salt as catalysts in the presence of 60 % aqueous H_2O_2 as oxidizing agent.¹¹ Another method, viz., Rhône-Poulenc process, uses strong mineral acids such as phosphoric acid and per-chloric acid with 70 % aqueous H₂O₂.^{12, 13} On the other hand, Ube-Rhone-Poulenc process involve the use of acid catalysts such as sulphuric or sulphonic acid with ketone peroxides (a-hydroxyhydroperoxides), and 60% aqueous H₂O₂.⁸ All these methods are based on homogeneous catalysts, the removal and reuse of the catalysts after the reaction is a great challenge. Therefore, the development of heterogeneous catalysts for the phenol hydroxylation is an attractive research area due to its catalytic efficiency, reusability, environmental friendly nature and more manufacturing control for the industrial chemist. The widely used heterogeneous catalysts are based on titanosilicates. Microporous titanosilicates TS-1¹⁴ and TS-2¹⁵ used for the production of

phenolic compounds such as catechol and hydroquinone through an environmentally benign process. Later Yoshihiro, et al developed a microporous titanium-based catalyst Ti-MCM-68, which showed excellent catalytic activity.¹⁶ However, the application of the microporous titanosilicate (TS) based catalyst is limited due to its small pore size and complex synthetic methods on preparation of TS molecular sieves. In order to address the above limitation, recent years researchers focuses on the preparation of phenolic derivative by direct hydroxylation of phenol by using peroxide.¹⁷ Commonly used oxidizing agents for the hydroxylation of phenol are alkyl hydroperoxides and hydrogen peroxide.^{18, 19} However, a disadvantage of hydrogen peroxide is its low product selectivity. In addition, hydrogen peroxide leads to further oxidation of phenolic rings by its vacant hydroxyl group which leads to bi-products such as acids and polymeric compounds.¹⁹ Another class of important oxidizing agents are organic peroxides, but their applications are limited because of their toxicity, explosive, corrosive, and environmentally destructive nature.²⁰ Therefore, selection of a suitable oxidizing agent and the catalyst for the hydroxylation process with good conversion and product selectivity is a crucial step. Transition metal-based complexes were widely used as catalysts for phenol hydroxylation reactions. Transition metal-based catalysts facilitate some side reactions and gives bi-products such as quinones and macromolecular tars.²¹⁻²⁴ Among various transition metals, copper-based catalysts have been extensively studied. Variety of copper based molecular sieves show outstanding catalytic activity for phenol hydroxylation. Wang et al. reported the copper substituted mesoporous SBA-15 as an excellent catalyst for hydroxylation of phenol with high selectivity for catechol.²⁵ The Cu²⁺⁻exchanged with HY, H β , USHY, NaY and HZSM-5 zeolites were also displayed good catalytic activity for phenol hydroxylation using hydrogen peroxide as the oxidant in an atmospheric batch reactor. These catalysts were observed to be more active than TS

based catalysts.²⁶ Additionally, the copper based catalysts such as Cu/MCM-41,^{1, 27} Cu/ZSM-5,²⁸ Cu/HMS²⁹ also exhibited good catalytic activity for phenol hydroxylation. Further, Karakhanov *et al.* reported, iron and copper based complexes with N,O and N,N ligands for the hydroxylation of phenol which was a comparatively good method with excellent selectivity for catechol under mild reaction conditions.¹⁷ However, these catalysts were observed to be less stable, emphasising the need for improvements in the phenol hydroxylation reaction. Metal phthalocyanine complexes of copper, vanadium and cobalt encapsulated in zeolite-Y are known to have good catalytic activity for phenol hydroxylation.³⁰ Studies showed that the transition metal complexes of biologically relevant ligands act as efficient catalysts for a variety of industrially important organic transformations. Porphyrin is one of the potential biological ligands and porphyrin based metallo-complexes of naturally existing macrocyclic ligand, porphyrin, and the catalytic activity of porphyrin in several biologically important processes have drawn our attention. In particular, we have investigated copper based porphyrin systems as catalysts for the phenol hydroxylation reaction.

2. Experimental Procedures

The solvents and the starting materials required for the synthesis and purification of metal complex and heterogenised samples were dried as per the standard procedure previously reported.³³⁻³⁷ Further, the ligands (*meso*-tetrakis-(4carboxyphenyl)porphyrin & *meso*-tetraphenylporphyrin) and its copper complex were prepared using Schlenk line set up. The complete synthetic procedures for the synthesis of copper-*meso*-tetrakis(4-carboxyphenyl)porphyrin (Cu-TCPP), copper-*meso*-tetraphenylporphyrin (Cu-TPP), aminated

SBA 15 (SBA-AM), grafting of metal complex, *i.e.* Cu-TCPP and Cu-TPP on amino functionalized SBA-15 are summarized below.

2.1. Synthesis of Copper-meso-tetrakis-(4-carboxyphenyl)porphyrin (Cu-TCPP):

The synthesis of ligand *meso*-tetrakis-(4-carboxyphenyl)porphyrin (TCPP) was achieved by taking terephthaladehydic acid (0.338 g, 2.25 mmol) and dried pyrrole (0.2 mL, 0.193 g, 2.88 mmol) in two neck round bottom flask containing propionic acid (100 mL). The reaction mixture was refluxed in inert atmosphere (N2 atmosphere) for two hours. After the completion of the reaction, the mixture was cooled to room temperature and the precipitated product was filtered, washed with cold methanol and dried. Subsequently, the product was recrystallized in 1:1 chloroform-acetone mixture and purple coloured crystals were obtained (12 % yield). For the preparation of copper-meso-tetrakis-(4-carboxyphenyl)porphyrin (Cu-TCPP) complex, metal salt cupric chloride was dissolved in 5 mL of dry methanol. Dropwise addition of the dissolved salt was then carried out in to the round bottom flask containing solution of 1 mmol of TCPP in dry acetone (45 mL) under nitrogen atmosphere. The final reaction mixture was refluxed for 24 h under N2 atmosphere. After reaction completion, the solvent was evaporated and impurities were removed by washing the crude product with methanol and acetone. Finally, the dark green coloured solid product was isolated, (Yield: 86 %).³³⁻³⁷(¹H NMR, 400 MHz, DMSO-d₆: δ (ppm) 8.77 (8H, d, β-pyrrole proton), 8.30 (8H, d, o-phenyl), 8.25 (8H, d, m, p-phenyl). (¹³C NMR, 400 MHz, DMSO-d₆: δ (ppm) 167.90 (COOH carbon), 145.91, 134.93, 130.98 (phenyl carbons), 119.82 (meso carbon), 128.38 (pyrrolic carbon). HR-MS (ESI-MS) Calcd: 851.1203(C₄₈H₂₈N₄O₈Cu).

2.2. Synthesis of Copper-meso-tetra-phenylporphyrin (Cu-TPP):

First the ligand *meso*-Tetra-phenylporphyrin (TPP) was prepared by refluxing a mixture of benzaldehyde (0.028 mol) and dried pyrrole (0.027 mol) in the propionic acid (120mL) under N₂ atmosphere as per the reported procedure³³⁻³⁷ (Yield : 12 %). Afterwards, preparation of Cu-TPP was carried out by dissolving cupric chloride (1mmol) in 5mL dried methanol and added dropwise to the round bottom flask containing brown coloured solution of 1 mmol of ligand TPP in 45 mL of dried acetone. The obtained dark green colour reaction mixture was refluxed for 24 h. The reaction mixture was cooled to room temperature after the completion of the reaction. The dark green coloured precipitate formed was collected, washed several times with acetone and methanol to eliminate the unreacted reactants and the final product obtained was dried, (Yield: 89 %).³³⁻³⁷ (¹H NMR (400 MHz, DMSO-d₃): δ (ppm) 8.84 (8H, d, β -pyrrole proton), 8.24 (8H, s, *o*-phenyl), 7.85 (12H, m, *m*, *p*-phenyl), (¹³C NMR, 400 MHz, DMSO-d₆: δ (ppm) 134.59, 126.70, 127.73 (phenyl carbons), 120.17 (*meso* carbon), 142.22 (pyrrolic carbon), HR-MS (ESI-MS) Calcd: 675.1610 (C₄₄H₂₈N₄Cu).

2.3 Synthesis of amino functionalized SBA 15 (SBA-AM)

Mesoporous SBA-15 molecular sieve was synthesized by the previously reported procedure. ^{39–41} The triblock co-polymer pluronic P123 and tetraethyl orthosilicate were used as surfactant and silica source, respectively. Treatment of calcined SBA-15 (3 g) with 3-aminopropyltrimethoxysilane (3mmol per gram) yielded the amino functionalized SBA-15 (SBA-AM).³⁹⁻⁴⁴

2.4 Grafting of Cu-TCPP and Cu-TPP complex on amino functionalized SBA-15

For the grafting of Cu-TPP and Cu-TCPP complexes on the surface of aminated SBA-15 material, 0.05 mmol of Cu-TPP and Cu-TCPP were dissolved in dry methanol (5 mL). The metal complex was introduced dropwise in to the round bottom flask containing 1 g of amino

functionalized SBA-15 (SBA-AM) in dry methanol (45 mL). The reaction mixture obtained was refluxed for 24 h under inert N_2 atmosphere. After the completion of the reaction, the precipitated product was collected by filtration, washed thoroughly with dried methanol followed by dichloromethane.³³⁻³⁶ The Cu-TCPP and Cu-TPP grafted materials were designated as Cu-TCPP–SBA-AM and Cu-TPP-SBA-AM respectively.

2.5. Catalytic reaction

In a typical reaction (Scheme 1), 9 mmol of phenol was added to the round bottom flask containing solution of required amount of catalyst (0.01 g in the case of Cu-TCPP and Cu-TPP and 0.05 g in the case of Cu-TCPP-SBA-AM and Cu-TPP-SBA-AM) in 3 mL of methanol. Subsequently, 18 mmol of oxidant cumene hydroperoxide was added to the reaction mixture and the reaction was stirred at room temperature for 1h. After completion of reaction, the products were separated,⁴⁵ and identified by gas chromatography (GC) analysis using commercially available authentic samples (hydroquinone and Catechol; SRL chemicals). The results were analysed quantitatively by GC (Mayura Analytical model 2100) in temperature program mode (heating from 70 to 180 °C, in 10° per minute) using an FID detector equipped with an HP 88 column.

2.6 Characterization Methods

In order to identify functional groups in ligands (TCPP, TPP) and copper complexes (Cu-TCPP, Cu-TPP), FT-IR was performed in the range of 400–4000 cm⁻¹ with 4 cm⁻¹ resolutions and 120 scans by the KBr method using a PerkinElmer spectrum-2 FT-IR spectrometer. UV–Vis spectra were measured using Shimadzu UV2600 spectrometer to find out the coordination nature of the copper complexes. The ¹H and ¹³C nuclear magnetic resonance (NMR) spectra of the molecules TCPP, TPP, Cu-TCPP and Cu-TPP were recorded on a Brücker AVANCE III 400 instrument

using tetramethylsilane as internal standard. The CDCl₃- d_6 and DMF- d_7 were used as the NMR solvents for ligand and copper complex respectively. Bruckerma Xis mass spectrometer was used to analyse mass spectra by electrospray ionization method and methanol as solvent. Elemental analyses were carried out on the Elementar-vario MICRO cube by using fine powdered sample packed in an aluminium foil. The N₂ sorption measurements were performed to obtain the textural properties of the heterogenised samples using an automatic micropore physisorption analyser (Quanta Chrome Nova 2200e) at -196 °C. Prior to each run, the samples were degassed under a pressure of 10^{-3} Torr at 110 °C for 10 h. Shimadzu MAXima_X XRD-700 X-ray diffractometer with Cu K α radiation ($\alpha = 1.5418$) were used for recording the powder X-ray diffraction patterns of all the heterogenised samples in the 2 θ range of 0.5–10° with a scan speed of 0.5°/min and step size of 0.02°. The EVO MA15 Zeiss scanning electron microscope (SEM) operated at 10–20 kV was used to obtain the external morphology and particle sizes of in heterogenised samples. The LaB6 FEI-TECNAIG2-20 TWIN filament was used for Transmission electron microscopy (TEM) images of the heterogenised samples.

3. **Results and Discussion**

FT-IR spectra (Figure 1 and 2) of TCPP, CuTCPP, TPP, and CuTPP showed characteristic vibration peaks in the range of 4000 to 450 cm⁻¹. Most of the bands appeared in the region of 450–970 cm⁻¹ corresponding to the in-plane bending, out-of-plane bending, ring rotation, and ring torsion modes of the TCPP and TPP skeleton.³⁵ In TCPP, the vibrational band at 964 cm⁻¹ is characteristic of the bending mode of N–H plane of the pyrrole ring which disappeared upon the formation of the Cu-TCPP complex. A new band appeared at 828 cm⁻¹ corresponding to Cu-N bond (Figure 1). Similarly, the peak corresponding to N–H bending mode of pyrrole ring present in TPP skeleton at 980 cm⁻¹ disappeared upon Cu incorporation and a new shoulder peak at 963

 cm^{-1} was observed corresponding to the Cu-N bond in Cu-TPP (Figure 2).⁴⁶ Furthermore, in TCPP and Cu-TCPP the vibrational modes of C=O aromatic C=C and C-O were observed at 1687 cm^{-1} , 1600 cm^{-1} and 1170 cm^{-1} , respectively. The other vibrational bands for TPP and Cu-TPP complex followed a similar trend.³³⁻³⁷

The CuTPP and CuTCPP formation was analyzed by ¹H NMR studies (Table 1). In the spectra, a typical peak corresponding to the N–H protons of the pyrrole unit in TPP appeared at δ –2.74 ppm. This peak disappeared upon copper incorporation into CuTPP, (Figure S1 in ESI*) supporting the copper linkage to the nitrogen center of the TPP ligand.³⁴⁻³⁷ In the case of CuTCPP complex, no peak was observed at δ -2.79 ppm, due to the presence of N–H protons in TCPP, again supporting the linkage of copper ion with "N" center of TCPP (Figure S2 in ESI*).³⁴⁻³⁷ The remaining peaks in the NMR spectra of CuTPP and CuTCPP, remained identical to that of the pure ligands (TPP and TCPP), characteristic of the TPP and TCPP frameworks which is summarized in table 1.33-37 The ¹³C NMR spectra of CuTCPP and CuTPP shows characteristic peaks at 120 and 119 ppm respectively, corresponding to meso-carbon.³⁴⁻³⁷ The additional signals appeared at 145, 134, 130, 128 and 167 ppm correspond to phenyl, pyrrolic, and carboxylic moiety of the CuTCPP frame-work (Figure S3 in ESI*).³⁴⁻³⁷ Similarly, in CuTPP the peaks at 126, 127, 134, 130, 145 ppm corresponds to phenyl and pyrrolic carbons (Figure S4 in ESI*).³⁴⁻³⁷ CHN analysis also supports the formation of copper complex and the results are summarized in table 2. The theoretical value (%) of C, H, and N are well matches with the experimental value.

The ligand TCPP showed soret band at 420 nm and Q bands at 514, 551, 592 and 646 nm in the UV-Vis spectra (Figure 2) which are characteristic peaks of porphyrin skeleton.³⁴⁻³⁷ After the formation of copper complex (Cu-TCPP), it was observed that the intensity of soret band

decreased with a small blue shift towards 414 nm. ³⁴⁻³⁷ In addition, the number of Q bands is reduced to one at 537 nm. This may be due to the reduction in energy gap and increase in structural symmetry (D_{4h}) of the copper porphyrin complex as compared to the symmetry of the pure ligand (D_{2h}).^{33-37, 47, 48} A similar trend was observed in the TPP and Cu-TPP complex as shown in figure 2.

After the confirmation and thorough characterization of Cu-TCPP and Cu-TPP structures using various characterization techniques, the copper complexes were grafted on the amino functionalized SBA-15 (SBA-AM) to synthesize Cu-TCPP-SBA-AM and Cu-TPP-SBA-AM. The synthesized heterogenized samples were also characterized using various analytical and spectral techniques. The grafting of the Cu-TCPP and Cu-TPP complex on the surface of the aminated SBA-15 material (SBA-AM) was observed and confirmed through FT-IR, N₂ sorption studies and powder XRD. Amine (NH₂) functional groups on the surface of SBA-AM was evident from the wagging modes of vibration at 1441 cm⁻¹ in the FT-IR spectra (Figure 1 & 2). In the FT-IR spectra of Cu-TCPP-SBA-AM, the vibrational band at 1656 cm⁻¹ is characteristic of amide linkage between the Cu-TCPP complexes and amino functionalized SBA-15 material. A typical band around 1080–1200 cm⁻¹ was observed in both Cu-TCPP-SBA-AM and Cu-TPP-SBA-AM, complexes, characteristic of the as-symmetric Si-O-Si stretching vibrational mode of the SBA-15 framework. Even after the immobilization of bulk Cu-TCPP and Cu-TPP complexes on the amino functionalized SBA-15 remains intact.

The grafting of bulk copper complexes *i.e.* CuTPP and CuTCPP on the functional molecular sieve was evident from the low-angle diffraction patterns of CuTPP and CuTCPP grafted materials (Figure 4). The X-ray pattern of CuTPP and CuTCPP heterogenized samples showed

the characteristic X-ray reflections at 2θ values of around 1.4°, with the typical line broadening as well as reduction in relative intensities as that of mesoporous SBA-15 structure.⁴¹⁻⁴⁴ The presence of organo-linker and bulk CuTPP and CuTCPP resulted, shift in 2θ value towards higher angle in both the samples compared to parent SBA-15 materials and also the broadening the signal. ^{34-37, 41-44} In both cases, the structure remains intact even after incorporation of bulk macromolecules.

The N₂ sorption studies showed a decrease in pore volume and surface area. The SBA-15 shows surface area of 824.2 m²g⁻¹ with pore size of 7.2 nm. After the grafting of copper complex, it showed surface area of 203 and 200 m²g⁻¹ with pore size 4.9 nm and 4.8 in the case of Cu-TCPP-SBA-AM and Cu-TPP-SBA-AM, respectively (Table 3). The decrease in pore size, surface area, and pore volume of the immobilized samples compared to the amine functionalized sample (SBA-AM) supported the grafting of Cu-TCPPP and Cu-TPP into the mesoporous channels of the aminated SBA-15 through axial position.³⁴⁻³⁷ In addition, the pore size distribution appeared in the range of 4.8 – 4.9 nm supporting the mesoporous intactness, which is beneficial for the molecular diffusion and catalytic transformations.³³⁻³⁷

As per the IUPAC classification, the nitrogen sorption isotherm (Figure 5) showed typical type IV isotherm A vell-defined sharp inflection appeared between relative pressure range of 0.4 and 0.8 due to capillary condensation of nitrogen inside the primary mesoporous channels. After thorough characterization of the CuTCPP and CuTPP, homogeneous complexes and their heterogenised analogues were explored for their catalytic activity towards phenol hydroxylation under liquid phase condition.

4. Catalytic studies

The catalytic activity of synthesized copper complexes catalytic activity for the hydroxylation of phenol in liquid phase medium using organic-peroxide were explored (Scheme 1). The reaction conditions were optimized using different oxidants, solvents, various temperatures, etc., and the results are summarized in the following section.

4.1 Effect of different oxidant

The reaction was initially carried out using various oxidants such as 30 % aq. H_2O_2 , TBHP in water (70 %) and cumene hydro peroxide and the results are summarized in table 4. The use of H_2O_2 as oxidant with CuTCPP catalyst showed only 17% conversion of phenol with 34% selectivity of catechol and 66% selectivity of hydroquinone. Similarly, TBHP in water showed about 18% conversion with 46% catechol and 54% of hydroquinone selectivity. The use of cumene hydroperoxide as an oxidant and the CuTCPP as a catalyst yielded comparably good conversion of 72 % with the formation of catechol as major product (98% selectivity). The presence of water in the aqueous peroxide may interact with macromolecules, and hence block the active sites suggesting much lower conversion.³⁷ The use of organic peroxide with organic solvent thus facilitates better conversion. Hence, for the further studies, cumene hydroperoxide may facilitate good conversion and selectivity for the phenol hydroxylation.

4.1 Effects of Solvent

In general, solvents play a key role on the catalytic activity in any chemical reaction and especially in the case of homogeneous catalysts. Attempts were made to understand the exact role of a solvent in the phenol hydroxylation reaction catalyzed by Cu-TCPP. The results are summarized in table 5. The reactions were monitored in various solvents such as methanol, *tertiary*-butyl alcohol, isopropyl alcohol and acetonitrile. Among these solvents, maximum

conversion of 72% was observed with methanol yielded catechol as the major product (98%). The above finding is in agreement with the literature.^{49,50} The conversion of phenol using different solvents follows the decreasing order as methanol > *t*ertiary-butanol > isopropyl alcohol > acetonitrile. The polarity of the chosen solvents are as follows acetonitrile > methanol > *tertiary*-butanol ~ isopropyl alcohol. Although, acetonitrile is strongly polar in nature, the non-protic acetonitrile gives comparable conversion. Among the various protic solvents, phenol conversion steadily increases with increase in the polarity of the solvent.^{49, 50} Therefore, methanol was used as the solvent for further studies.

4.3 Effects of temperature

The reaction was carried out at various temperatures ranging from 0 to 60 °C and the results are displayed in Figure 6. The increase in phenol conversion was observed with increase in temperature from 0- 25 °C with exclusive formation of catechol as product. Further increase in temperature from 25 to 60 °C, yields no appreciable change in conversion of phenol and hence the 25 °C (i.e. at room temperature) was considered as optimal temperature condition for the chosen reaction. In all of the cases, catechol was obtained as the major product.

4.4 Effects of time

The reaction was carried out at different intervals such as 10, 20, 30, 40, 50, 60, 120 and 180 minutes at different reaction temperatures (Figure 7). It was observed that as the reaction time increases from 10 to 60 minutes, phenol hydroxylation increases linearly and the conversion was steady state afterwards. At 60 minutes the catalyst CuTCPP, showed almost 70% conversion with the formation of catechol as the major product. Hence 60 minutes was chosen as reaction time for phenol hydroxylation. The reaction was carried out at various temperatures and

observed that irrespective of the reaction temperature the conversion of phenol showed almost constant, i.e. after 60 minutes, there was no appreciable change observed in phenol conversion.

4.5 Determination of rate and activation energy of phenol hydroxylation

The reaction was carried out at various temperatures and time intervals in order to find out the rate of reaction and activation energy (Figure 8). The plot with log of the concentration of the reactant versus time yielded a straight-line indicting that the reaction follows first-order kinetics with respect to substrate phenol (Figure 8a). In addition, the *lnK* versus *1/T* yielded a negative slope of 2774.4. The activation energy of the reaction was calculated and found to be 23.06 KJ/mol., which is comparable to the activation energy reported in the literature.⁵¹⁻⁵⁶

4.6 Recyclability Study

The optimal reaction conditions, the catalytic efficiency of both homogeneous (Cu-TCPP, Cu-TPP) and heterogeneous catalysts (Cu-TCPP-SBA-AM, Cu-TPP-SBA-AM) were evaluated (figure 9). Among CuTPP and CuTCPP homogeneous catalysts, Cu-TCPP showed better phenol conversion (72%) and Cu-TPP shows a slight lower conversion i.e.; 65%. Both of the homogeneous catalysts gave exclusively catechol as the product (98%). Both the heterogeneous catalysts, Cu-TCPP-SBA-AM and Cu-TPP-SBA-AM, showed almost similar conversion of phenol which is about 65%. In all the cases catechol was obtained as the major product (> 95%). The recyclability of both homogeneous (Cu-TCPP and Cu-TPP) and heterogeneous (Cu-TCPP-SBA-AM and Cu-TPP-SBA-AM) catalysts was further explored (Figure 10). In the case of homogeneous catalysis, 9 mmol of reactant (phenol) was added into the reaction vessel after each run, and the reaction was continued further under identical experimental conditions. Both Cu-TCPP and Cu-TPP showed a gradual decrease in phenol hydroxylation. The Cu-TCPP displayed 72% conversion approximately in the first run and was decreased to 43% in the fifth

run. In addition, the selectivity of catechol was decreased from 98% to 79%. Similar tends were observed in the case of Cu-TPP catalysts and heterogeneous catalysts, (Cu-TCPP-SBA-AM and Cu-TPP-SBA-AM). In the first run both of the catalysts showed conversion of almost 65% with a 95% selectivity of catechol and in the fifth run it showed 43 % conversion with 78% of catechol selectivity, which is represented in figure 10. The water formed as by product during the reaction may interact through axial position of the complexes and may reduce the activity during the recycle studies.

4.7 Substrate scope

The scope of homogeneous (CuTCPP) and heterogeneous (Cu-TCPP-SBA-AM) catalyst were explored for hydroxylation of different phenolic substrates and the results are summarized in table 6. All of the reactions were performed in methanol for 1 h at room temperature. Both homogeneous and heterogeneous catalysts showed comparable conversion. Substituted phenols such as 2,5-dimethylphenol, 3,5-dimethyl phenol and 2,3,5-trimethylphenol gave comparable conversion with the formation of corresponding hydroquinone as a major product. Benzene showed very less conversion, with the formation of phenol as the major product with comparably good selectivity. Anisole yielded both *para-* and *ortho-* substituted hydroxylated products in which the *para-* substituted product, 4-methoxyphenol was formed as major product (73%). Whereas the isceugenol, yielded vanillin and vanillic acid with 36% conversion with the oxidation of propenyl chain.

4.8 Mechanism of phenol oxidation by cumene hydroperoxide

Based on the results and previous studies⁵⁷⁻⁶¹, it is proposed that the reaction may proceed via the pathway as shown in Scheme 2. Initially in the presence of solvent, the proximal oxygen of peroxo species will coordinate with the metal center *i.e.* copper center which acts as Lewis acid.

Subsequently, the hydroxyl species will remove from the peroxide and attack the *ortho-* or *para*position of phenol and form corresponding products, viz., catechol and hydroquinone respectively. Finally, the catalysts were regenerated and forming hydroxy cumene as bi-product.

5. Conclusion

Copper-containing porphyrin complexes (CuTCPP, CuTPP) were synthesized for the first time and heterogenized on the amino functionalized SBA-15 molecular sieve. The synthesized copper complexes were characterized and confirmed through FT-IR, CHN, ¹HNMR, ¹³CNMR and mass spectral analyses. The heterogenization of copper complex on aminated SBA-15 was confirmed by powder XRD, FT-IR, and adsorption-desorption analyses. The catalytic application of the synthesized copper complexes, CuTPP, CuTCPP heterogeneous complex, CuTPP-SBA-AM and CuTCPP-SBA-AM for the hydroxylation of phenolic compounds, anisole, benzene and substituted phenols were studied. The catalysts showed comparable conversion (65-72 %) with the formation of *ortho-* and *para-* substituted products. The reaction was found to be first order with activation energy of 23.06 KJ/mol., which is comparable to the previously reported values. Further the homogeneous and heterogeneous catalysts showed comparable recyclability and reusability.

Conflicts of interest

There are no conflicts to declare.

Declaration of interests

 \boxtimes The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supporting Information

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Figure 1: FT-IR spectra of TCPP, CuTCPP and CuTCPP-SBA-AM.





Figure 2: Powder XRD pattern of SBA-15, Cu-TCPP-SBA-AM, and Cu-TPP-SBA-AM.

20(degree)

4

2

6

CuTPP-SBA-AM

CuTCPP-SBA-AM

8

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Figure 6: Effect of temperature on phenol hydroxylation over Cu-TCPP catalyst. (Reaction Conditions: Methanol (Solvent) =3mL, Cu-TCPP (Catalyst) =10mg, Phenol (Substrate) = 0.8mL (9mmol), Cumene hydroperoxide (oxidant) = 2mL (18mmol), Time = 1 hr.



Figure 7: Effect of reaction duration (a) at 25 °C (b) at different temperature using CuTCPP as catalyst.



Figure 8: Kinetic study on phenol hydroxylation using CuTCPP; (a) Log concentration of the reactant vs time plot for the first order, and (b) rate constant vs 1/T plot to find out slope and activation energy.



Figure 9: Effect of various copper macromolecular catalysts on phenol hydroxylation.

Reaction Conditions: Methanol (Solvent) =3mL, Cu-TCPP/Cu-TPP (Catalyst) =10mg, Cu-TCPP-SBA-AM/Cu-TPP-SBA-AM = 50mg, Phenol (Substrate) = 0.8mL (9mmol), Cumene hydroperoxide (oxidant) = 2mL (18mmol), Time = 1 hr



Figure 10: Recyclability of (a) Cu-TCPP (b) Cu-TCPP, (c) Cu-TCPP-SBA-AM and (d) Cu-TPP-SBA-AM on phenol hydroxylation.

Reaction Conditions: Methanol (Solvent) =3mL, Cu-TCPP/Cu-TPP (Catalyst) =10mg, Cu-TCPP-SBA-AM/Cu-TPP-SBA-AM = 50mg, Phenol (Substrate) = 0.8mL (9mmol), Cumene hydroperoxide (oxidant) = 2mL (18mmol), Time = 1 hr



Scheme 2: Proposed mechanism for the phenol hydroxylation using cumene hydroperoide as oxidant and Cu based catalyst.

Journal Pression

Table 1: ¹H-NMR of macromolecular ligands TPP (tetraphenylporphyrin), TCPP (Tetrakis (4carboxyphenyl)porphyrin) and its copper complexes CuTPP (Copper-tetraphenylporphyrin),

| Sample code | Pyrrole | N-H | ortho | meta,para |
|----------------|---------|-------|-------|-----------|
| TPP | 8.87 | -2.74 | 8.25 | 7.75 |
| CuTPP | 8.84 | | 8.24 | 7.85 |
| ТСРР | 8.87 | -2.79 | 8.25 | 7.79 |
| CuTCPP | 8.77 | | 8.30 | 8.25 |

CuTCPP (Copper-tetrakis(4-carboxyphenyl)porphyrin).

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Table 2: CHNS of macromolecular ligands TPP (tetraphenylporphyrin), TCPP (Tetrakis (4-carboxyphenyl)porphyrin) and its copper complexes CuTPP (Copper-tetraphenylporphyrin),

| Sample code | % of C | | % of H | | % of N | |
|-------------|--------|--------|--------|--------|--------|--------|
| | Expt. | Theor. | Expt. | Theor. | Expt. | Theor. |
| TPP | 85.35 | 85.90 | 4.98 | 4.88 | 9.17 | 9.11 |
| CuTPP | 77.95 | 78.15 | 3.98 | 4.17 | 8.14 | 8.28 |
| TCPP | 71.2 | 72.9 | 4.6 | 3.8 | 6.2 | 7.0 |
| CuTCPP | 67.21 | 67.64 | 3.14 | 3.31 | 6.24 | 6.57 |

CuTCPP (Copper-tetrakis(4-carboxyphenyl)porphyrin).

Table 3: Textural properties of heterogeneous copper porphyrin complexes.

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| Sample code | BET Surface area (m ² g ⁻¹) | BJH Pore volume (cm ³ g ⁻¹) | BJH Pore size (nm) |
|----------------|---|---|-----------------------|
| SBA-15 | 824 | 1.05 | 7.2 |
| Cu-TPP-SBA-AM | 200 | 0.27 | 4.8 |
| Cu-TCPP-SBA-AM | 203 | 0.26 | 4.9 |

| Ovidant | Conversion (%) | Selectivity (%) | | |
|-------------------------------|----------------|-----------------|-------------------|--|
| Oxidant | | Catechol | Hydroquinone (HQ) | |
| H ₂ O ₂ | 17 | 34 | 66 | |
| TBHP in water | 19 | 46 | 54 | |
| Cumene hydroperoxide | 72 | 98 | 2 | |

Table 4: Role of oxidant on phenol hydroxylation using CuTCPP catalyst.

Reaction Conditions: Methanol (Solvent) =3mL, Cu-TCPP (Catalyst) =10mg, Phenol (Substrate) = 0.8mL (9mmol), oxidant= 18mmol, t = 1 hr; T = 25 °C.

ound

| | | Selecti | | |
|-------------------|----------------|----------|----------------------|----------------|
| Solvent | Conversion (%) | Catechol | Hydroquinone (HQ) | Polarity Index |
| Methanol | 72 | 98 | 2 | 5.1 |
| t-butanol | 69 | 82 | 18 | 3.9 |
| Isopropyl alcohol | 59 | 86 | 14 | 3.9 |
| Acetonitrile | 54 | 99 | 1 | 5.8 |

Table 5: Effect of solvent on hydroxylation of phenol using CuTCPP catalyst.

Reaction Conditions: Solvent =3mL, Cu-TCPP (Catalyst) =0.01 g, Phenol (Substrate) = 0.8mL (9mmol), Cumene hydroproxide (oxidant) = 18mmol, t = 1 hr, T = 25 °C.

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| | | | CuTCPP CuTCPP | | PP-SB | SBA-AM | | |
|-------|-----------------------------|---------------------------------------|---------------|-----------------|-------|-------------|-------------|-----|
| Entry | Substrate | Product | Conv. (%) | Sel. (%) | TON | Conv (%) | Sel. (%) | TON |
| 1 | benzene | Phenol | 9 | 83 | 73 | 11 | 78 | 20 |
| 2 | OH 2,5-dimethylphenol | HO 2,5-dimethylbenzene-1,4-diol | 21 | 76 | 172 | 26 | 72 | 47 |
| 3 | OH 3,5-dimethylphenol | HO 2,6-dimethylbenzene-1,4-diol | 13 | 82 | 106 | 17 | 82 | 30 |
| 4 | OH 2,3,5-trimethylphenol | HO 2,3,5-trimethylbenzene-1,4-diol | 17 | 78 | 139 | 32 | 67 | 58 |
| 5 | HO | HO O Vanillin | 36 | 63 [#] | 294 | 31 | 71# | 56 |
| 6 | anisole | HO 4-methoxyphenol | 11 | 73 | 90 | 13 | 68 | 23 |

| Table 6: Conversion of value | arious phenolic substrates i | using CuTCPP and CuTCPP-SBA-AM c | catalysts. |
|-------------------------------------|------------------------------|----------------------------------|------------|
|-------------------------------------|------------------------------|----------------------------------|------------|

Reaction Conditions: Methanol (Solvent) = 3mL, Cu-TCPP/Cu-TPP (Catalyst) = 10mg, Cu-TCPP-SBA-AM/Cu-TPP-SBA-AM = 50mg, Phenol (Substrate) = 0.8mL (9mmol), Cumene hydroperoxide (oxidant) = 2mL (18mmol), t = 1 hr; T = 25 °C, TON: Turn over number. [#] Remaining product is vanillic acid.

