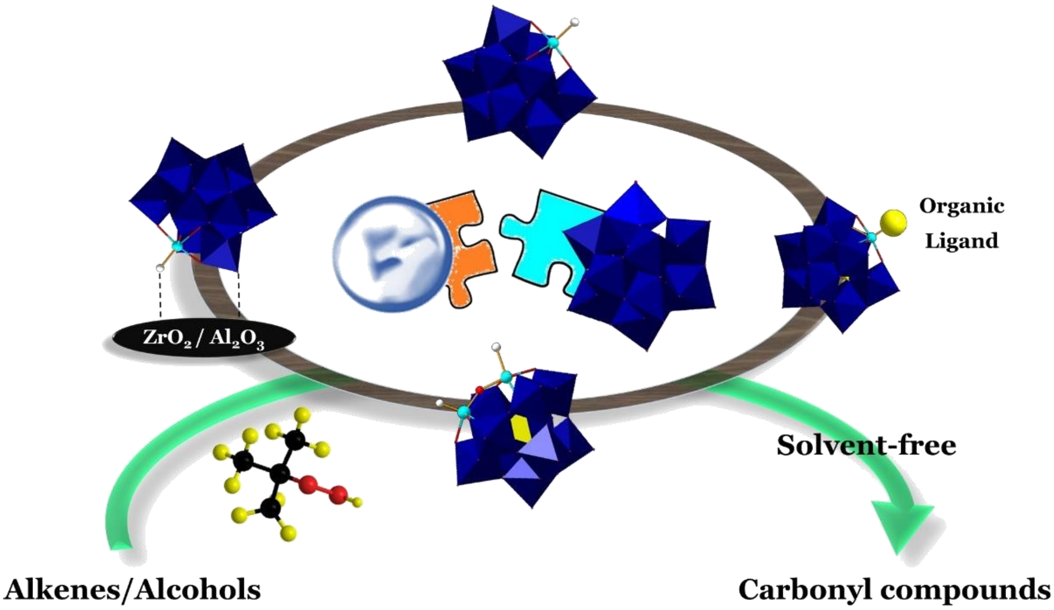
Synopsis of thesis entitled

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 multielectron 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 iono-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

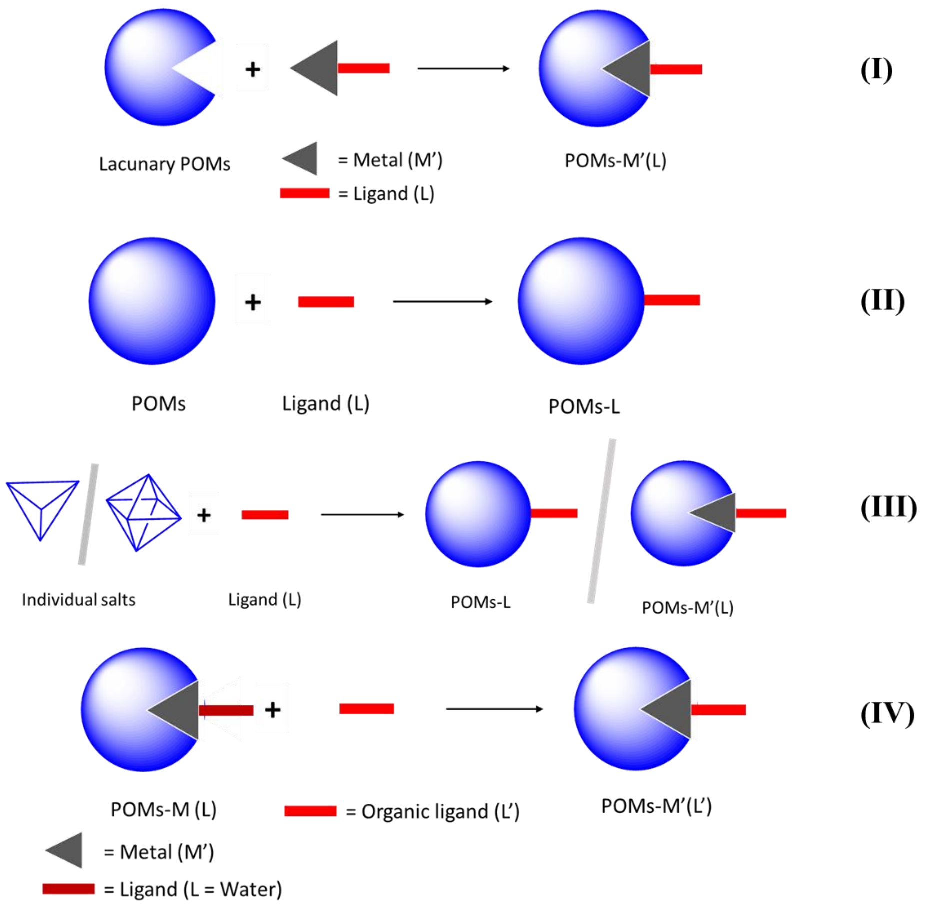


Figure 1. Strategies for synthesis of functionalized materials

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, TGA-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 alkenes and alcohols.
- To support the synthesized material on various supports (ZrO_2 and Al_2O_3) and characterize the same using various techniques
- To use the supported catalysts for oxidation of alkenes and alcohols, and to identify the better support.
- Further, to synthesize and characterize hybrid inorganic-organic materials using normal as well as chiral organic moieties [Imidazole, R-(-)- and S-(+)-1-phenyl ethylamine and R-(-)-cyclohexylethylamine] , and use the same as catalysts for various organic transformations.
- To carry out kinetic and mechanistic studies for each reaction, thereby understand the role of each component of the reaction.
- To study the recyclability and reusability of the different catalysts
- Finally, to generate a comparative study between all catalysts, and thereby choose the best catalyst amongst all

The work is divided into three parts

Part A: Copper substituted phosohotungstate

- Mono-copper substituted phosohotungstate
- Di-copper substituted phosphotungstate

Part B: Supported mono-copper substituted phosphotungstate

- Hydrous ZrO_2
- Neutral Al_2O_3

Part C: Inorganic-Organic hybrid materials based on mono-copper substituted phosphotungstate

- Imidazole
- 1-Phenyl ethylamine

Part A: Copper substituted phosohotungstate

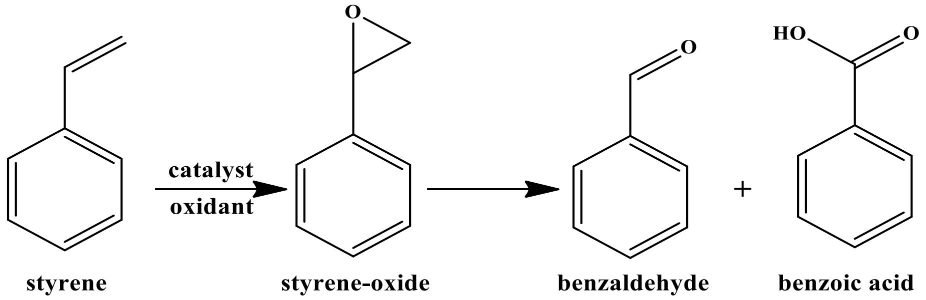
Chapter 1 describes the synthesis and characterization of mono-copper substituted phosphotungstate as well as its catalytic evaluation for oxidation of alkenes using TBHP oxidant.

2.88 g (1 mmol) of $H_3PW_{12}O_{40}.nH_2O$ was dissolved in 10 mL of water and the pH of the solution was adjusted to 4.8 using supersaturated NaOH solution. The solution was heated to 90^{o}C with stirring. To this hot solution, 0.17 g (1 mmol) of $CuCl_2.2H_2O$ dissolved in minimum amount of water, was added. The solution was air refluxed at 90^{o}C for 90 minutes with constant stirring. This was filtered hot, then 0.5 g solid CsCl was immediately added. The resulting greenish blue precipitates were filtered, dried at room temperature and designated as $RPW_{11}Cu$.

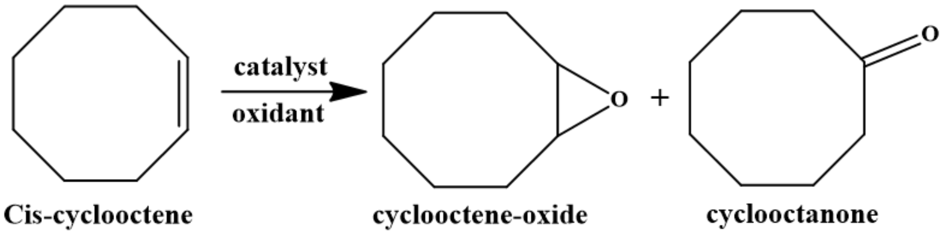
In addition to this, a novel microwave technique was developed for the synthesis of the same, in which instead of the reflux, the mixture of $H_3PW_{12}O_{40}.nH_2O$ and $CuCl_2.2H_2O$ was microwaved for 30 s at intervals of 10, 5, 5, 5 and 5 s. further addition of CsCl followed by filtration gives greenish blue precipitates designated as $MPW_{11}Cu$.

The complex obtained from both the techniques have been characterized using various physico-chemical techniques like TG-DTA, ICP, FT-IR, ^{31}PNMR, UV-Visible spectrophotometry, powder XRD, ESR and Cyclic Voltammetry. FT-IR confirmed the formation of PW_{11} from the parent 12-tungstophosphoric acid, while ^{31}P NMR confirmed formation of a single isomer. ESR and UV confirmed the incorporation of Cu(II) into the lacuna in a distorted octahedron geometry, and powder XRD showcased the better textural properties of microwave product over the reflux product.

The catalytic activity for the synthesized materials was evaluated for oxidation of styrene and cis-cyclooctene.



Benzaldehyde is one of the most valuable compounds with widespread applications in perfumery, dye and agro chemical industries. It is second only to vanillin amongst aromatic compounds used in cosmetics and flavour industry. Similarly, epoxides like styrene oxide are widely used as raw materials in synthesis of resins, paints, surfactants and intermediates for various organic reactions.



Similarly, cyclooctene-oxide can be converted to 1,2-diol, which can further be used to synthesize C8 carboxylic acids. And cyclooctanone is used as an intermediate for various industrially important compounds; it is also used in total synthesis of the natural product (-)-vulgarolide, which is used as a flavoring agent.

Initially, a preliminary study was carried out using H_2O_2 as the oxidant. Since there was no significant conversion (2%), TBHP was used as the oxidant and various parameters such as reaction temperature, catalyst amount, reaction time and amount of TBHP were optimized. In order to study the effect of time, the reaction was carried out at different times, and the results are presented in Figure 2a. With increase in time from 8 to 16 h, there is a steady increase in %

conversion. At the same time, the selectivity of benzaldehyde decreases and the selectivity for styrene-oxide increases. But when the reaction proceeds further to 20 h, the selectivity of both benzaldehyde as well as styrene oxide, decreases. It is well known that styrene-oxide is the intermediate that is formed during the oxidation of styrene, and the decrease in selectivity of the products may be attributed to complete oxidation of styrene to benzaldehyde and further to benzoic acid. Hence, reaction time was optimized at 16 h.

The reaction was then carried out at different catalyst amounts and the results are presented in figure 2b**.** It can be seen that with increase in catalyst amount from 5 mg to 15 mg, there is a steady increase in conversion of styrene. However, the selectivity of benzaldehyde initially decreases up to 10 mg and then increases, while the selectivity of styrene oxide initially increases and then decreases. This may be because with increase in catalyst amount, the reaction tends to move forward towards completion. Beyond 15 mg, the increase in conversion as well as selectivity of benzaldehyde is negligible. Hence, 15 mg was optimized as the catalyst amount.

The amount of TBHP was then varied to study the effect of oxidant and the results are presented in Figure 2c. With increase in TBHP amount from 1 mL to 2.5 mL, there is an increase conversion and selectivity of benzaldehyde along with decrease in selectivity for styrene-oxide, which is the expected trend. Excess of TBHP would lead to increase in oxygen concentration, and this would lead to further oxidation of benzaldehyde to benzoic acid, as seen in case of 2.5 mL TBHP. Hence, 2 mL TBHP was considered optimum for the reaction.

Finally, the reaction was carried at different temperatures and the results are presented in Figure 2d. When the temperature was increased from 50^{o}C to 60^{o}C, there is an increase in conversion as well as selectivity of styrene-oxide. But on increasing temperature beyond 60^{o}C, there is a significant decrease in the selectivity of benzaldehyde as well as styrene-oxide. This may be due to the degradation of TBHP at higher temperatures, thereby resulting in polymerization of styrene. Hence, temperature was optimized at 60^{o}C.

The reaction conditions for oxidation of styrene were optimized as follows: catalyst amount – 15 mg; reaction time – 16 h; TBHP – 2 mL; reaction temperature – 60 ^{o}C. It is necessary to bring to notice that in the present systems, optimization has been carried out keeping in priority the selectivity of styrene-oxide. These conditions may be varied by the chemist depending on the requirement of the products.

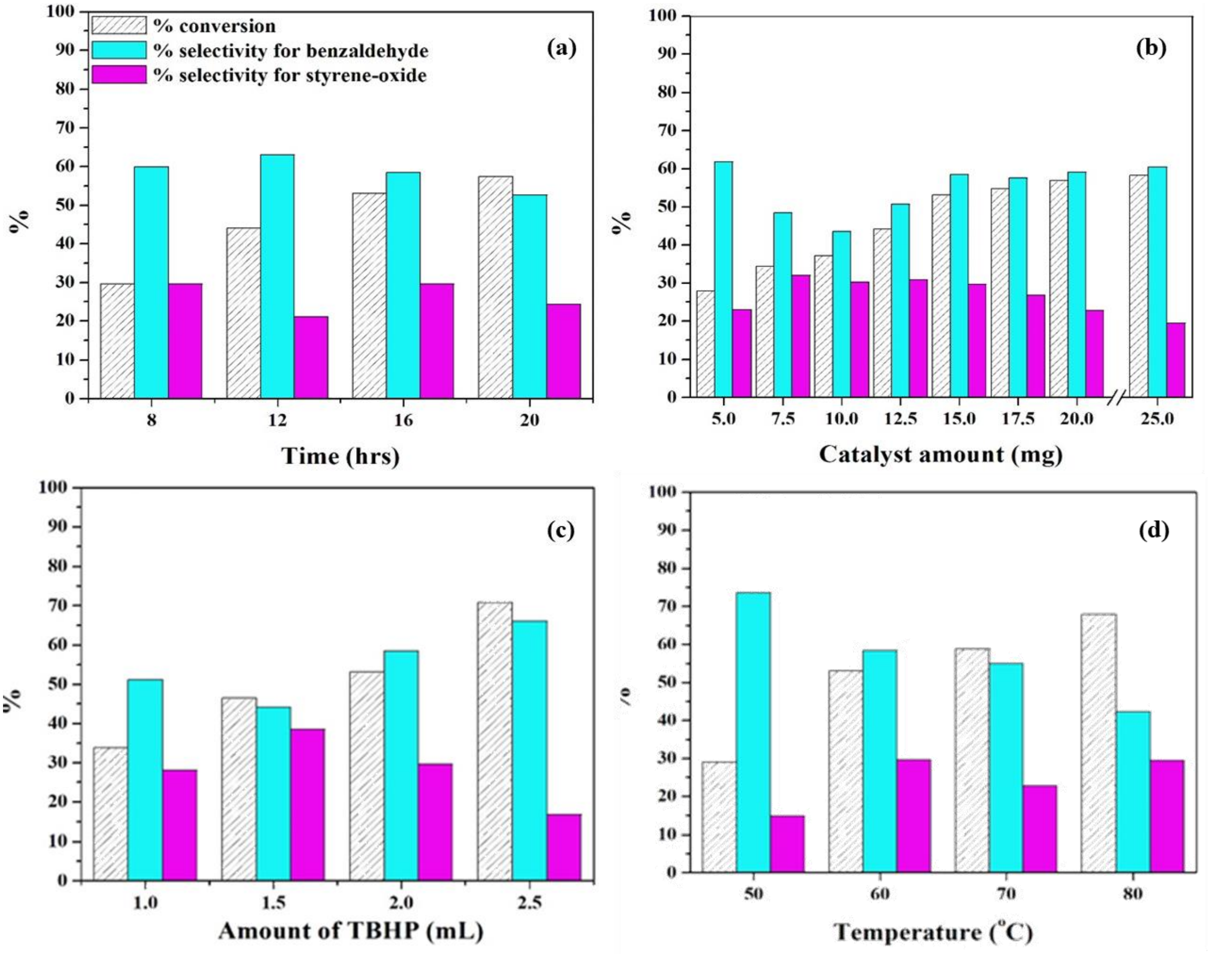


Figure 2. Optimization of parameters for oxidation of styrene (a) Effect of time (Catalyst amount – 15 mg; temp – 60 ºC; TBHP – 2 mL); (b) Effect of catalyst amount (Time – 16 h; temp – 60 ºC; TBHP – 2 mL); (c) Effect of amount of TBHP (catalyst amount – 15 mg; temp – 60 ºC; time – 16 h); (d) Effect of temperature (catalyst amount – 15 mg; time – 16 h; TBHP – 2 mL)

Stability of the catalyst during the course of the reaction is of utmost importance as leaching of active species would make the catalyst unappealing. Hence, the catalyst was tested leaching of copper. Absence of characteristic absorption peaks for Cu(II) in the UV-Vis spectrum of reaction mixture confirmed that the catalyst does not leach during the course of the reaction.

To check the heterogeneity of the catalyst, the reaction was first run for 12 h, after which the catalyst was filtered out from the reaction mixture. The reaction was then allowed to proceed further up to 16 h. No change in the conversion as well as selectivity of the products (Table 1) indicates that the catalyst is truly heterogeneous in nature.

Table 1. Test for heterogeneity

Catalyst	% conversion	% selectivity	
		Benzaldehyde	Styrene-oxide
$PW_{11}Cu$ (12 h)	44	63	21
Filtrate (16 h)	45	64	22

Catalyst amount: 15 mg; Temp: 60ºC; TBHP: 2 mL.

Control experiments were carried out to understand the role of each component on the reaction. Experiments were performed without the catalyst, with $CsPW_{11}$ and $CuCl_2$, and the results are presented in table 2.

Table 2. Control Experiments

Catalyst	% conversion	% selectivity		Turn Over Number (TON)
		Benzaldehyde	Styrene-oxide	
$^{a}CsPW_{11}$	4	88	5	-
$^{b}CuCl_2$	51	74	15	1208
$^{c}PW_{11}Cu$	54	59	30	1260

[a] Catalyst amount-13.16 mg; TBHP – 2 mL; Temperature–60ºC; Time–16h.
[b] Catalyst amount-0.72 mg (active amount of Cu-0.27 mg); TBHP – 2 mL; Temperature–60ºC; Time–16h.
[c] Catalyst amount-15 mg (active amount of Cu-0.27 mg); TBHP – 2 mL; Temperature–60ºC; Time–16h

Control experiments were carried out with $CsPW_{11}$, $CuCl_2$ and $PW_{11}Cu$ and the results are presented in Table 2. Higher conversion (54%) and higher selectivity for epoxide are obtained when $PW_{11}Cu$ is used as catalyst. This may be attributed to the synergic effect between Cu and PW_{11}. Also, it is well known that polyoxometalate moiety can stabilize lower oxidation state of transition metals. Here, Cu(II) is reduced to Cu(I) during the course of the reaction, which is stabilized by PW_{11}. This in turn is able to stabilize the reactive intermediate species that is formed, and hence, higher selectivity for the epoxide is seen.

Characterization of regenerated catalyst

The regenerated catalyst was characterized by UV, ESR and FT-IR spectroscopy. The UV-Vis spectra of the regenerated catalyst showed the characteristic peak for Cu^{2+} at 867 nm. This suggests that copper does not leach into the reaction mixture. The ESR spectra of fresh and recycled $MPW_{11}Cu$ are shown in the figure 11. It can be clearly seen that both the spectra are similar, as the five line spectrum is obtained back in the recycled $MPW_{11}Cu$ further confirming the intact structure of the catalyst. The FT-IR spectrum of Rec PWC1 shows characteristic bands at 1103, 1056, 964, 887 and 813 cm^{-1} corresponding to P–O, W=O, and

W–O–W stretching frequencies respectively. The Cu-O band can be clearly seen at 433 cm^{-1}. No significant shifting of bands clearly indicates that the catalyst does not degrade and the structural morphology of the complex remains unchanged during the course of the reaction. The slight decrease in the sharpness of the bands in recycled catalyst may be due to impurities that remain on the catalyst after recycling.

Kinetic studies

A detailed kinetic study of the reaction was carried out on order to understand the effect of each component on the rate of reaction. Experiments were carried out with different initial concentrations of styrene and TBHP, keeping the catalyst amount constant. Equation 1 establishes a relation between the individual concentration of the reactants and time.

$$\frac{2.303}{(b-a)} log \frac{a(b-x)}{b(a-x)} = kt \qquad (1)$$

where 'a' is the initial concentration of styrene, 'b' is the initial concentration of TBHP and 'x' is the concentration at time t. A plot of log[(b-x)/(a-x)] versus time shows a straight line (Figure 3a), indicating that the reaction is first order with respect to styrene and TBHP, individually. Similarly, an experiment was then carried out keeping the concentration of styrene as well as TBHP the same. Equation 2 establishes a relation between the concentration and time.

$$\frac{1}{(a-x)} = kt + c \qquad (2)$$

where 'a' is the initial concentrations of styrene and TBHP and 'x' is the conversion of styrene at time t. As in the previous case, a plot of 1/(a-x) versus time shows a linear relationship, (Figure 3b) indicating that the reaction follows second order overall with respect to concentration of styrene and TBHP. The effect of reaction rate with respect to catalyst concentration was studied a plot of rate constants at different catalyst concentrations and is shown in Figure 3c. When the concentration is increased from 1.545 x 10^{-3} mmol to 4.573 x 10^{-3} mmol, there is a linear increase in rate of the reaction, indicating that the reaction follows first order kinetics with respect to catalyst concentration as well [6].

As most oxidation reactions are highly sensitive to temperatures, the effect of temperature plays a very significant role. When temperature is increased from 323K to 353K, a gradual increase in the conversion of styrene is seen. Thus, 1/T shows a linear relationship with lnk, and the activation energy was evaluated using the Arrhenius equation. In a two phase reaction system like the present one, it is necessary to know that the reaction is governed by a truly chemical step and is not diffusion/mass transfer limited. Generally, the Ea of a mass transfer limited reaction is known to be about 10-15 kJ/mol, while a truly chemical reaction has Ea value greater than 25 kJ/mol. In the present case, the significantly higher activation energy of 64.81 kJ/mol (Figure 3d) indicates that the reaction is truly governed by a chemical step and also that the catalyst has been exploited to its maximum capacity.

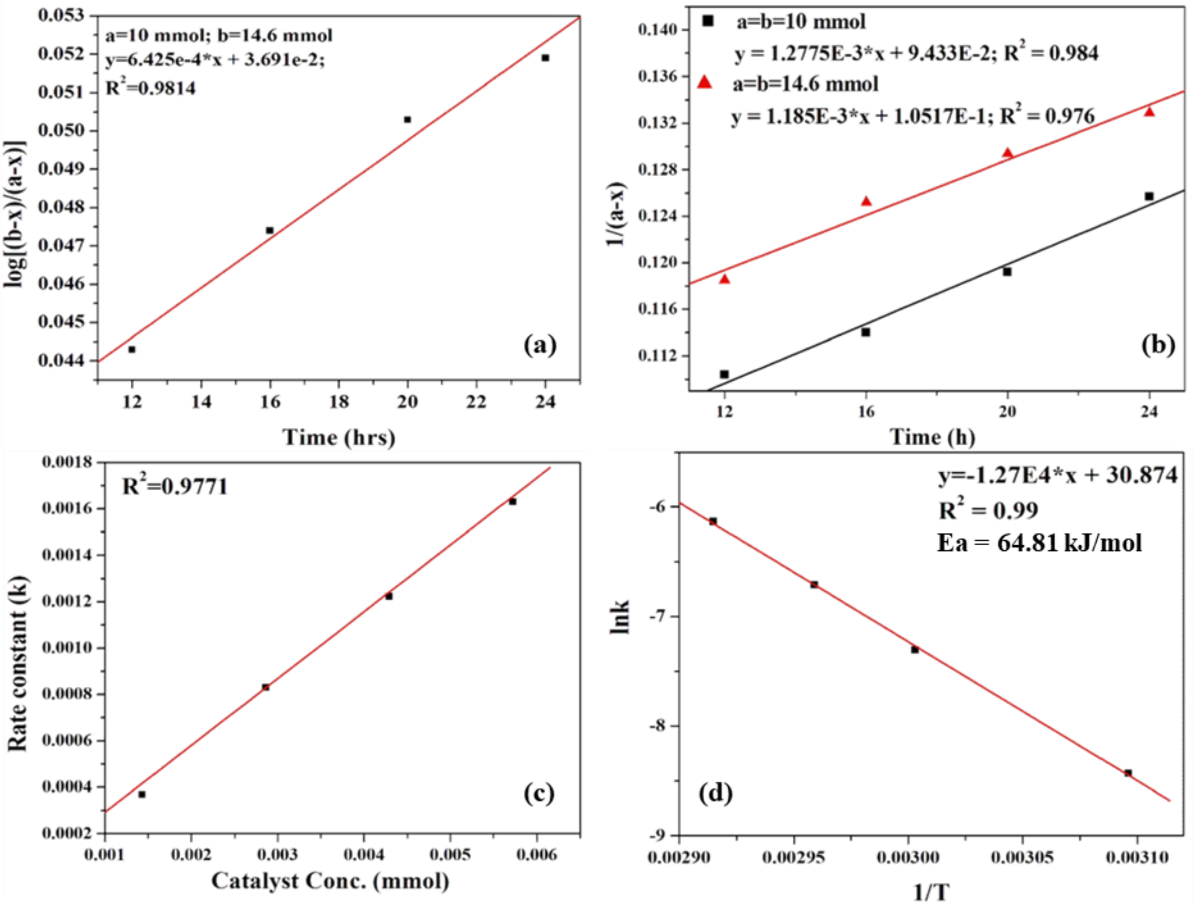


Figure 3. (a) Plot of log[(b-x)/(a-x)] versus time; (b) Plot of 1/(a-x) versus time; (c) Plot of rate of reaction versus catalyst concentration; (d) Plot for determination of activation energy

On similar lines, oxidation of cis-cyclooctene was carried out and under optimized conditions, 24% conversion and 86% selectivity for cyclooctene-oxide was obtained. The optimized conditions are: catalyst amount – 15 mg; reaction time – 20 h; TBHP – 2 mL; reaction temperature – 65 °C. Heterogeneity test confirmed that the catalysts were truly heterogeneous in nature, while radical inhibitor experiment confirmed the reaction following radical mechanism. The catalysts were recycled and reused up to three cycles without significant loss in catalytic activity. A detailed kinetic study showed first order dependence with respect to each component, individually, and an overall second order dependence.

Chapter 2 describes the synthesis and characterization of di-copper substituted phosphotungstate as well as its catalytic evaluation for oxidation of alkenes using TBHP oxidant.

Synthesis of di-copper substituted phosphotungstate by reflux as well as microwave techniques followed same procedure as mono-copper phosphotungstates, except that .340 g of $CuCl_2.2H_2O$ (2 mmol) was used and the pH set was 6.4. The reaction mixture was refluxed for 2 h. the two products obtained were designated $RPW_{10}Cu_2$ and $MPW_{10}Cu_2$ respectively.

Characterization of the synthesized complexes showed that both the synthetic routes yielded the same material, with the physical texture of microwave product being slightly better. The synthesized materials were used as catalysts for solvent free oxidation of alkenes (with focus on selectivity of epoxide) and various reaction conditions were optimized. The optimized conditions obtained were: (I) Oxidation of styrene: Time – 8 h; Catalyst amount – 15 mg; Temperature – 60 ^{0}C; Amount of TBHP – 2 mL. Under optimized conditions, 78% conversion with 29% selectivity for benzaldehyde and 52% selectivity for styrene-oxide was obtained. (II) Oxidation of cis-cyclooctene: Time – 20 h; Catalyst amount – 15 mg; Temperature – 60 ^{0}C; Amount of TBHP – 2 mL. Under optimized conditions, 34% conversion with 81% selectivity for cyclooctene-oxide was obtained.

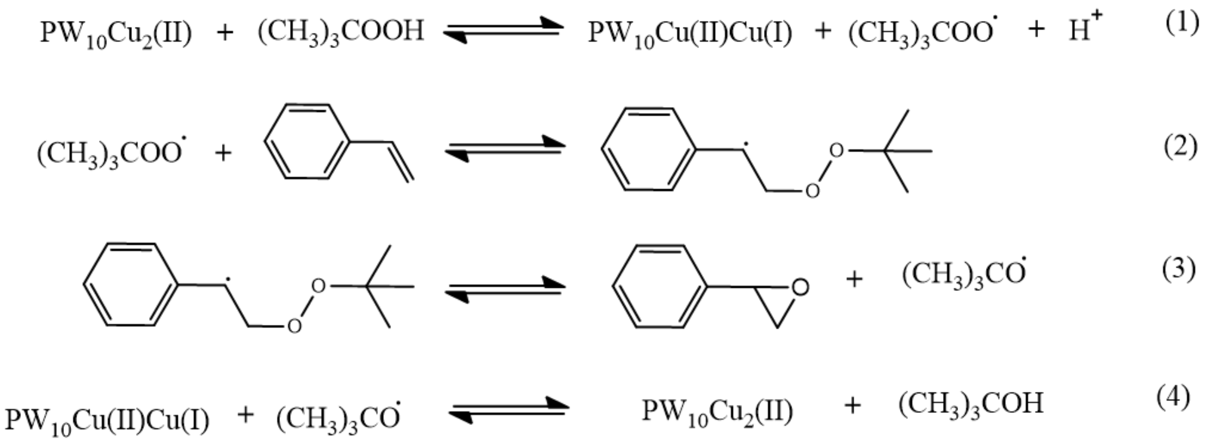
Heterogeneity test confirmed that the catalysts were truly heterogeneous in nature, while radical inhibitor experiment confirmed the reaction following radical mechanism. The catalysts were recycled and reused up to three cycles without significant loss in catalytic activity. A detailed kinetic study showed first order dependence with respect to each component, individually, and an overall second order dependence. Finally a comparative study of the activities of the two catalysts for both the reactions showed that activity in case of $PW_{10}Cu_2$ was double to that of $PW_{11}Cu$, further confirming that copper is the main active site in the catalysts. The results are presented in table 3.

Table 3. Comparison of catalysts.

Reaction	Catalyst	% conversion	% selectivity		Activation energy (Ea)
			Aldehyde/ Ketone	Epoxide	
Oxidation of styrene [a]	**$MPW_{11}Cu$**	44	63	21	64.81 $kJmol^{-1}$
	$MPW_{10}Cu_2$	83	35	33	57.64 $kJmol^{-1}$
Oxidation of cis-cyclooctene [b]	**$MPW_{11}Cu$**	18	15	85	105.88 $kJmol^{-1}$
	$MPW_{10}Cu_2$	34	19	81	21.13 $kJmol^{-1}$

[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.

The mechanism for transition metal catalyzed oxidation of olefins using TBHP has always been a matter of controversy and many mechanistic schemes have been proposed. In the present case, in order to confirm whether the reaction involves oxygen transfer or electron transfer, detailed ESR, CV studies as well as iodometric titrations were carried out. Based on the results obtained, the following mechanism was proposed [7].



Scheme 1. Proposed mechanism for oxidation of styrene using TBHP

Part B: Supported mono copper substituted phosohotungstate

Chapter 3 describes the synthesis and characterization of mono-copper substituted phosphotungstate supported on zirconia as well as its catalytic evaluation for oxidation of alkenes using TBHP oxidant.

Hydrous zirconia was synthesized using a technique previously reported by our group, while $PW_{11}Cu$ was synthesized by reflux method as mentioned earlier. 30% $PW_{11}Cu$ supported over zirconia was synthesized by wet impregnation method. To the aqueous solution of $PW_{11}Cu$ (0.3 g/30 mL), 1 g ZrO_2 was added and dried at 100 °C for 10 h and the resulting material was designated 30% $PW_{11}Cu/ZrO_2$. On similar lines, 10%, 20% and 40% $PW_{11}Cu/ZrO_2$ were prepared taking 0.1 g/10 mL, 0.2 g/20 mL and 0.4 g/40 mL aqueous solutions of $PW_{11}Cu$ respectively and designated as 10% $PW_{11}Cu/ZrO_2$, 20% $PW_{11}Cu/ZrO_2$ and 40% $PW_{11}Cu/ZrO_2$ respectively.

A preliminary catalytic reaction study showed 30% $PW_{11}Cu/ZrO_2$ to have best activity. Hence, detailed characterizations and catalytic evaluations were carried out for 30% $PW_{11}Cu/ZrO_2$. FT-IR, ^{31}P MAS NMR and TPR studies confirm the chemical interaction of $PW_{11}Cu$ with the -OH groups of ZrO_2 [8, 9]. Further, FT-IR and FT-Raman confirm the intact Keggin unit of $PW_{11}Cu$, while powder XRD confirms homogeneous dispersion of the active species on the support. The synthesized materials were used as catalysts for solvent free oxidation of alkenes (with focus on selectivity of epoxide) and various reaction conditions were optimized. The optimized conditions for oxidation of styrene were: Time – 16 h; Catalyst amount – 25 mg (6.25 mg $PW_{11}Cu$); Temperature – 60 ^{0}C; Amount of TBHP – 2 mL. Under optimized conditions, 44% conversion with 44% selectivity for benzaldehyde and 37% selectivity for epoxide were obtained. Similarly, the optimized conditions for oxidation of cis-cyclooctene are: Time – 24 h; Catalyst amount – 50 mg (12.5 mg $PW_{11}Cu$); Temperature – 60 ^{0}C; Amount of TBHP – 1.5 mL. Heterogeneity test confirmed that the catalysts were truly heterogeneous in nature, while radical inhibitor experiment confirmed the reaction following radical mechanism. The catalysts were recycled and reused up to three cycles without significant loss in catalytic activity. A detailed kinetic study for $PW_{11}Cu/ZrO_2$ catalyst showed first order dependence with respect to each component, individually, and an overall second order dependence.

Chapter 4 describes the synthesis and characterization of mono-copper substituted phosphotungstate supported on neutral alumina as well as its catalytic evaluation for oxidation of styrene using TBHP oxidant.

While neutral alumina was procured from the market, $PW_{11}Cu$ was synthesized by reflux method as mentioned in chapter 1. 30% $PW_{11}Cu$ supported over zirconia was synthesized by wet impregnation method. To the aqueous solution of $PW_{11}Cu$ (0.3 g/30 mL), 1 g Al_2O_3 was added and aged for 35 h at room temperature. This was then dried at 100 ^{o}C for 10 h and the resulting material was designated 30% $PW_{11}Cu/Al_2O_3$. On similar lines, 10%, 20% and 40% $PW_{11}Cu/Al_2O_3$ were prepared taking 0.1 g/10 mL, 0.2 g/20 mL and 0.4 g/40 mL aqueous solutions of $PW_{11}Cu$ respectively and designated as 10% $PW_{11}Cu/Al_2O_3$, 20% $PW_{11}Cu/Al_2O_3$ and 40% $PW_{11}Cu/Al_2O_3$ respectively.

A preliminary catalytic reaction study showed 30% $PW_{11}Cu/Al_2O_3$ to have best activity. Hence, detailed characterizations and catalytic evaluations were carried out for 30% $PW_{11}Cu/Al_2O_3$. FT-IR, and TPR studies indicated the chemical interaction of $PW_{11}Cu$ with the terminal oxygen of Al_2O_3. Further, FT-IR and FT-Raman confirm the intact Keggin unit of $PW_{11}Cu$ even after impregnation. Other characterizations are in progress. The synthesized materials were used as catalysts for solvent free oxidation of styrene (with focus on selectivity of epoxide) and various reaction conditions were optimized. The optimized conditions for oxidation of styrene were: Time – 16 h; Catalyst amount – 25 mg (6.25 mg $PW_{11}Cu$); Temperature – 60 ^{0}; Amount of TBHP – 2 mL. Under optimized conditions, 63% conversion was obtained, with 60% selectivity for benzaldehyde and 19% selectivity for epoxide. Heterogeneity test confirmed that the catalysts were truly heterogeneous in nature, while radical inhibitor experiment confirmed the reaction following radical mechanism. The catalysts were recycled and reused up to three cycles without significant loss in catalytic activity. A comparative study of the supported catalysts (tables 4 and 5) showed that alumina supported catalyst showed better reactivity compared to zirconia supported one.

Table 4. Oxidation of styrene over $PW_{11}Cu/ZrO_2$ as well as $PW_{11}Cu/Al_2O_3$: Comparison under optimized conditions

Catalyst	% conversion	% selectivity	
		Benzaldehyde	Styrene oxide
$PW_{11}Cu/ZrO_2$	44	44	37
$PW_{11}Cu/Al_2O_3$	63	60	19

Catalyst amount-25 mg (active amount of PW11Cu-6.25 mg); Time–16h; TBHP – 2 mL; Temp–60 ^{0}C

Table 5. Oxidation of styrene over $PW_{11}Cu/ZrO_2$ as well as $PW_{11}Cu/Al_2O_3$: Comparison with respect to similar conversion

Catalyst	% conversion	% selectivity	
		Benzaldehyde	Styrene oxide
$PW_{11}Cu/ZrO_2$[a]	50	60	27
$PW_{11}Cu/Al_2O_3$[b]	49	58	28

[a] Catalyst amount-25 mg (active amount of PW11Cu-6.25 mg); Time - 16 h; temp - 65°C; TBHP - 2 mL
[b] Catalyst amount-25 mg (active amount of PW11Cu-6.25 mg); Time–12 h; temp–60 ^{0}C; TBHP – 2 mL

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

Chapter 5 describes the synthesis and characterization of imidazole functionalized mono-copper substituted phosphotungstate as well as its catalytic evaluation for oxidation of alkenes using TBHP oxidant.

Imidazole is a pentacyclic aromatic compound, with two N coordination centres to extend structure. Also, it is a stronger ligand which may offer the possibility to replace the aqua ligand. Thus, a combination TMSPOMs and imidazole or its derivatives would resulted in hybrid materials by direct introduction of N - containing moiety into the mono-TMSPOM, with improved polarity, acidity and redox properties.

Functionalization of $PW_{11}Cu$ by imidazole was carried out by ligand substitution method. 0.35g (0.1 mmol) of $PW_{11}Cu$ was dissolved in 10 mL water by heating. 10 mg (0.1 mmol) of Imidazole was dissolved 10 mL methanol. The methanolic solution of imidazole was added drop-wise to the hot solution of $PW_{11}Cu$ while stirring. The pH was adjusted to 6.4 using NaOH. The resultant mixture was refluxed for 10 h at 90 ^{0}C, cooled, filtered and dried at 100 0C. The obtained violet coloured powder was designated as $PW_{11}Cu$-Im.

Further, to confirm the formation of a truly hybrid material, a physical mixture of the same was also synthesized by taking 0.35 g PW11Cu and 10 mg of Imidazole in a mortar and grinding them thoroughly with a pestle till fine light violet coloured powder was obtained. This material was designated $PW_{11}Cu$ + Im.

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 (with focus on selectivity of epoxide) and various reaction conditions were optimized as follows: Time – 10 h; Catalyst amount – 15 mg; Temperature – 60 ^{0}C; Amount of TBHP – 2 mL. Under optimized conditions, 91% conversion was obtained, with 45% selectivity for benzaldehyde and 42% selectivity for styrene-oxide.

Control experiments were carried out to understand the exact role of imidazole [10], and also to affirm chemical interaction between inorganic and organic moieties. It confirms the dual role of imidazole, as an initiator of the reaction, as well as a suppressor of the overall acidity of the catalyst. Catalytic studies were also used as a tool to explain the interactions between organic and inorganic component very well. Heterogeneity test confirmed that the catalyst was truly heterogeneous in nature. The catalyst was recycled and reused up to three cycles without significant loss in catalytic activity. Characterization of regenerated catalyst clearly indicated the intact structure of the compound after recycling. A detailed kinetic study for $PW_{11}Cu$-Im catalyst showed first order dependence with respect to each component, individually, and an overall second order dependence.

Chapter 6 describes the functionalization of $PW_{11}Cu$ by R- and S-1-phenylethylamine (PEA), in an attempt to induce chirality into the catalyst. 0.35g (0.1 mmol) of $PW_{11}Cu$ was dissolved in 10 mL water by heating. 0.15 mL mg (0.1 mmol) of R-PEA was dissolved 10 mL methanol. The methanolic solution of R-PEA was added drop-wise to the hot solution of $PW_{11}Cu$ while stirring. The resultant mixture was refluxed for 24 h at 80 ^{0}C, cooled, filtered and dried at 100 ^{0}C. The obtained precipitate was designated as $PW_{11}Cu$-R-PEA. On similar line, $PW_{11}Cu$-S-PEA was also synthesized and as designated.

The synthesized materials were characterized by various physico-chemical techniques as mentioned earlier and evaluated for their catalytic activity for the oxidation of styrene by varying different reaction parameters.

Summary

Environmentally benign heterogeneous catalysts were developed based on phosphotungstate and copper. Acidic and redox properties of phosphotungstate have been tuned by formation of mono- as well as di-copper substituted phosphotungstates.

A novel, green, microwave synthetic technique was successfully developed for synthesis of $PW_{11}Cu$ and $PW_{10}Cu_2$, which can be extended for other TMSPOMs

Further modifications of mono-copper substituted phosphotungstate were carried out by supporting on different supports as well as by introducing organic ligands. The synthesized catalysts were successfully characterized by various physicochemical techniques. Catalytic activity of the synthesized materials was evaluated for the solvent free flexible oxidation of alkenes and reaction conditions were optimized for best possible conversion and selectivity of desired products (epoxides). All the catalysts are recyclable and truly heterogeneous in nature. Successful regeneration of the catalysts were possible due to their heterogeneous nature and multiple recycle study showed negligible loss in catalytic activity. Detailed kinetic studies were carried out for each reaction and it was concluded that the reaction showed first order dependence for each reactant, individually, and an overall second order dependence

Modifications of $PW_{11}Cu$ by supporting or functionalization opens new avenues in the development of heterogeneous, environmentally benign catalysts and their scope can be extended to other organic transformations.

References

1. Hu Y-Y, Zhang T-T, Zhang X, Zhao D-C, Cui X-B, Huo Q-S, Xu J-Q, Dalton Trans., 2016, 45, 2562-2573
2. Khan RNN, Lv C, Zhang J, Hao J, Wei Y, Dalton Trans., 2015, 44, 4568-4575
3. Sun W, Hu J., React Kinet Mech Catal., 2016,119(1), 305-18
4. Gao Q, Li F, Sun Z, Xu L, Sun M, Dalton Trans., 2016, 45, 2422-2425.
5. Walsh JJ, Bond AM, Forster RJ, Keyes TE, Coord. Chem. Rev., 2016 306, 217-234.
6. Liang Y, Yi C, Tricard S, Fang J, Zhao J, Shen W, RSC Adv., 2015, 5, 17993-17999.
7. Hossain M.M., Huang W.-K., Chen H.-J., Wang P.-H., Shyu S.-G., Green Chem., 2014, 16, 3013–3017.
8. Liu S, Chen L, Wang G, Liu J, Gao Y, Li C, et al. J. Energy Chem., 2016, 25(1), 85-92
9. Alcañiz-Monge J, Bakkali BE, Trautwein G, Reinoso S., Appl Catal B: Environ., 2018, 224, 194-203
10. Kamata K, Sugahara K, Ishimoto R, Nojima S, Okazaki M, Matsumoto T, Mizuno N., ChemCatChem, 2014, 6, 2327-2332

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