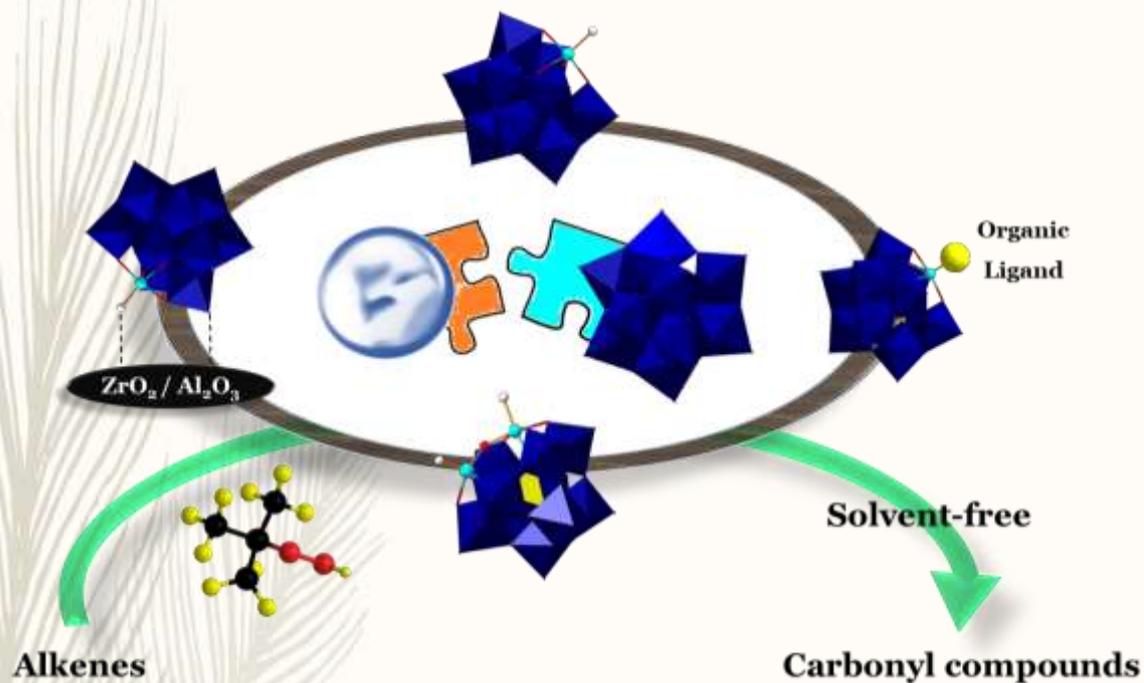


Summary of thesis entitled

*Copper substituted Phosphotungstates:
Design, Characterization and Catalytic Activity*



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Introduction

Polyoxometalates (POMs) are early transition metal oxygen anion clusters, with metals in their higher oxidation state like W(VI), Mo(VI), V(V). They are of significant importance as they possess a wide variety of applications in many areas such as structural chemistry, analytical chemistry, surface chemistry, medicine, electrochemistry, photochemistry and catalysis. They are promising green catalysts as they possess a unique set of physicochemical properties, intrinsic multifunctionality. Of all the different types of POMs, Keggin type phosphotungstates are the most widely used because of their high stability, high acidity, ease of synthesis, environmentally benign nature and finally their ability to be modified at molecular level.

The modification of parent phosphotungstates can lead to the development of new generation catalysts with enhanced properties of acidity, redox potential and stability. The acidic and redox properties of POMs can be controlled at a molecular level, and can be predominantly done in three ways: (i) Removal of M=O unit from the Keggin unit can lead to the formation of lacunary Polyoxometalate (LPOM); (ii) Transition metals can be substituted in the lacuna forming transition metal substituted Polyoxometalate (TMSPOMs) (iii) supporting on various supports and (iv) functionalization [1, 2].

Removal of one, two or three addenda atoms or M's give rise to mono-, di-, or tri-lacunary phosphotungstates with molecular formulae $[PW_{11}O_{39}]^{n-}$, $[PW_{10}O_{36}]^{n-}$ and $[PW_9O_{34}]^{n-}$ respectively. Further substitution with other transition metals give rise to mono-, di- or sandwich type Transition Metal Substituted Phosphotungstates (TMSPs), $[PW_{11}M'O_{39}]^{n-}$, $[PW_{10}M'_2O_{38}]^{n-}$ and $[P_2W_{18}M'_3O_{68}]^{n-}$ respectively. Due to the structural diversity as well as the unique electronic properties, TMSPs are of potential importance from the view point of catalysis.

Amongst the various TMSPs, those based on Mn, Co, Fe, Ni and Ru are of great interest as catalysts for various organic transformations, especially oxidation reactions. At the same time, very few reports are available in art for copper substituted POMs, even though it is of great value as copper has unique redox properties, relatively inexpensive and low toxic nature. Also, our group has been working on transition metal substituted polyoxometalates using metals like Mn, Fe, Co, Ni and Ru. As an extension, it was thought of interest to use copper metal to design TMSPs and note the characteristics and catalytic activities of the same.

The greatest disadvantage of catalysts in bulk form is their low surface area, which reduces the efficiency of the catalyst [3]. Moreover, homogeneous catalysts always have the drawback of reusability as they cannot be easily be recycled. In order to overcome these drawbacks, anchoring of catalytic materials on various supports via dative, covalent, acid-basic, or electrostatic interactions has emerged as an upcoming research area. POMs anchored to various supports have received increasing attention as they can undergo fast reversible multi-electron redox transformations under mild conditions. Use of different supports like mesoporous silica, zirconia, zeolites, and alumina to immobilize POMs have been explored for various organic transformations.

Further, tailoring and synthesis of Functionalized (organic-inorganic hybrid) materials constructed from distinctive building blocks represents an outstanding research area in various fields of chemistry. Incorporation of organic substructures into inorganic oxide framework provides a powerful method for structural modification and synthesis of novel organic-inorganic hybrid materials. This combines the unique features of both the organic and inorganic components [4, 5].

TMSPs have unique co-ordination geometries, variable oxidation states and possess the ability to co-ordinate with organic ligands. In TMSPs, the transition metal is coordinated with five oxygen atoms from the POM while the sixth coordination site is occupied by an aqua ligand. This aqua ligand is labile and

can be replaced by an organic moiety. Hence they are the most suitable for functionalization. The various advantages of functionalized TMSPs are: (i) Activation of surface oxygen; (ii) Increases POMs reactivity; (iii) Provide structural and spectroscopic model for substrate binding to have better catalytic activity and (iv) form a class of multifunctional oxidation catalysts that display selective recognition of substrates and provide higher selectivity.

The structure and properties obtained from such materials depend on the nature of both the components and can be mainly of two classes depending upon nature of the interaction between the organic and inorganic components: Class I – where no covalent bonds are shared between the organic and the inorganic moieties. Only electrostatic interactions, hydrogen bonds, or van der Waals interactions are involved and Class II – in which, the organic and inorganic moieties are linked via strong covalent or ionic-covalent bonds. In each of the above cases, the organic moiety may be present in the role of counter-cation, or simply as an attachment with POM, or act as an electron donor.

Four basic strategies have been explored for the synthesis of functionalized material based on POMs as shown in figure 1.

(I) Coordination competition. This approach consists of lacunary POMs (LPOMs) as ligands. These LPOMs react with organic metal complexes through coordination competition to form new POMs coordinated metal complexes.

(II) Terminal modification. This route involves modification of the POMs surface by substituting terminal O atoms of POMs with organic species. Generally, such kind of synthesis was carried out in organic solvents

(III) In situ synthesis. This strategy consists of self-condensation of the simple inorganic and organic units (sometimes pre-synthesized POMs/TMSPOMs). Most of the successful syntheses using this route were carried out under hydrothermal conditions

(IV) Ligand substitution. This method consists of TMSPOMs as starting materials, in which, five oxygen atoms of the POM coordinate with the transition

metal from five sides, while an aqua ligand occupies the sixth coordination site. Thus aqua ligand is labile and can be replaced by any organic group or even by organometallic groups

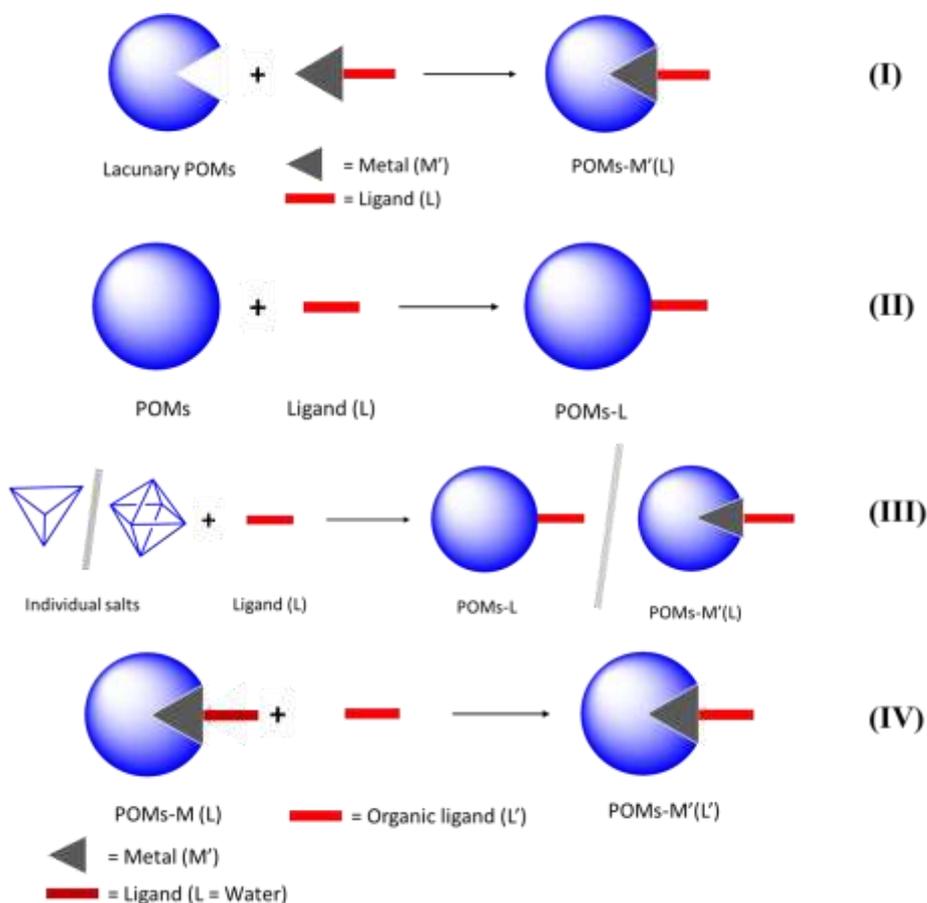


Figure 1. Strategies for synthesis of functionalized materials

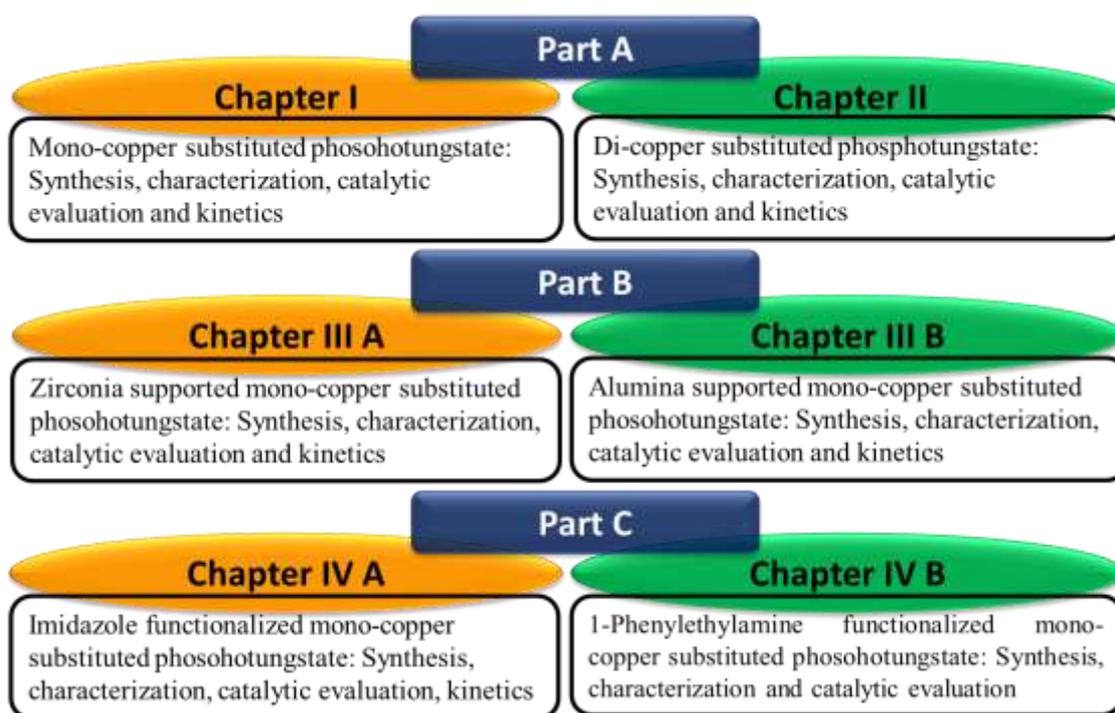
On these lines, the following objectives were proposed.

Objectives of the work

- To tune the properties of phosphotungstates (PW_{12}) at the molecular level by synthesizing mono- as well as di-copper substituted phosphotungstates.
- To characterize the synthesized materials using EDX, TG-DTA, FT-IR, ^{31}P NMR, UV-Vis, ESR, Powder XRD and CV.
- To use the synthesized materials as catalysts for the liquid phase oxidation of styrene and cis-cyclooctene under mild conditions.

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- To support the synthesized material on different supports (ZrO_2 and Al_2O_3), characterize and evaluate the catalytic activities of the same for oxidation of styrene and cis-cyclooctene, and to identify the better support.
 - Further, to synthesize and characterize hybrid inorganic-organic materials using normal as well as chiral organic moieties [Imidazole, (S)-1-phenyl ethylamine], and use the same as catalysts for oxidation of alkenes.
 - To study the recyclability and reusability of the different catalysts.
 - To study the chemical kinetics and mechanism for each catalytic system.
 - Finally, to generate a comparative study between all catalysts, and thereby choose the best catalyst from each series.

The work is divided into three parts comprising two chapters each



Part A: Copper substituted phosphotungstate

Chapter I describes the synthesis and characterization of mono-copper substituted phosphotungstate ($PW_{11}Cu$). Along with the traditional one-pot technique, a green and sustainable microwave technique has also been developed. Structure as well as similarity were confirmed by various spectral techniques.

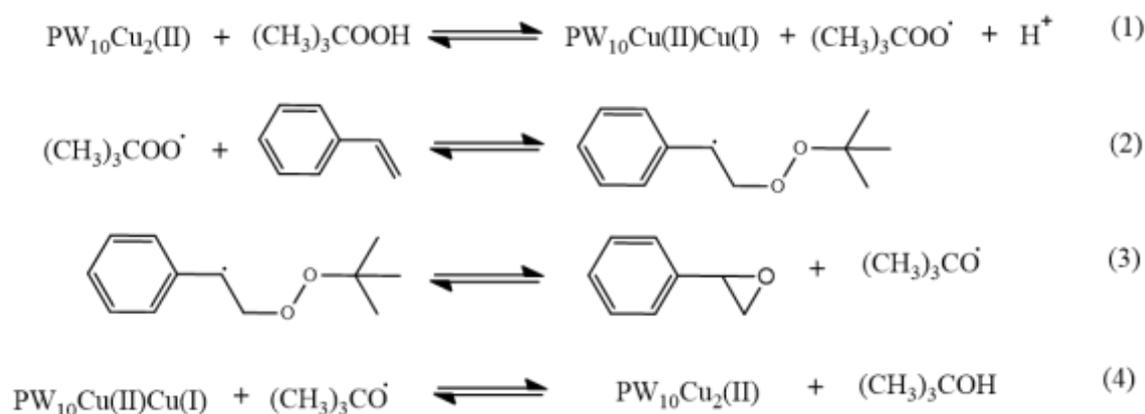
This was followed by a detailed study to explore the catalytic activity of the synthesized complexes for the oxidation of styrene and cis-cyclooctene using 3°-butyl hydroperoxide (TBHP) as the oxidant. The conditions for maximum conversion and selectivity of the desired products have been optimized by varying different reaction parameters. **54% conversion along with 59% selectivity for benzaldehyde and 30% selectivity for styrene-oxide were obtained. The reaction conditions were optimized as follows: catalyst amount - 15 mg (Active amount of Cu - 0.27 mg); styrene - 10 mmol; reaction time - 16 h; TBHP - 2 mL; reaction temperature - 60 °C. Similarly, the optimized conditions for 24% conversion and 86.3% selectivity of the epoxide are: Temperature: 65 °C; amount of catalyst: 15 mg (Active amount of Cu: 0.27 mg); Cis-cyclooctene - 10 mmol; reaction time: 20 h and amount of TBHP: 2 mL.**

In order to get an insight on the role of each component in the reaction, a comprehensive kinetic study has been carried out and the order of reaction and activation energy have been determined, which indicate that the reaction is truly chemical in nature with no mass/diffusion limitation. All the experimental data helped us to propose a possible mechanism for the reaction in which reduction of Cu(II) leads to decomposition of TBHP to initiate the radical mechanism. Finally, the catalyst was regenerated and reused thrice without any significant loss in % conversion as well as % selectivity and may be reused for further cycles.

Chapter II describes the synthesis of di-copper substituted phosphotungstate ($PW_{10}Cu_2$) by one-pot as well as microwave techniques and its characterization. A detailed study to explore the use of synthesized complex for

the oxidation of styrene and cis-cyclooctene with TBHP as the oxidant has been carried out under mild reaction conditions, by varying different parameters. 78% conversion along with 29% selectivity for benzaldehyde and 52% selectivity for styrene-oxide were obtained. The conditions were optimized as follows: catalyst amount - 15 mg (Active amount of Cu - 0.51 mg); reaction time - 8 h; TBHP - 2 mL; reaction temperature - 60 °C. Similarly, the conditions optimized for 34% conversion of cis-cyclooctene and 81% selectivity for the epoxide were as follows: catalyst amount - 15 mg (Active amount of Cu - 0.51 mg); reaction time - 20 h; TBHP - 2 mL; reaction temperature - 60 °C. Further, a detailed kinetics and mechanistic study has also been carried out and high E_a values indicated that the reactions are truly chemically driven and not limited to mass transfer/diffusion.

Based on detailed ESR, CV studies as well as iodometric titrations the following mechanism was proposed for the oxidation reaction [7].



Scheme 1. Proposed mechanism for oxidation of styrene using TBHP

A comparison of the catalytic activities of PW_{11}Cu as well as $\text{PW}_{10}\text{Cu}_2$ showed double conversion and higher selectivity for the epoxide, at lower activation energies for the di-copper substituted one, indicating the role of copper as the active species and POM unit as the stabilizing agent.

Table 1. Comparison of catalysts.

Reaction	Catalyst	% conversion	% selectivity		Activation energy (E _a)
			Aldehyde/ Ketone	Epoxide	
Oxidation of styrene ^a	PW ₁₁ Cu	44	63	21	64.81 kJmol ⁻¹
	PW ₁₀ Cu ₂	83	35	33	57.64 kJmol ⁻¹
Oxidation of cis-cyclooctene ^b	PW ₁₁ Cu	18	15	85	105.88 kJmol ⁻¹
	PW ₁₀ Cu ₂	34	19	81	82.57 kJmol ⁻¹

^a Catalyst amount: 15 mg; Time: 12 h; temp: 60 °C; TBHP: 2 mL.

^b Catalyst amount: 15 mg; Time: 20 h; temp: 60 °C; TBHP: 2 mL.

Part B: Supported mono copper substituted phosphotungstate

Chapter III is divided into two sections.

Chapter III A describes the supporting of $PW_{11}Cu$ to hydrous zirconia by wet impregnation technique, and retention of individual structures as well as chemical interactions were confirmed by various spectral characterizations. The synthesized material was evaluated for oxidation of styrene and cis-cyclooctene. **44% conversion along with 44% selectivity for benzaldehyde and 37% selectivity for styrene-oxide were obtained. The optimized conditions are as follows: catalyst amount - 25 mg (active species - 6.25 mg); reaction time - 16 h; TBHP - 2 mL; reaction temperature - 60 °C. Similarly, the conditions optimized for 35% conversion of cis-cyclooctene and 89% selectivity of epoxide were as follows: catalyst amount - 50 mg (active amount of $PW_{11}Cu$ - 12.5 mg); reaction time - 24 h; TBHP - 1.5 mL and temperature - 60 °C.** The supported catalyst displayed better conversion as well as selectivity for epoxides with lower E_a as compared to $PW_{11}Cu$, thus showcasing its superiority. Further, the active species did not leach out of the support, and the catalyst exhibited true heterogeneity under the reaction conditions.

Chapter III B describes the successful implementation of wet impregnation technique to support $PW_{11}Cu$ on to neutral alumina and further characterizations confirmed intact structure, homogeneous dispersion as well as strong chemical interactions between $PW_{11}Cu$ and the support. The synthesized material was evaluated for oxidation of styrene and cis-cyclooctene. **63% conversion along with 60% selectivity for benzaldehyde and 19% selectivity for styrene-oxide were obtained for styrene oxidation. The optimized conditions are as follows: catalyst amount - 25 mg (active species - 6.25 mg); reaction time - 16 h; TBHP - 2 mL; reaction temperature - 60 °C.** $PW_{11}Cu/Al_2O_3$ showed better catalytic activity compared to $PW_{11}Cu$ for the oxidation of styrene with higher selectivity for benzaldehyde and substantially higher TON. Unfortunately, cis-cyclooctene did not show good conversion and hence, was not continued. This was attributed

to the nucleophilicity of the substrates as well as the presence of strong Lewis acid sites in the form of aluminum metal.

Table 2. Comparison of catalysts for oxidation of styrene.

Catalyst	% conversion	% selectivity		Activation Energy (E _a)
		Benzaldehyde	Styrene oxide	
PW ₁₁ Cu/ZrO ₂	44	44	37	40.31 kJmol ⁻¹
PW ₁₁ Cu/Al ₂ O ₃	63	60	19	69.30 kJmol ⁻¹

Catalyst amount - 25 mg (active amount of PW₁₁Cu - 6.25 mg); Time - 16h; TBHP - 2 mL;
Temp - 60 °C

Part C: Inorganic-organic hybrid materials based on mono-copper substituted Phosphotungstate

Chapter IV is divided into two part

Chapter IV A describes the functionalization of PW₁₁Cu with imidazole by ligand substitution technique and characterized in detail. The spectral studies shows that the POM retains its structure even after introduction of imidazole. The NMR and IR studies indicate the formation of N→Cu dative bond. A comparison with the physical mixture further confirmed the same.

The synthesized material was used as catalyst for solvent free oxidation of styrene and cis-cyclooctene, and various reaction conditions were optimized. 91% conversion of styrene with 45% selectivity of benzaldehyde and 41% selectivity of styrene-oxide were obtained. **The conditions were optimized as follows: Time-10 h; Catalyst amount - 15 mg; Temperature - 60 °C; Amount of TBHP - 2 mL. Similarly, the conditions for 47% conversion of cis-cyclooctene and 85% selectivity of the epoxide were optimized as follows: Catalyst amount - 25 mg; Time - 20 h; Amount of TBHP - 1.5 mL and Temperature - 60 °C.** Catalytic evaluation and kinetic studies showed considerable increase in conversion and selectivity of epoxide compared to unfunctionalized complex at considerably lower Ea.

Table 3. Comparison of substrates

Substrate	% conversion	% selectivity		Activation energy (Ea, kJ/mol)
		Epoxide	Aldehyde/ Ketone	
Styrene	91	42	45	32.66
Cis-cyclooctene	10	93	7	82.18

^a Catalyst amount: 15 mg; Time: 12h; temp: 60 °C; TBHP: 2 mL

Chapter IV B describes the functionalization of $PW_{11}Cu$ by *S*-1-phenylethylamine ($PW_{11}Cu$ -*S*-PEA), in an attempt to induce chirality into the catalyst. FT-IR and ^{13}C MAS NMR confirmed the formation of $N \rightarrow Cu$ dative bond, while optical rotation studies and CD spectroscopy affirmed the chirality of the material. The material was evaluated for its activity for asymmetric oxidation of styrene, and with a view to obtain high *enantiomeric excess*, different oxidants were used. While TBHP gave high selectivity for epoxide, the best *ee* was obtained with molecular oxygen. This is attributed to the inability of oxygen to undergo self-disproportionation, as a result of which, it forms the reactive intermediate with the chiral catalyst to give high enantioselectivity.

Table 4. Effect of oxidants

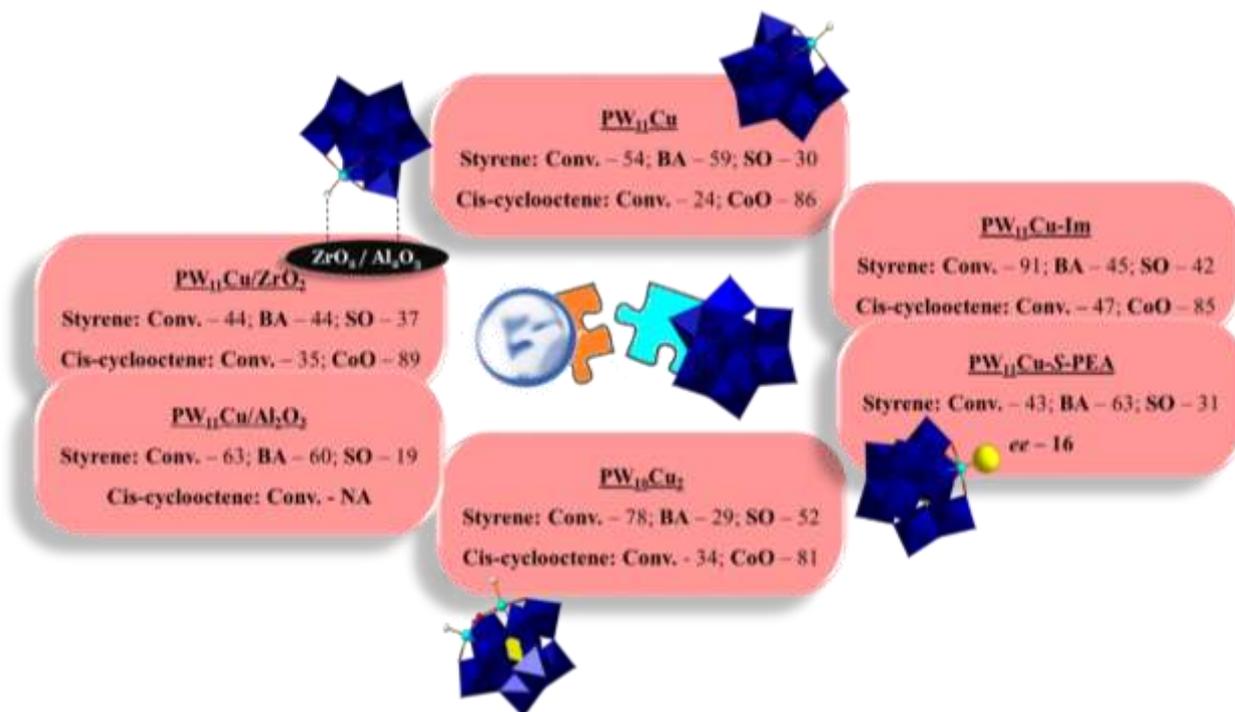
Oxidant	% conversion	% selectivity			<i>ee</i>
		Benzaldehyde	<i>R</i> -styrene oxide	<i>S</i> -styrene oxide	
^a TBHP	35	40	25	28	6
^b H ₂ O ₂	N.A.	-	-	-	-
^c O ₂	43	63	13	18	16

^a Catalyst amount – 20 mg, Time – 12 h; TBHP – 2 mL; Temp – 60 °C

^b Catalyst amount – 20 mg, Time – 12 h; Styrene:H₂O₂ – 1:3; Temp – 80 °C

^c Catalyst amount – 20 mg, Time – 12 h; Styrene – 100 mmol; TBHP – 0.2 mL; Temp – 80 °C

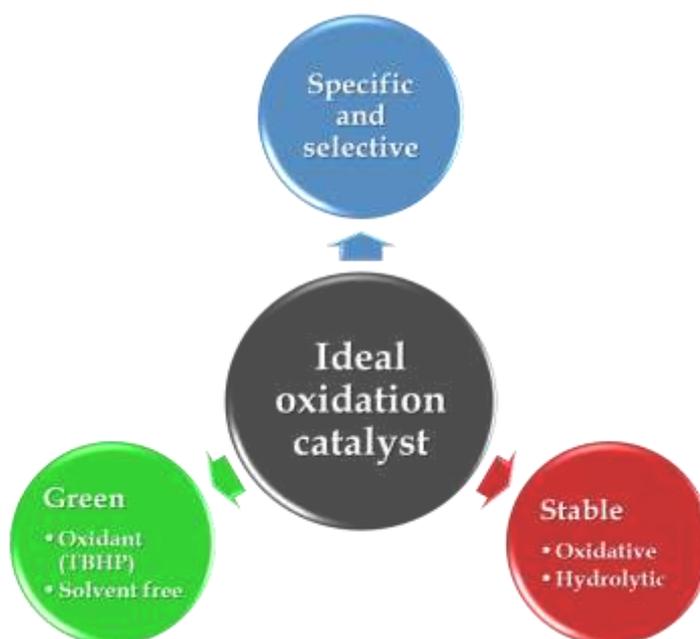
Main Conclusions



- Successful designing of catalytic materials based on copper substituted phosphotungstates and modifications via supporting as well as functionalization
- Due to presence of Lewis acid sites, alumina supported PW₁₁Cu gave higher conversion of styrene and selectivity for benzaldehyde but was unsuccessful in oxidizing cis-cyclooctene. This signifies that the role of support is indeed very substantial.
- Functionalization is the best technique to enhance the catalytic activity of PW₁₁Cu for oxidation reactions.

Novelty of the work

- Microwave technique was introduced for the first time to synthesize copper substituted phosphotungstates, the scope for which can be extended to other POM based materials
- Designing of different Cu-POM based materials was successfully accomplished and further modifications of different types, viz., supporting as well as functionalization was also achieved.
- The entire catalytic evaluation study was carried out under solvent-free conditions, using TBHP alone, as a green oxidant. Further, we were able to develop a flexible oxidation system, in which the major product could be selected based on the choice of the chemist.
- We were successful in inducing chirality in POM, which can open doors for the synthesis of hybrid, chiral 4th generation catalysts, especially for asymmetric oxidation.



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