

Immobilization of Copper Complex by Phosphotungstate, Their Characterization and Application in Catalysis

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Abstract: The synthesized ternary metal complex was immobilized onto ammonium salt of phosphotungstate $(\text{NH}_4)_3(\text{PW}_{12}\text{O}_{40})$ under solvothermal condition to synthesize a new organic-inorganic hybrid $(\text{NH}_4)_3[(\text{CuComplex})(\text{PW}_{12}\text{O}_{40})]$. The synthesized metal complex and the hybrid $(\text{NH}_4)_3[(\text{CuComplex})(\text{PW}_{12}\text{O}_{40})]$ were characterized by FT-IR, CHNO elemental analysis, SEM, powder-XRD, DR UV-Vis. Hybrid was further characterized by EDX. The metal complex as well as organic-inorganic hybrid were studied for their catalytic activity in oxidative conversion of alkyl aromatic, cycloalkane and cycloalcohols. The products formed during catalysis were analyzed by gas chromatography (GC) –mass spectroscopy (MS). The heterogeneous catalyst was recycled and reused multiple times with no substantial loss of their catalytic activity. A green procedure was followed and no toxic chemicals were released during solvothermal synthesis of heterogeneous catalyst. The resulting catalytic oxidation products are valuable intermediates and are employed for various medicinal and pharmaceutical industrial synthesis.

Keywords: Homogeneous catalysis, heterogeneous catalysis, polyoxometalate, green procedure.

1 Introduction

Cyclopentanone was used to synthesize fused pyran, pyridine, thiophene derivatives which have high inhibitory effects toward some cancer cell lines [1], it is also used as a precursor for the synthesis of cyclopentobarbital. Keto derivative of 1,2,3,4-tetrahydro-naphthalene (tetralin) is 3,4-dihydronaphthalen-1(2H)-one (tetralone), this derivative is used as reactive intermediate for the synthesis of antidepressant sertraline, antihypertensive drug benazepril and insecticide carbaryl [2-4]. Cyclohexanone is also used as valuable intermediate in medicinal industries.

A lot of research papers are published for selective oxidation of alkyl aromatics, cycloalkanes and cycloalcohols to higher-added value ketones using metal complexes as homogeneous catalysts [5-9]. Various procedures have been established for the immobilization of homogeneous catalysts [10]. To synthesize heterogeneous catalysts metal complexes were immobilized onto polyoxometalates (POMs) [11,12]. As an anionic early transition metal oxide clusters POMs bear many properties that make them attractive for applications in catalytic, biological, magnetic, optical and medicinal properties [13-17]. The introduction of metal organic groups to POMs may yield materials with fascinating structures and desirable properties [18]. Heterogeneous catalysts have lot of

benefits as compared to homogeneous catalysts such as easy separation, recovery, reutilizing and stability of heterogeneous catalysts. The separation of catalyst and recyclability of catalytic system are of significant industrial interest. The heteropolyacids are environment friendly solid catalysts which offer several advantages in terms of catalytic performance, strong acidic and redox site and selectivity to particular reaction product by selective stabilization of reaction intermediates. Copper plays an important role in biological system, it act as an oxygen carrier in hemocyanins [19] and as redox center in oxidation reactions of catechol oxidase enzymes [20]. Polypyridine and phosphine based mixed-ligand copper(I) complexes appear to have significant potential for photocatalytic applications, due to their diversity in excited state [21].

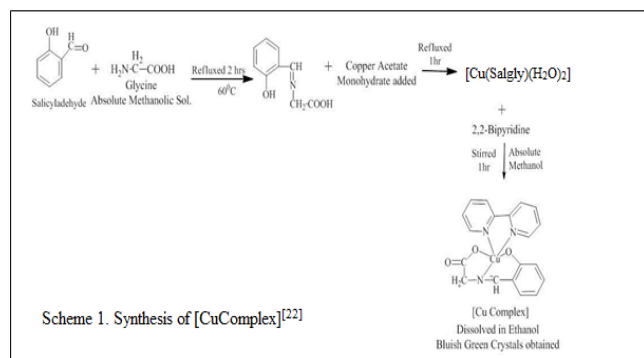
In the present work we have synthesized [CuComplex] (Scheme 1) according to the procedure as described by P.A.N. Reddy et.al., and then immobilized this [CuComplex], onto the surface of ammonium salt of phosphotungstate $(\text{NH}_4)_3(\text{PW}_{12}\text{O}_{40})$, thus synthesizing a new organic-inorganic hybrid $(\text{NH}_4)_3[(\text{CuComplex})(\text{PW}_{12}\text{O}_{40})]$. The [CuComplex] and organic-inorganic hybrid were studied for their catalytic

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activity in the oxidation of alkyl aromatic, cycloalkane and cycloalcohols with green oxidant H_2O_2 . The products obtained by catalysis, are valuable intermediates and used in the manufacture of final products in various dyes, agrochemical, pharmaceutical, medicinal industries.

2 Experimental

Copper acetate monohydrate, salicylaldehyde, glycine, 2,2-bipyridine, phosphotungstic acid were purchased from Sigma Aldrich and used without further purification. IR spectra were recorded in KBr pellets with a Nicolet170 SXFT-IR spectrophotometer in the $4000\text{--}500\text{ cm}^{-1}$ region. Nova Nano FE-SEM 450 (FEI) is coupled to EDAX detector for measuring the elemental composition of materials. Room temperature magnetic data were recorded for polycrystalline samples using a PPMS VersaLab cryostat. Diamagnetic corrections were made using Pascal's constants. Thermo Scientific TSQ 8000 Gas Chromatograph - Mass Spectrometer was used for product analysis.



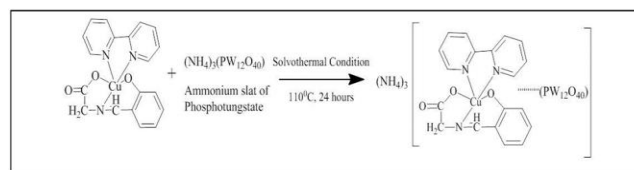
Synthesis of Organic Inorganic Hybrid $(\text{NH}_4)_3[(\text{CuComplex})(\text{PW}_{12}\text{O}_{40})]$:

Firstly, $[\text{Cu}(\text{salgly})(\text{H}_2\text{O})_2]$ was synthesized according to the procedure as described by P.A.N. Reddy et al. [22]. $[\text{CuComplex}]$ $\text{C}_{19}\text{H}_{23}\text{N}_3\text{O}_7\text{Cu}$ (%) (Mol. wt. 468.95) C, 48.54; H, 4.96; N, 8.82. Found (%) C, 48.68; H, 4.90; N, 8.98%. FT-IR (KBr): 3377, 1730, 1637, 1570, 1492, 1363, 1279, 1169, 773 cm^{-1} .

The $[\text{CuComplex}]$ shows no weight loss in the temperature range of $100\text{--}200^\circ\text{C}$ which suggest that in the complex no co-ordinated water molecule is retained. After synthesizing $[\text{CuComplex}]$, ammonium salt of phosphotungstate $(\text{NH}_4)_3(\text{PW}_{12}\text{O}_{40})$ was synthesized by adding ammonium hydroxide solution, with constant stirring, to aqueous solution of PWA (1mmole), pH 7 was maintained, pH was monitored by pH meter. By evaporation on water bath excess ammonia was removed and absolute ethanol was added in excess 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. $(\text{NH}_4)_3(\text{PW}_{12}\text{O}_{40})$ 1 mmole was added to $[\text{CuComplex}]$ (1mmole) solution in absolute methanol

(10ml) and stirred for 1 hour. The solution mixture was constantly stirred for 1 hour and then transferred to a sealed teflon reactor and heated at 110°C for 24 hours (Scheme 2). After 24 hours of constant heating at an autogenous pressure the reactor was cooled down to room temperature, the hybrid was collected, filtered and washed with double distilled water.

Thus green colored solid powder product of $(\text{NH}_4)_3[(\text{CuComplex})(\text{PW}_{12}\text{O}_{40})]$ was obtained. Elemental analysis calculated for $(\text{NH}_4)_3[(\text{CuComplex})(\text{PW}_{12}\text{O}_{40})]$ $\text{C}_{19}\text{H}_{23}\text{CuN}_3\text{O}_{47}\text{W}_{12}$ (%) (Mol. wt. 3369.12) C, 6.77; H, 1.05; N, 2.49; O, 22.32 Found (%) C, 6.80; H, 0.98; N, 1.27. IR spectra (KBr): 527, 590, 750, 810, 890, 949, 990, 1082 cm^{-1} . Ammonium salt of phosphotungstate $(\text{NH}_4)_3(\text{PW}_{12}\text{O}_{40})$ was also kept under similar solvothermal condition and characterized by FT-IR, powder-XRD.

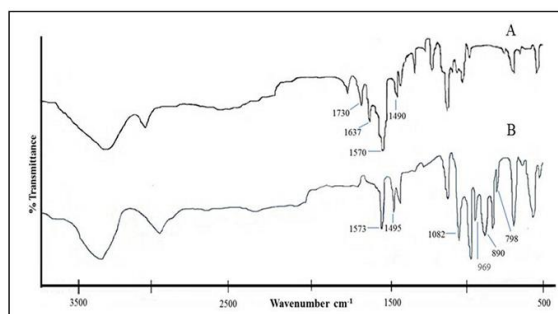


Scheme 2. Synthesis of heterogeneous catalyst

3 Result and Discussion

The characteristic IR band in [fig. 1(A)] at 1637 cm^{-1} ($\text{C}=\text{O}$) for $[\text{CuComplex}]$ disappeared in $(\text{NH}_4)_3[(\text{CuComplex})(\text{PW}_{12}\text{O}_{40})]$ because possibly the oxygen atom of $\text{C}=\text{O}$ has been attached to $(\text{NH}_4)_3(\text{PW}_{12}\text{O}_{40})$.

IR bands as shown in [Figure 1(B)] at 798 cm^{-1} ($\nu_{\text{asym}}\text{W-O-W}$), 890 cm^{-1} ($\nu_{\text{asym}}\text{W-O-W}$), 969 cm^{-1} ($\nu_{\text{asym}}\text{W-O}$) indicate that Keggin type structure was retained. The presence of these characteristic bands along with 3442 cm^{-1} , 1589 cm^{-1} , 1495 cm^{-1} indicate positive interaction between $[\text{CuComplex}]$ and $(\text{NH}_4)_3(\text{PW}_{12}\text{O}_{40})$.



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

The DRS UV-Vis spectrum of $[\text{CuComplex}]$ and $(\text{NH}_4)_3[(\text{CuComplex})(\text{PW}_{12}\text{O}_{40})]$ as shown in [fig. 2(A), (B)] represents the absorption band in the region of 514 nm to 533 nm, for $[\text{CuComplex}]$ and the hybrid appear in the same region, showing almost no change in the co-

ordination geometry of Cu ion in the complex and in the hybrid. UV-Vis band is significant because it provides information about the geometry of the metal complex. Room temperature magnetic moment μ_{eff} was found to be 1.82 which is close to spin only value expected for low symmetry ligand field suggesting a $\{d_{x^2-y^2}\}$ ground state. The [CuComplex] shows distorted square pyramidal-trigonal bipyramidal geometry which remains in the hybrid.

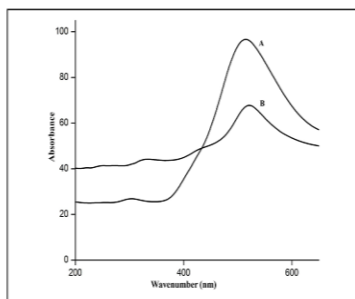


Figure 2 DR UV-Vis. spectra of (A) [CuComplex] (B) $(\text{NH}_4)_3[(\text{CuComplex})(\text{PW}_{12}\text{O}_{40})]$

The powder-XRD pattern of $(\text{NH}_4)_3[(\text{CuComplex})(\text{PW}_{12}\text{O}_{40})]$ shows reflection around $2\theta = 9^\circ$, which represents that metal complex was immobilized by $(\text{NH}_4)_3(\text{PW}_{12}\text{O}_{40})$, since Keggin type of structure was maintained in the hybrid [23]. Minor shift in 2θ values of the hybrid as compared to [CuComplex] may be due to incorporation of complex into polyoxometalate structure.

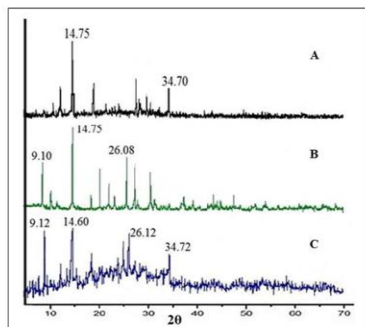


Figure 3 Powder XRD of (A) [CuComplex] (B) $(\text{NH}_4)_3(\text{PW}_{12}\text{O}_{40})$ (C) $(\text{NH}_4)_3[(\text{CuComplex})(\text{PW}_{12}\text{O}_{40})]$

SEM images clearly show the drastic change in the surface morphology of the hybrid as compared to [CuComplex] and $(\text{NH}_4)_3(\text{PW}_{12}\text{O}_{40})$ which indicates immobilization of complex onto the surface of $(\text{NH}_4)_3(\text{PW}_{12}\text{O}_{40})$, thus forming a new hybrid with different surface morphology. SEM micrographs of [CuComplex] and $(\text{NH}_4)_3[(\text{CuComplex})(\text{PW}_{12}\text{O}_{40})]$ is shown in (fig. 4 B, 4 C). SEM image of $(\text{NH}_4)_3(\text{PW}_{12}\text{O}_{40})$ (fig. 4 A) was taken when it was kept under similar solvothermal condition as $(\text{NH}_4)_3[(\text{CuComplex})(\text{PW}_{12}\text{O}_{40})]$.

Through EDX analysis (Fig. 5) the presence of all elements that were expected to be present in the hybrid

was confirmed with the formula, $(\text{NH}_4)_3[(\text{CuComplex})(\text{PW}_{12}\text{O}_{40})]$. The EDX analysis of hybrid shows that the stoichiometric ratio of Cu atom to W atom is 1 Cu atom per 12 W atoms, in $(\text{NH}_4)_3[(\text{CuComplex})(\text{PW}_{12}\text{O}_{40})]$, thus we can conclude that one Keggin unit ($\text{PW}_{12}\text{O}_{40}$) is successfully combined with one [CuComplex] unit.



Figure 4 SEM Images of (A) $(\text{NH}_4)_3(\text{PW}_{12}\text{O}_{40})$ (B) [CuComplex] (C) $(\text{NH}_4)_3[(\text{CuComplex})(\text{PW}_{12}\text{O}_{40})]$

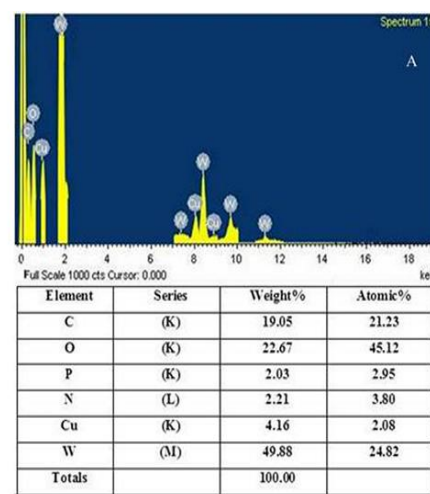
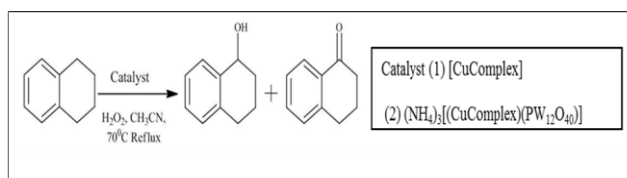


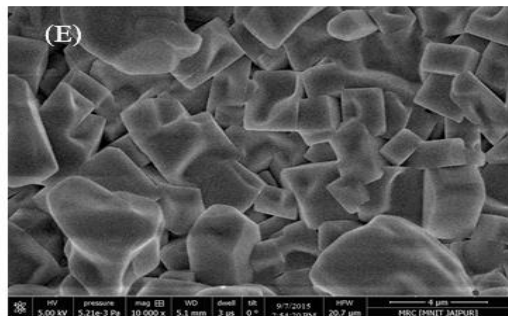
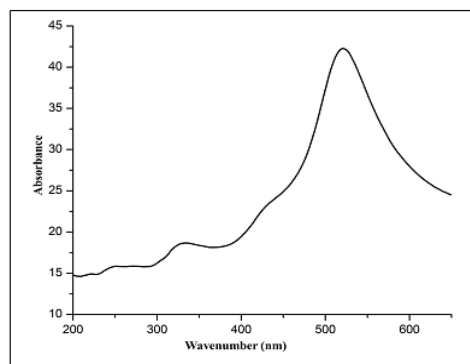
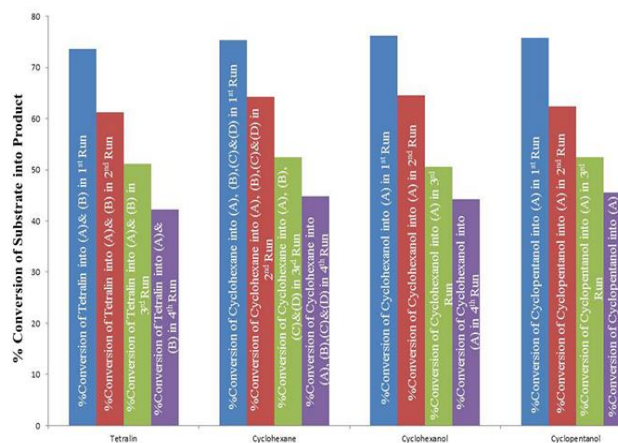
Figure 5 EDX of $(\text{NH}_4)_3[(\text{CuComplex})(\text{PW}_{12}\text{O}_{40})]$

3.1 Catalytic Evaluation

The catalytic activity of both the homogeneous and heterogeneous catalysts were compared under similar catalytic condition and these catalyst were used to catalyze the oxidation reaction of 1,2,3,4-tetrahydronaphthalene (tetralin), cyclohexane and cycloalcohols. Green oxidizing agent i.e., hydrogen peroxide of 30% strength, was used as an oxidant and acetonitrile as solvent. The catalytic experiment was refluxed at 70°C . 0.1 mmole of catalyst, 1ml of substrates and 2 ml of H_2O_2 were added to 5ml of acetonitrile, the reaction mixture was stirred and refluxed. After the completion of catalytic reaction the reaction mixture was diluted with D.D. water (25 ml), the products and substrates were extracted with CH_2Cl_2 (4X5 ml). The products obtained after catalysis were washed several times. The catalytic activity was monitored by gas chromatography. The products were confirmed and identified by mass spectroscopy. The conversion percent of



Scheme 3. Showing catalytic conversion of tetralin into desired product

Figure 6 SEM Images of $(\text{NH}_4)_3[(\text{CuComplex})(\text{PW}_{12}\text{O}_{40})]$ after fourth catalytic runFigure 7 DR UV-Vis of $(\text{NH}_4)_3[(\text{CuComplex})(\text{PW}_{12}\text{O}_{40})]$ after fourth catalytic runGraph 1
Conversion% of substrates to products by $(\text{NH}_4)_3[(\text{CuComplex})(\text{PW}_{12}\text{O}_{40})]$ catalyst

S. No.	Substrate	Product	Conversion %	Selectivity%	Time (hr)
(i)	1,2,3,4-tetrahydronaphthalene	(A) 1,2,3,4-tetrahydronaphthalen-1(2H)-one	58.84 ⁽ⁱ⁾	81.97 ⁽ⁱ⁾	5 ⁽ⁱ⁾
		(B) 1,2,3,4-tetrahydronaphthalen-1-ol	73.56 ⁽ⁱⁱ⁾	90.12 ⁽ⁱⁱ⁾	3 ⁽ⁱⁱ⁾
(ii)	Cyclohexane	(A) Cyclohexanone	60.04 ⁽ⁱ⁾	68.22 ⁽ⁱⁱ⁾	5 ⁽ⁱ⁾
		(B) Cyclohexanol	75.30 ⁽ⁱⁱ⁾	10.59 ⁽ⁱⁱ⁾	4 ⁽ⁱⁱ⁾
(iii)	Cyclohexanol	(A) Cyclohexanone	59.22 ⁽ⁱ⁾	100 ⁽ⁱⁱ⁾	4 ⁽ⁱ⁾
		(B) 2-hydroxycyclohexanone	76.15 ⁽ⁱⁱ⁾	100 ⁽ⁱⁱ⁾	3 ⁽ⁱⁱ⁾
(iv)	Cyclopentanol	(A) Cyclopentanone	42.61 ⁽ⁱ⁾	100 ⁽ⁱⁱ⁾	4 ⁽ⁱ⁾
		(B) 4-hydroxycyclohexanone	75.78 ⁽ⁱⁱ⁾	100 ⁽ⁱⁱ⁾	3 ⁽ⁱⁱ⁾

Table 1
% Conversion and Selectivity shown by [CuComplex] as catalyst = (i)
% Conversion and Selectivity shown by $(\text{NH}_4)_3[(\text{CuComplex})(\text{PW}_{12}\text{O}_{40})]$ as catalyst = (ii)

the substrates into desired products and selectivity shown by the catalysts [CuComplex] and $(\text{NH}_4)_3[(\text{CuComplex})(\text{PW}_{12}\text{O}_{40})]$ is given in Table(1).

The heterogeneous catalyst was collected, washed with D.D. water, methanol, diethyl ether and reused after every catalytic run. The catalytic activity of $(\text{NH}_4)_3[(\text{CuComplex})(\text{PW}_{12}\text{O}_{40})]$, reduced slightly after every run and almost no catalytic activity was observed after the fourth catalytic run. The decrease in catalytic activity is due to the leaching of the active species, especially with the use of peroxide according to Sheldon [24]. (Fig. 6, 7) represent the DRUV-Vis spectra and SEM image of heterogeneous catalyst after fourth catalytic run. The absorption band of $(\text{NH}_4)_3[(\text{CuComplex})(\text{PW}_{12}\text{O}_{40})]$ in (Fig.7) is in the same wavelength region with very minute shift which proves that there is no significant change in coordination geometry of heterogeneous catalyst. The SEM image of $(\text{NH}_4)_3[(\text{CuComplex})(\text{PW}_{12}\text{O}_{40})]$ in (Fig. 7, 4 C) shows similar surface morphology which proves that the Keggin phase remains intact of heterogeneous catalyst even after fourth catalytic run. The catalytic activity for the percentage conversion of the substrates into their respective products by heterogeneous catalyst during first, second, third and fourth run are graphically shown in Graph (1).

A separate blank catalytic experiment one without using

oxidant (H_2O_2) and other without using both the catalyst was carried out, under similar conditions but no measurable products were obtained.

4 Conclusion

The [CuComplex] was successfully immobilized on $(\text{NH}_4)_3(\text{PW}_{12}\text{O}_{40})$. The catalytic activity of homogeneous and both heterogeneous catalysts were compared using cycloalcohols, cycloalkanes and tetralin as substrates. The heterogeneous catalyst $(\text{NH}_4)_3[(\text{CuComplex})(\text{PW}_{12}\text{O}_{40})]$ was 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 after the fourth catalytic run.

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