

Solvothermal Synthesis of Recyclable Heterogeneous Catalysts by Transition Metal Complex Anchored on Polyoxometalate Keggin Unit

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ABSTRACT-Metal complex comprising of copper (II) coordinated to nicotinamide and potassium thiocyanate ligands was synthesized and characterized. The metal complex was immobilized by anchoring on ammonium salt of phosphotungstate $[(\text{NH}_4)_3(\text{PW}_{12}\text{O}_{40})]$ and phosphomolybdate $[(\text{NH}_4)_3(\text{PMo}_{12}\text{O}_{40})]$ by hydrothermal method. Green procedure was followed during synthesis of organic-inorganic hybrids. The synthesized metal complex and organic-inorganic hybrids were characterized by elemental analysis, FT-IR., DR-UV-Vis, EDX, SEM and powder XRD. Powder XRD of organic-inorganic hybrids gave reflection at around $2\theta=9$, confirming the preservation of the Keggin structure. Since the Keggin structure was maintained after the immobilization of the complex, the immobilization strategy was successful. The metal complex as well as organic-inorganic hybrids were studied for their catalytic activity for oxidative conversion of alkyl aromatic, cycloalkane and cycloalcohols. Gas chromatography (GC) and mass spectroscopy (MS) was used for the determination of products formed during catalysis. The heterogeneous catalysts showed high catalytic activity and good product selectivity. The catalysts were recycled and reused multiple times with no substantial loss of their catalytic activity.

Keywords-Phosphotungstate, phosphomolybdate, heterogeneous catalyst, cyclohexane

I. INTRODUCTION

Since much is known about metal complex catalysts, which are generally soluble and therefore termed as homogenous. The immobilization of these entities onto the solids to create organic-inorganic hybrid catalysts can be accomplished with some aspects of design. Heterogeneous catalysts provide numerous opportunities for recovering and recycling catalysts from reaction environments. Various procedures have been established for the immobilization of homogeneous catalysts[1]. Features such as improved processing steps, better process economics, and environmental friendly industrial manufacturing are important motivating factors for creating recoverable catalysts. Benefits of heterogeneous catalysts as compared to homogeneous catalysts are easy separation, recovery, reutilizing and stability of heterogeneous catalysts. The recyclability and easy separation of catalyst from catalytic system are of significant industrial interest. Traditional heterogeneous catalysts are rather limited in the nature of their active sites and thus the scope of reactions that these catalysts can accomplish. Therefore, to overcome these obstacles various researchers used polyoxometalate (POM) clusters to synthesize heterogeneous catalysts. The goal is to incorporate these active metal complexes onto the POM as solid support to provide avenues to recovery and possible recyclability.

Quite a lot of recent studies have focused on the selective oxidation of alkyl aromatics, cycloalkanes and cycloalcohols to higher-added value ketones using hydrogen peroxide or oxygen as green oxidizing agents[2–6]. The products that were obtained during catalysis were used as intermediates in synthesizing various industrial products. Keto derivative of 1,2,3,4-tetrahydronaphthalene (tetralin) is 3,4-dihydronaphthalen-1(2H)-one (tetralone), which is used as reactive intermediate for the synthesis of insecticide carbaryl, the antidepressant sertraline, and the antihypertensive drug benazepril [7–9]. Similarly, cyclopentanone is a precursor to cyclopentobarbital and cyclohexanone is consumed as precursors in the production to Nylon 6,6 and Nylon 6. Copper(II) can easily interact and catalyze these reactions as it plays a major role in similar biological system [10-12].

In our research group we have earlier synthesized $[\text{Cu}_2-(\mu\text{-NCS})_2(\text{NCS})_2(\text{Nicotinamide})_4]$ and characterized it by single crystal XRD, CCDC No. 850081 [The detailed structural studies and its magnetic behavior will be reported later] [13]. Now in this work we have gone a step further by immobilizing the Cu(II) complex on ammonium salt of phosphotungstate $[(\text{NH}_4)_3(\text{PW}_{12}\text{O}_{40})]$ and ammonium salt of phosphomolybdate $[(\text{NH}_4)_3(\text{PMo}_{12}\text{O}_{40})]$ which

shows keggin type structure, thus synthesizing two new heterogeneous catalysts and studied the catalytic activity of Cu(II) complex and two newly synthesized heterogeneous catalysts for oxidative conversion of cycloalkanes and cycloalcohols.

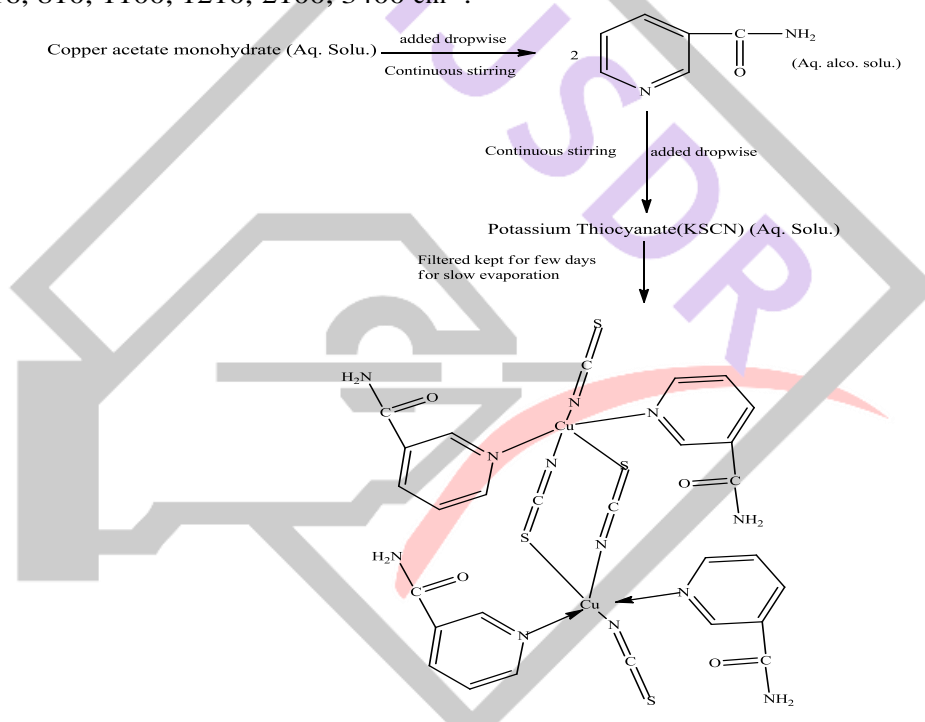
II. EXPERIMENTAL

Materials and Characterization Techniques

Copper acetate (Sigma Aldrich), potassium thiocyanate (Sigma Aldrich), nicotinamide (Sigma Aldrich), phosphotungstic acid (Sigma Aldrich), phosphomolybdic acid (Sigma Aldrich) were purchased and used without further purification. FT-IR spectra were recorded in KBr pellets with a Nicolet170 SXFT-IR spectrophotometer in the 4000–400 cm^{-1} region. Nova Nano FE-SEM 450 (FEI) is coupled to EDAX detector for measuring the elemental composition of materials. Thermo Scientific TSQ 8000 gas chromatograph-mass spectrometer was used for product analysis.

Synthesis of [CuComplex]

The complex, $[\text{Cu}_2(\mu\text{-NCS})_2(\text{NCS})_2(\text{Nicotinamide})_4]$ was synthesized by following similar procedure as reported in the Ph.D thesis [13] (scheme 1). To hot ethanol-water solution (10 ml) of nicotinamide (0.244g, 2 mmol) aqueous solution (10ml) of copper acetate (0.181g, 1 mmol) was added with constant stirring. Aqueous solution of potassium thiocyanate (0.196g, 2 mmol) was slowly added drop wise to the solution of copper acetate and nicotinamide. The blue color solution was filtered and kept for slow evaporation. After few days needle shaped crystals were obtained. Elemental analysis calculated for $[\text{Cu}_2(\text{NCS})_4(\text{C}_6\text{H}_6\text{N}_2\text{O})_4]$ (%) (Mol. wt. 847.08) C 17.0, H 2.8, N 6.6, O 3.7, Found (%) C 17.8, H 2.5, N 6.15, O 3.9. FT-IR (KBr phase) (cm^{-1}): 616, 810, 1100, 1210, 2100, 3400 cm^{-1} .



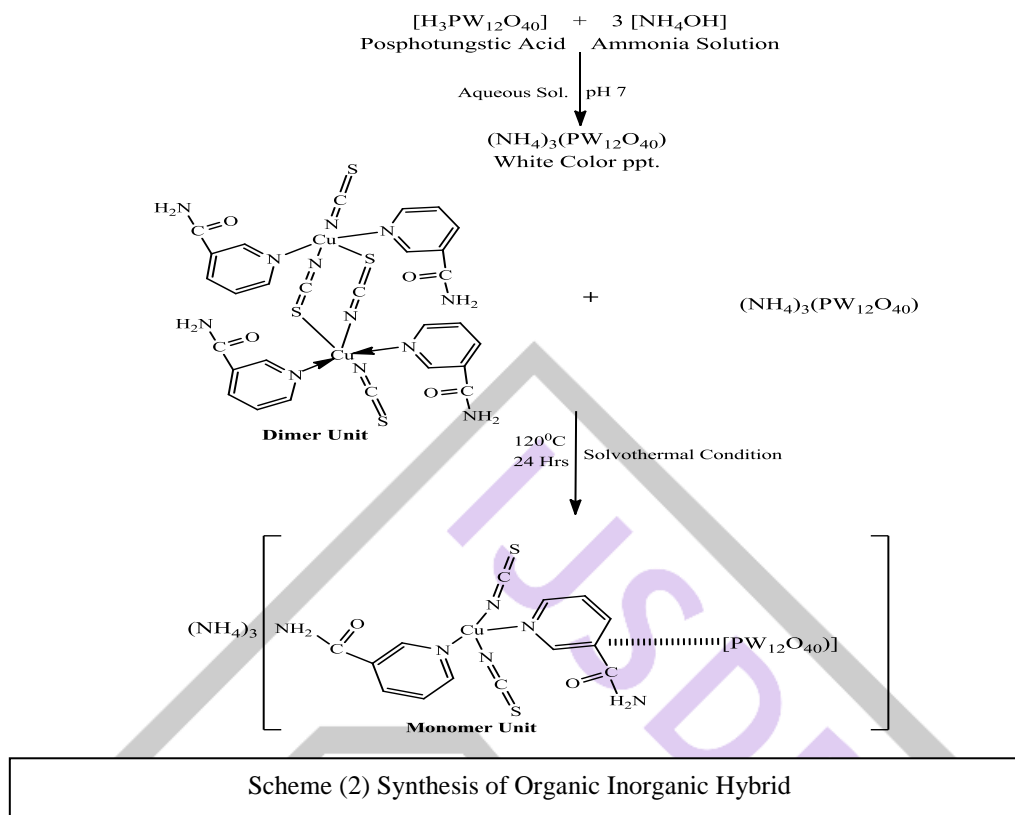
Scheme (1) Synthesis of [CuComplex]

Synthesis of Organic Inorganic Hybrid $(\text{NH}_4)_3[(\text{CuComplex})(\text{PW}_{12}\text{O}_{40})]$

To 1 mmol aqueous solution of phosphotungstic acid [PTA] ammonium hydroxide solution was added drop wise until pH=7 was maintained, pH was monitored by pH meter. Excess ammonia was removed by evaporation on water bath and absolute ethanol in excess was added to obtain white precipitate, the precipitate was vacuum dried and white salt of $[(\text{NH}_4)_3(\text{PW}_{12}\text{O}_{40})]$ was collected. 1 mmol (0.8470 gm) of [CuComplex] was added to methanolic solution of 1 mmol (2.9311 gm) $[(\text{NH}_4)_3(\text{PW}_{12}\text{O}_{40})]$. After stirring for an hour the solution mixture was transferred to a sealed teflon reactor and heated at 120°C for 1 day. The reactor was cooled down to room temperature, after constant heating for 1 day at autogenous pressure. The hybrid which was collected, filtered and washed with double distilled water and dried under vacuum. $(\text{NH}_4)_3[(\text{CuComplex})(\text{PW}_{12}\text{O}_{40})]$ was obtained as bluish green powder product. Elemental analysis calculated for $[\text{Cu}(\text{NCS})_2(\text{C}_6\text{H}_6\text{N}_2\text{O})_2(\text{NH}_3)_3(\text{PW}_{12}\text{O}_{40})]$ (%) (Mol. wt. 3352.08) C, 5.02; H, 0.63; N, 3.76; O, 20.05 Found (%) C, 5.08; H, 0.72; N, 3.80; O, 20.10 FTIR spectra of $(\text{NH}_4)_3[(\text{CuComplex})(\text{PW}_{12}\text{O}_{40})]$ 534, 710, 750, 810, 890, 969 cm^{-1} [14].

Synthesis of Organic Inorganic Hybrid $(\text{NH}_4)_3[(\text{CuComplex})(\text{PMo}_{12}\text{O}_{40})]$

During the synthesis of organic inorganic hybrid, $(\text{NH}_4)_3[(\text{CuComplex})(\text{PMo}_{12}\text{O}_{40})]$ similar procedure was followed, as mentioned in the synthesis of $(\text{NH}_4)_3[(\text{CuComplex})(\text{PW}_{12}\text{O}_{40})]$ but in place of PTA phosphomolybdic (PMA) was used. Elemental analysis calculated for $[\text{Cu}(\text{NCS})_2(\text{C}_6\text{H}_6\text{N}_2\text{O})_2(\text{NH}_3)_3(\text{PMo}_{12}\text{O}_{40})]$ (%) (Mol. wt. 2297.52) C, 7.32; H, 0.92; N, 5.49; O, 29.25 Found (%) C, 7.41; H, 0.93; N, 5.52; O, 29.95. FTIR spectra of $(\text{NH}_4)_3[(\text{CuComplex})(\text{PMo}_{12}\text{O}_{40})]$ 785, 888, 1059 cm^{-1} [15].



RESULTS AND DISCUSSION

FT-IR spectra of [CuComplex] in Fig.1A shows broad band in the range of 3400 cm^{-1} and is assigned to asymmetric and symmetric stretching vibration of NH_2 group of nicotinamide. Nicotinamide show a broad band in the region ($1418 \text{ cm}^{-1} \sim 1318 \text{ cm}^{-1}$) for ring stretching of $\nu(\text{CN})$ of the primary amide. The peak near 2190 cm^{-1} assigned to stretching mode $\nu(\text{CN})$, of bridged thiocyanate ligand. This peak points out, that thiocyanate coordinates in bridging (Cu-NCS-Cu) manner. The spectrum presents single band near 2012 cm^{-1} which may be assigned to the (CN) stretching mode of unbridged thiocyanate [18]. The peak near 743 cm^{-1} is responsible for (CS) stretching of thiocyanate group. The characteristic peak at 2012 cm^{-1} , 743 cm^{-1} in [CuComplex], shifted to 2002 cm^{-1} , 738 cm^{-1} in $(\text{NH}_4)_3[(\text{CuComplex})(\text{PW}_{12}\text{O}_{40})]$ and 2014 cm^{-1} , 723 cm^{-1} in $(\text{NH}_4)_3[(\text{CuComplex})(\text{PMo}_{12}\text{O}_{40})]$, which confirms the presence of thiocyanate group. Disappearance of absorption at 2190 cm^{-1} from the spectra of hybrid suggest the unbridged monomeric nature of complex. Appearance of IR peaks (cm^{-1}) in Fig. 1B of $(\text{NH}_4)_3[(\text{CuComplex})(\text{PW}_{12}\text{O}_{40})]$ 534 (ν symmetric WOW) 750 (ν asymmetric (asym) WOW), 890 (ν asym WOW), 949 (ν asym W=O), 969 (ν asym W=O) in addition to these bands, presence of 3410, 2012, 1413 shows positive interaction between [CuComplex] and $(\text{NH}_4)_3[(\text{CuComplex})(\text{PW}_{12}\text{O}_{40})]$. The characteristic bands of FTIR spectra (cm^{-1}) as shown in Fig. 1C in $(\text{NH}_4)_3[(\text{CuComplex})(\text{PMo}_{12}\text{O}_{40})]$ at 1059, 888, 785 are assigned to the symmetric stretching of P-O, Mo-Oc-Mo, Mo-Oe-Mo, respectively. Here c tends, for the corner sharing oxygen atom, and e for the edge sharing oxygen connecting Mo. Along with characteristic IR bands (cm^{-1}) 1059, 969, 888, 785 which are due to PMA Keggin species presence of 3400, 1413, 1260 bands indicate positive immobilization of [CuComplex] onto $(\text{NH}_4)_3(\text{PMo}_{12}\text{O}_{40})$.

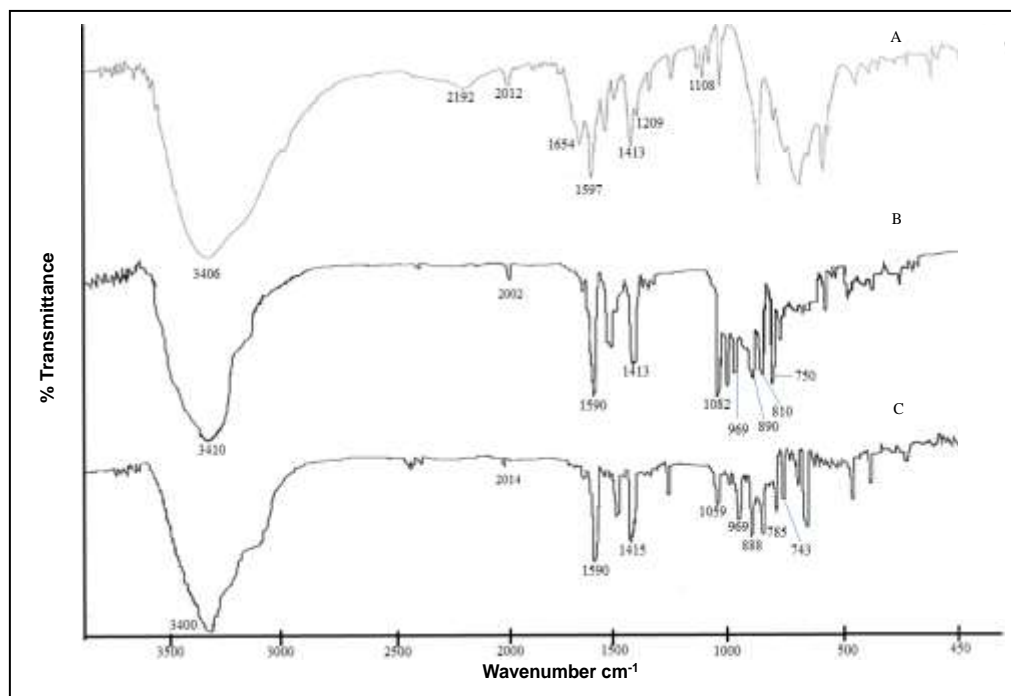


Figure 1 FT-IR of (A) [CuComplex] (B) $(\text{NH}_4)_3[(\text{CuComplex})(\text{PW}_{12}\text{O}_{40})]$ (C) $(\text{NH}_4)_3[(\text{CuComplex})(\text{PMo}_{12}\text{O}_{40})]$

Figure 2B, 2D shows the powder XRD of solid $(\text{NH}_4)_3(\text{PW}_{12}\text{O}_{40})$ and $(\text{NH}_4)_3(\text{PMo}_{12}\text{O}_{40})$ which were obtained after going through similar solvothermal condition as the hybrids, $(\text{NH}_4)_3[(\text{CuComplex})(\text{PW}_{12}\text{O}_{40})]$ and $(\text{NH}_4)_3[(\text{CuComplex})(\text{PMo}_{12}\text{O}_{40})]$. The XRD pattern of $(\text{NH}_4)_3[(\text{CuComplex})(\text{PW}_{12}\text{O}_{40})]$ and $(\text{NH}_4)_3[(\text{CuComplex})(\text{PMo}_{12}\text{O}_{40})]$ shows reflection around $2\theta=9^\circ$ Fig. 2C, 2E, which represents that metal complex Fig. 2A was immobilized by $(\text{NH}_4)_3(\text{PW}_{12}\text{O}_{40})$ and $(\text{NH}_4)_3(\text{PMo}_{12}\text{O}_{40})$ respectively, since Keggin type of structure was maintained in the hybrid [16]. The XRD pattern of organic inorganic hybrids shows the presence of characteristic peaks with minor shift which are present in [CuComplex], $(\text{NH}_4)_3(\text{PW}_{12}\text{O}_{40})$ and $(\text{NH}_4)_3(\text{PMo}_{12}\text{O}_{40})$.

The DRS UV-Vis spectrum Fig. 3A, 3B, 3C, represent [CuComplex], $(\text{NH}_4)_3[(\text{CuComplex})(\text{PW}_{12}\text{O}_{40})]$ and $(\text{NH}_4)_3[(\text{CuComplex})(\text{PMo}_{12}\text{O}_{40})]$, the absorption band in the region of 514 nm to 533 nm, for [CuComplex] and the hybrids appear in the same region with a minor shift showing almost no change in the co-ordination geometry of Cu ion in the complex and in the hybrids. UV-Vis band is significant because it provides information about the geometry of the metal complex. The [CuComplex] shows distorted square pyramidal-trigonal bipyramidal geometry which remains in the hybrid.

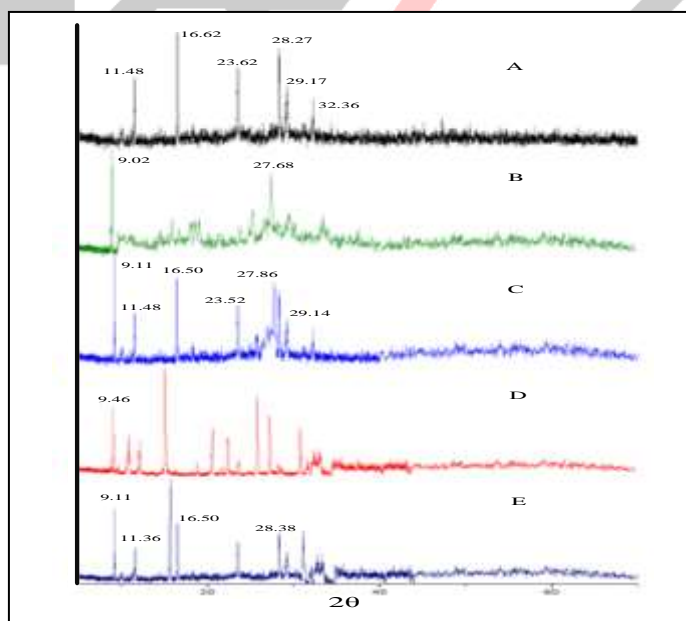


Figure 2 Powder XRD of (A) [CuComplex] (B) $(\text{NH}_4)_3(\text{PW}_{12}\text{O}_{40})$ (C) $(\text{NH}_4)_3[(\text{CuComplex})(\text{PW}_{12}\text{O}_{40})]$ (D) $(\text{NH}_4)_3[(\text{CuComplex})(\text{PMo}_{12}\text{O}_{40})]$ (E) $(\text{NH}_4)_3(\text{PMo}_{12}\text{O}_{40})$

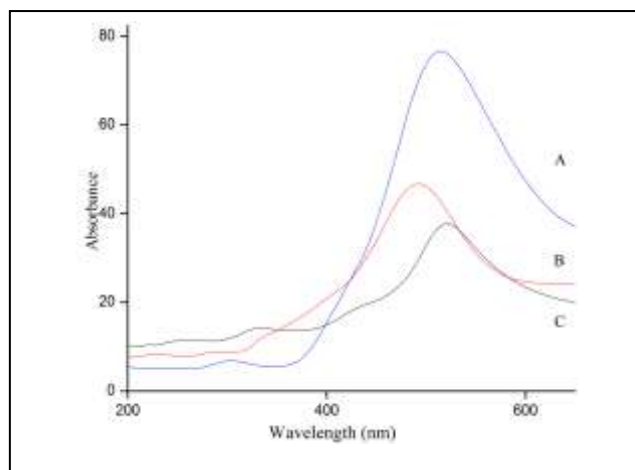


Figure 3 DRS UV-Vis of (A) [CuComplex] (B) $(\text{NH}_4)_3[(\text{CuComplex})(\text{PW}_{12}\text{O}_{40})]$
(C) $(\text{NH}_4)_3[(\text{CuComplex})(\text{PMo}_{12}\text{O}_{40})]$

Scanning Electron images, Fig. 4C, 4E, of $(\text{NH}_4)_3[(\text{CuComplex})(\text{PW}_{12}\text{O}_{40})]$ and $(\text{NH}_4)_3[(\text{CuComplex})(\text{PMo}_{12}\text{O}_{40})]$ shows drastic change in surface morphology as compared with [CuComplex], $(\text{NH}_4)_3(\text{PW}_{12}\text{O}_{40})$ and $(\text{NH}_4)_3(\text{PMo}_{12}\text{O}_{40})$ as shown in Fig. 4 A, 4 B, 4 D, which indicate that the [CuComplex] was immobilized onto the surface of $(\text{NH}_4)_3(\text{PW}_{12}\text{O}_{40})$ and $(\text{NH}_4)_3(\text{PMo}_{12}\text{O}_{40})$, thus forming two new hybrids. EDX spectrum of $(\text{NH}_4)_3[(\text{CuComplex})(\text{PW}_{12}\text{O}_{40})]$ and $(\text{NH}_4)_3[(\text{CuComplex})(\text{PMo}_{12}\text{O}_{40})]$ [Fig. 5 (A), (B)] which not only reveals the presence of all expected elements in the synthesized hybrids but also the stoichiometric ratio of Cu atom to W atom in $(\text{NH}_4)_3[(\text{CuComplex})(\text{PW}_{12}\text{O}_{40})]$ is 1 Cu atom per 12 W atoms and Cu atom to Mo atom in $(\text{NH}_4)_3[(\text{CuComplex})(\text{PMo}_{12}\text{O}_{40})]$ is 1 Cu atom per 12 Mo. The stoichiometric ratio of 1Cu to 12W atoms and 1Cu to 12Mo atoms shows that the monomeric unit of [CuComplex] has combined with $(\text{NH}_4)_3(\text{PW}_{12}\text{O}_{40})$ and $(\text{NH}_4)_3(\text{PMo}_{12}\text{O}_{40})$.

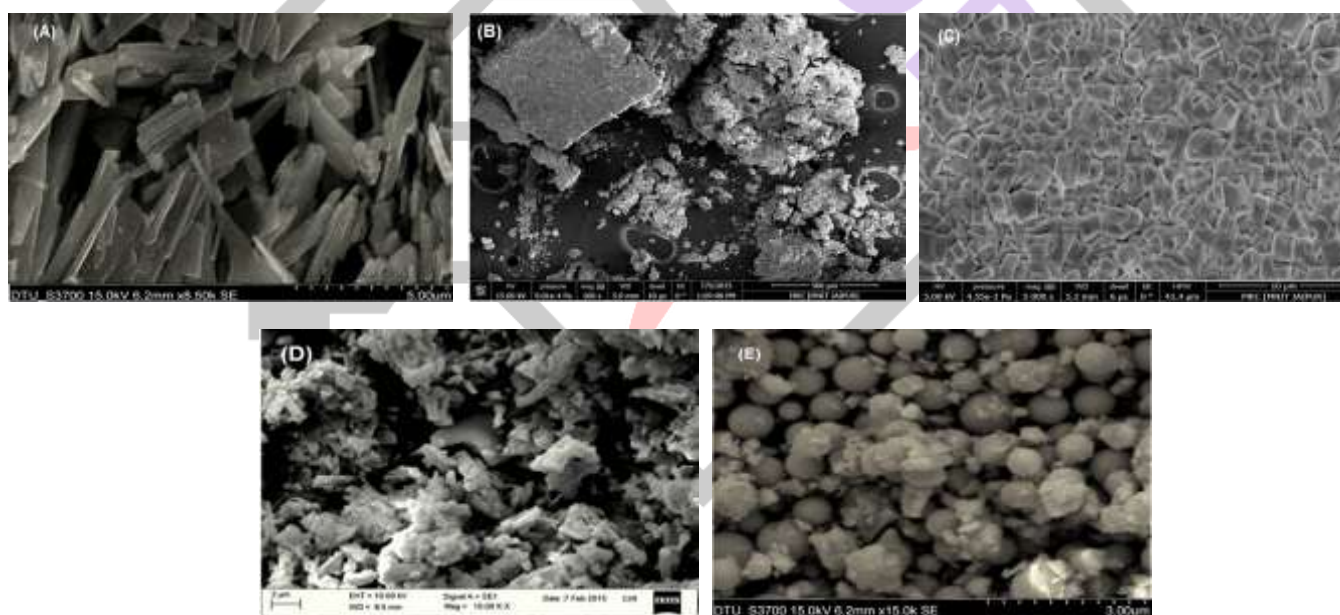
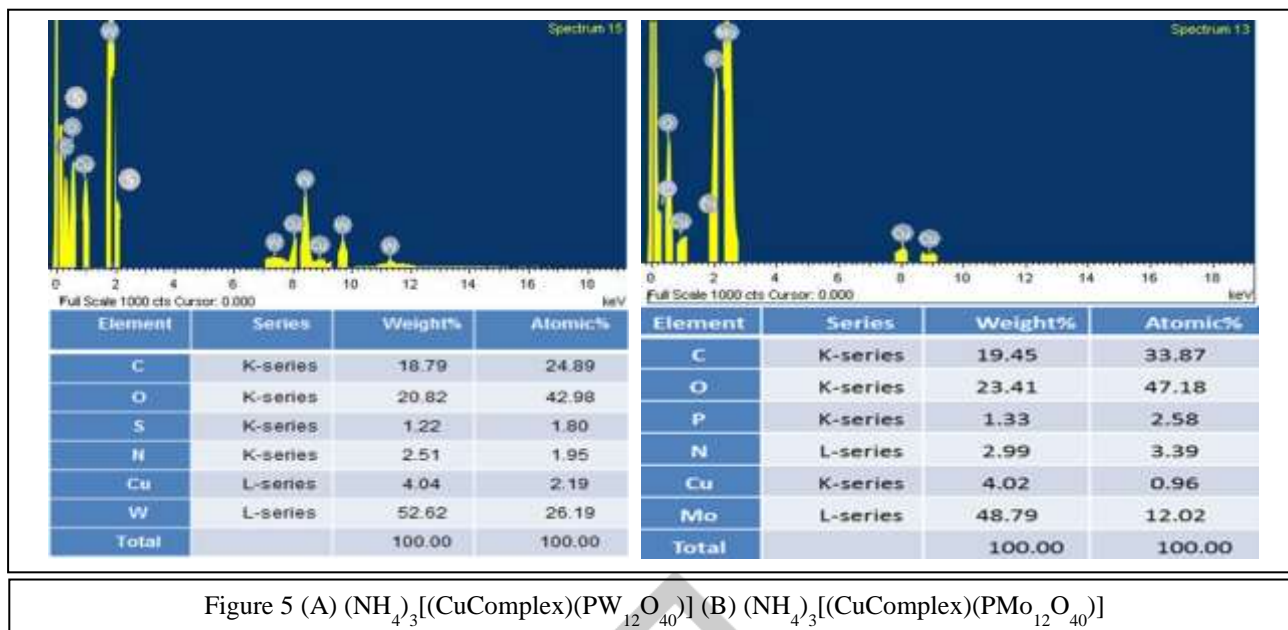


Figure 4 (A) [CuComplex] (B) $(\text{NH}_4)_3(\text{PW}_{12}\text{O}_{40})$ (C) $(\text{NH}_4)_3[(\text{CuComplex})(\text{PW}_{12}\text{O}_{40})]$ (D) $(\text{NH}_4)_3(\text{PMo}_{12}\text{O}_{40})$ (E)
 $(\text{NH}_4)_3[(\text{CuComplex})(\text{PMo}_{12}\text{O}_{40})]$



CATALYTIC EVALUATION

The catalytic activity of the [CuComplex] as homogeneous catalyst and two newly synthesized heterogeneous catalysts i.e. $(\text{NH}_4)_3[(\text{CuComplex})(\text{PW}_{12}\text{O}_{40})]$ and $(\text{NH}_4)_3[(\text{CuComplex})(\text{PMo}_{12}\text{O}_{40})]$ were compared under similar catalytic condition. The synthesized catalysts were tested for the oxidation of tetralin, cyclohexane and cycloalcohols. The heterogeneous catalysts were reused multiple times in the oxidation of tetralin, cyclohexane and cycloalcohols. During oxidative catalysis of substrates with homogeneous catalyst i.e. [CuComplex] readily react with substrates in acetonitrile solution to form possibly an unstable brown copper(I) species which on exposure to H_2O_2 converts back to the parent copper(II) complex which was blue in color [17]. All the catalytic experiments were carried out at 70°C temperature. Among various oxidants a green oxidizing agent i.e. hydrogen peroxide of 30% strength was used for oxidation and acetonitrile as solvent. In our experiment 0.1 mmol of catalysts, 1ml of substrates were added to 5ml of acetonitrile and 1 ml of H_2O_2 , the progress of the reaction was monitored after each hour and mixture was stirred and refluxed for 8 Hrs. After the completion of reaction the reaction mixture was diluted with D.D. water (25 ml), then dichloromethane (DCM) (4X5 ml) was added to extract the products. Products were washed with DCM several times. The products were confirmed and identified by gas chromatography GC and mass spectroscopy MS. Table 1 represents the percent conversion of substrate to their respective products by the catalysts.

Under similar condition blank catalytic experiments were also performed without using the catalysts, but no oxidation products were obtained. The catalytic experiment was also performed under similar condition using $(\text{NH}_4)_3(\text{PW}_{12}\text{O}_{40})$ and $(\text{NH}_4)_3(\text{PMo}_{12}\text{O}_{40})$ but no oxidation products were obtained. After the every run of catalytic experiment, the heterogeneous catalysts i.e. $(\text{NH}_4)_3[(\text{CuComplex})(\text{PW}_{12}\text{O}_{40})]$ and $(\text{NH}_4)_3[(\text{CuComplex})(\text{PMo}_{12}\text{O}_{40})]$ were washed with D.D. water, methanol, diethyl ether and reused. Graph 1 represents the percent conversion of substrates to the respective products during first, second, third and fourth catalytic run by heterogeneous catalysts. The SEM image of $(\text{NH}_4)_3[(\text{CuComplex})(\text{PW}_{12}\text{O}_{40})]$ and $(\text{NH}_4)_3[(\text{CuComplex})(\text{PMo}_{12}\text{O}_{40})]$ (Fig.6 A, 6 B) was taken after fourth catalytic run shows similar surface morphology as given in Fig. 4C and 4E, similarly DRS UV-Vis spectra (Fig. 7 A, 7 B) of heterogeneous catalysts shows absorbance at similar wavelength (nm) as given in Fig. 3B and 3C. The catalytic activity, unfortunately, reduced after every run, and lastly, almost no catalytic activity was observed in the fourth catalytic run. Rapid decrease in catalytic activity is due to the leaching of the active species, especially with the use of peroxide as reported by Sheldon [18].

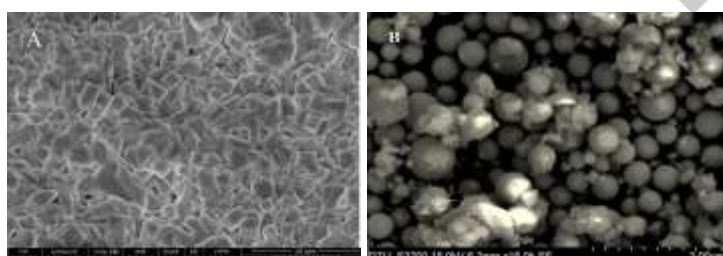


Figure 6 SEM after fourth catalytic run
(A) $(\text{NH}_4)_3[(\text{CuComplex})(\text{PW}_{12}\text{O}_{40})]$
(B) $(\text{NH}_4)_3[(\text{CuComplex})(\text{PMo}_{12}\text{O}_{40})]$

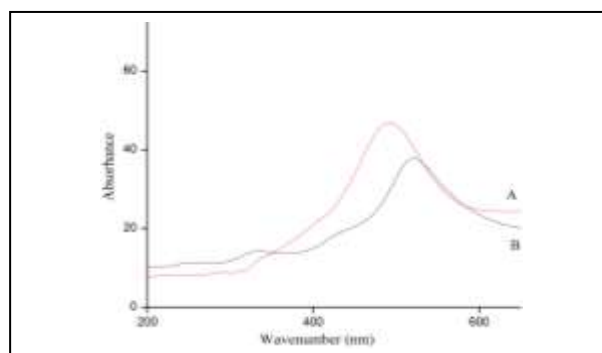
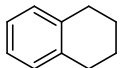



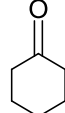
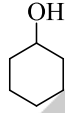
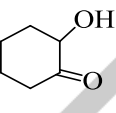
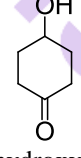
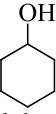
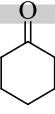
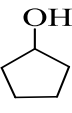
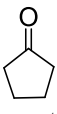


Figure 7 DRS UV-Vis after fourth catalytic run
(A) $(\text{NH}_4)_3[(\text{CuComplex})(\text{PW}_{12}\text{O}_{40})]$
(B) $(\text{NH}_4)_3[(\text{CuComplex})(\text{PMo}_{12}\text{O}_{40})]$

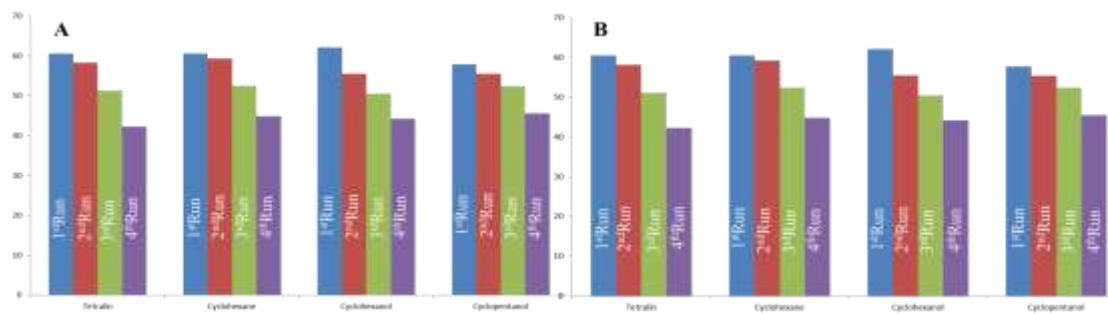
TABLE 1

| S. No. | Substrate | Product | Conversion % | Selectivity% | | | | Time (hr) | |
|--------|--|--|--|------------------------|------------------------|------------------------|-----------------------|-----------------------|--------------------|
| | | | | (A) | (B) | (C) | (D) | | |
| (i) |  1,2,3,4-tetrahydronaphthalene | (A)  3,4-dihydronaphthalen-1(2H)-one | (B)  1,2,3,4-tetrahydronaphthalen-1-ol | 58.84 ⁽ⁱ⁾ | 87.03 ⁽ⁱ⁾ | 12.96 ⁽ⁱ⁾ | | 5 ⁽ⁱ⁾ | |
| | | | | 62.02 ⁽ⁱⁱ⁾ | 89.98 ⁽ⁱ⁾ | 10.02 ⁽ⁱⁱ⁾ | | 3 ⁽ⁱⁱ⁾ | |
| | | | | 60.54 ⁽ⁱⁱⁱ⁾ | 87.47 ⁽ⁱⁱⁱ⁾ | 7.59 ⁽ⁱⁱⁱ⁾ | | 3 ⁽ⁱⁱⁱ⁾ | |
| (ii) |  Cyclohexane | (A)  Cyclohexanone | (B)  Cyclohexanol | 55.04 ⁽ⁱ⁾ | 66.14 ⁽ⁱ⁾ | 12.15 ⁽ⁱ⁾ | 14.18 ⁽ⁱ⁾ | 7.53 ⁽ⁱ⁾ | 5 ⁽ⁱ⁾ |
| | | (C)  2-hydroxycyclohexanone | (D)  4-hydroxycyclohexanone | 61.54 ⁽ⁱⁱ⁾ | 71.75 ⁽ⁱⁱ⁾ | 10.25 ⁽ⁱⁱ⁾ | 8.89 ⁽ⁱⁱ⁾ | 9.11 ⁽ⁱⁱ⁾ | 4 ⁽ⁱⁱ⁾ |
| | | | | 60.14 ⁽ⁱⁱⁱ⁾ | 70.14 ⁽ⁱⁱⁱ⁾ | 11.15 ⁽ⁱⁱⁱ⁾ | 9.48 ⁽ⁱⁱⁱ⁾ | 9.23 ⁽ⁱⁱⁱ⁾ | 4 ⁽ⁱⁱⁱ⁾ |
| (iii) |  Cyclohexanol | (A)  Cyclohexanone | | 59.22 ⁽ⁱ⁾ | | | | | 4 ⁽ⁱ⁾ |
| | | | | 65.44 ⁽ⁱⁱ⁾ | | | | | 3 ⁽ⁱⁱ⁾ |
| | | | | 62.28 ⁽ⁱⁱⁱ⁾ | | | | | 3 ⁽ⁱⁱⁱ⁾ |
| (iv) |  Cyclopentanol | (A)  Cyclopentanone | | 54.61 ⁽ⁱ⁾ | | | | | 4 ⁽ⁱ⁾ |
| | | | | 60.82 ⁽ⁱⁱ⁾ | | | | | 3 ⁽ⁱⁱ⁾ |
| | | | | 57.28 ⁽ⁱⁱⁱ⁾ | | | | | 3 ⁽ⁱⁱⁱ⁾ |

Conversion% and Selectivity% shown by [CuComplex] as catalyst = (i)

Conversion% and Selectivity% shown by (NH₄)₃[(CuComplex)(PW₁₂O₄₀)] as catalyst = (ii)

Conversion% and Selectivity% shown by (NH₄)₃[(CuComplex)(PMO₁₂O₄₀)] as catalyst = (iii)



Graph1 %Conversion of substrates during 1st, 2nd, 3rd and 4th catalytic run by (A) $(\text{NH}_4)_3[(\text{CuComplex})(\text{PW}_{12}\text{O}_{40})]$ (B) $(\text{NH}_4)_3[(\text{CuComplex})(\text{PMo}_{12}\text{O}_{40})]$

CONCLUSION

The [CuComplex] which was earlier synthesized in our research group was successfully immobilized on $(\text{NH}_4)_3(\text{PW}_{12}\text{O}_{40})$ and $(\text{NH}_4)_3(\text{PMo}_{12}\text{O}_{40})$. The catalytic activity of homogeneous and both heterogenised catalysts were compared using cycloalcohols, cycloalkanes and tetralin as substrates. The heterogeneous catalyst $(\text{NH}_4)_3[\text{CuComplex}][\text{PTA}]$ and $(\text{NH}_4)_3[\text{CuComplex}][\text{PMA}]$ were reused after washing with D.D. water, methanol, diethyl ether. The catalytic activity, unfortunately, reduced after every run, and lastly, almost no catalytic activity was observed in the third catalytic run.

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