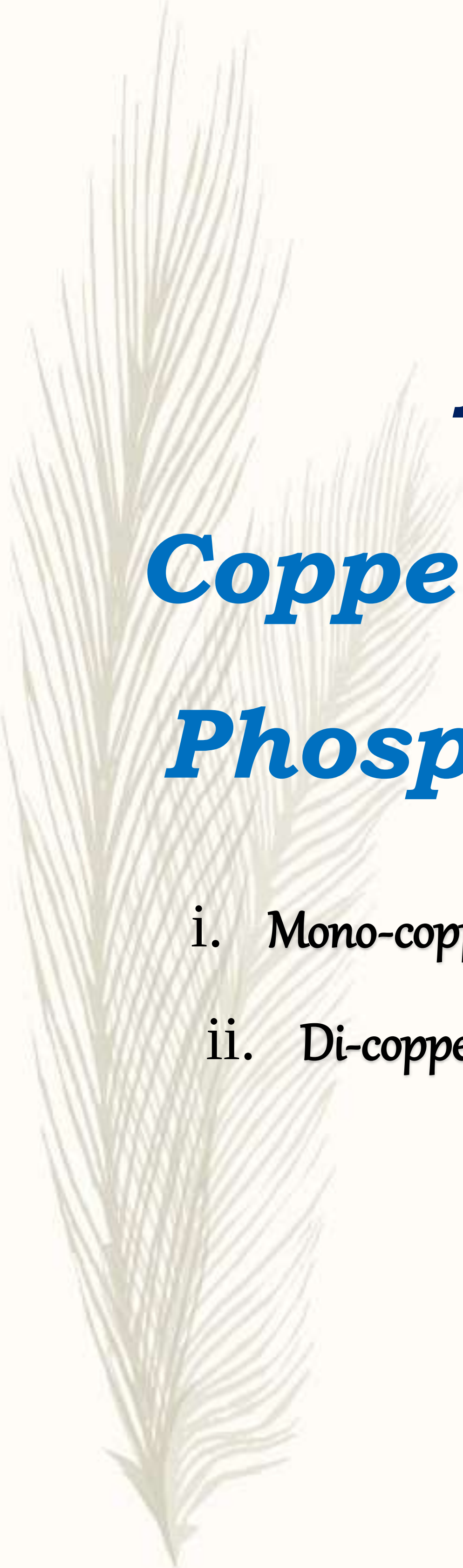
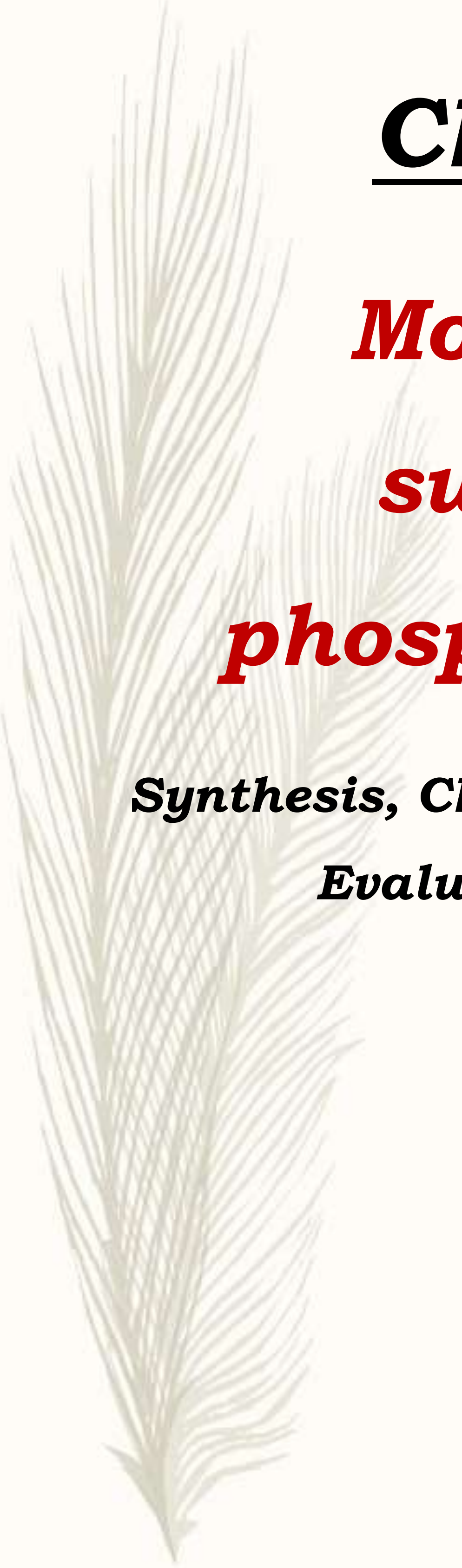


Part A

Copper substituted Phosphotungstate

i. Mono-copper substituted phosphotungstate

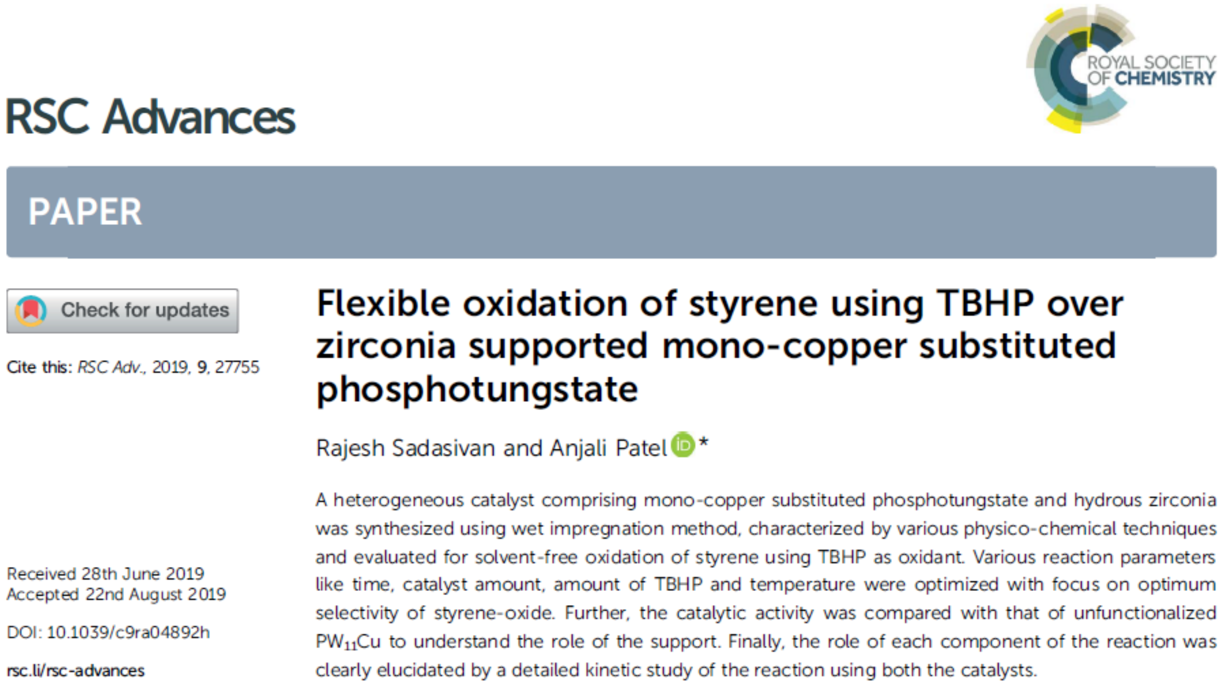
ii. Di-copper substituted phosphotungstate



Chapter 1

Mono-copper substituted phosphotungstate

Synthesis, Characterization, Catalytic Evaluation and Kinetics



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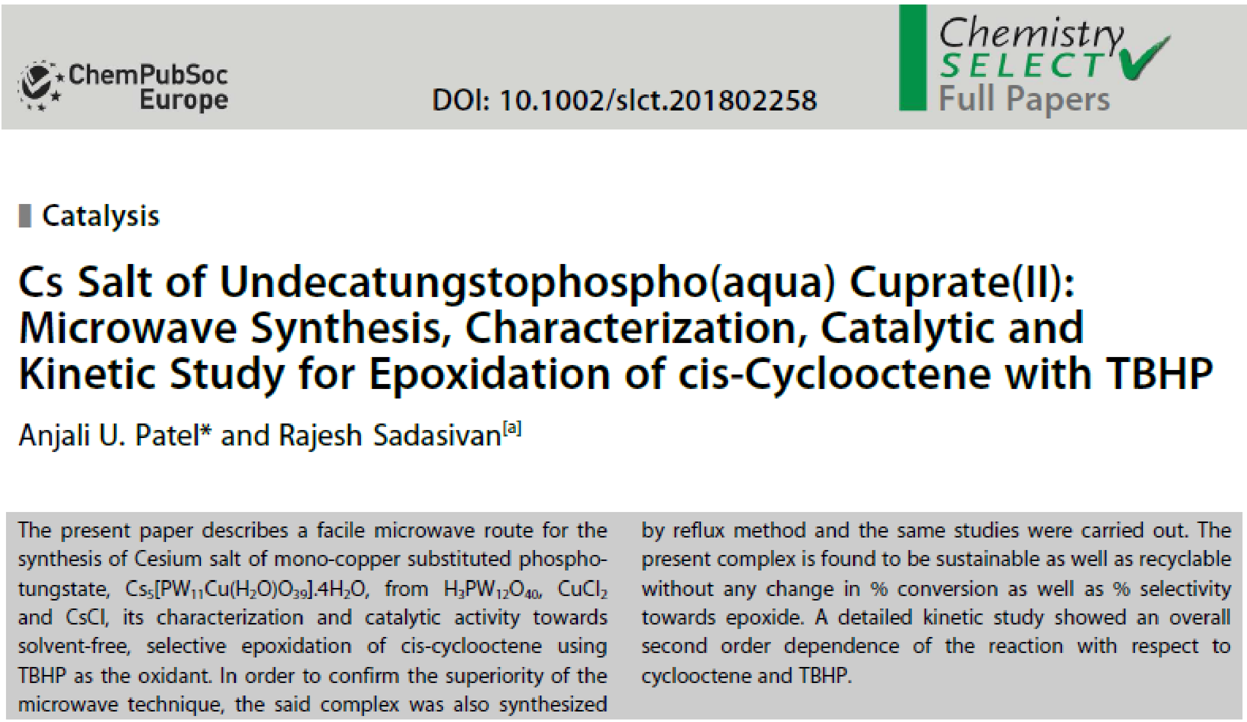
Flexible oxidation of styrene using TBHP over zirconia supported mono-copper substituted phosphotungstate

Rajesh Sadasivan and Anjali Patel*

A heterogeneous catalyst comprising mono-copper substituted phosphotungstate and hydrous zirconia was synthesized using wet impregnation method, characterized by various physico-chemical techniques and evaluated for solvent-free oxidation of styrene using TBHP as oxidant. Various reaction parameters like time, catalyst amount, amount of TBHP and temperature were optimized with focus on optimum selectivity of styrene-oxide. Further, the catalytic activity was compared with that of unfunctionalized $PW_{11}Cu$ to understand the role of the support. Finally, the role of each component of the reaction was clearly elucidated by a detailed kinetic study of the reaction using both the catalysts.



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Catalysis

Cs Salt of Undecatungstophospho(aqua) Cuprate(II): Microwave Synthesis, Characterization, Catalytic and Kinetic Study for Epoxidation of cis-Cyclooctene with TBHP

Anjali U. Patel* and Rajesh Sadasivan[a]

The present paper describes a facile microwave route for the synthesis of Cesium salt of mono-copper substituted phosphotungstate, $Cs_5[PW_{11}Cu(H_2O)O_{39}].4H_2O$, from $H_3PW_{12}O_{40}$, $CuCl_2$ and CsCl, its characterization and catalytic activity towards solvent-free, selective epoxidation of cis-cyclooctene using TBHP as the oxidant. In order to confirm the superiority of the microwave technique, the said complex was also synthesized by reflux method and the same studies were carried out. The present complex is found to be sustainable as well as recyclable without any change in % conversion as well as % selectivity towards epoxide. A detailed kinetic study showed an overall second order dependence of the reaction with respect to cyclooctene and TBHP.

As mentioned in the general introduction, amongst the different transition metals, copper substituted phosphotungstates are of great interest because copper has unique redox properties, relatively inexpensive and low toxic nature [1-4]. In spite of these distinct advantages, very few reports are available in art for copper substituted POMs.

For the first time in 1970, Tourne et al synthesized 11-tungstocupro(II)-phosphate, -silicate, -germanate, -borate and -zincate and also 11-molybdocupro(II)-silicate, -germanate and -phosphate from the monovacant precursors and $CuSO_4.5H_2O$, and were obtained as K, Rb or NH_4 salts [5]. Almost 30 years later, in 1999, Cavaleiro et al synthesized tetra-butyl ammonium salt of $PW_{11}Cu$ from the individual salts, i.e., Na_2HPO_4, Na_2WO_4 and $Cu(NO_3)_2$. This was then screened for its catalytic activity for the oxidation of cyclohexane using aqueous hydrogen peroxide as the oxidant [1]. In 2003, the same group synthesized different polymorphs of the tetra-butyl ammonium salts of $PW_{11}CuO_{39}$, by different synthetic routes. The cubic phase was obtained from the potassium salt of monovacant phosphotungstate by cation metathesis in aqueous solution. On the other hand, the tetragonal phase was obtained by dissolving the cubic phase in acetonitrile and evaporating to dryness at room temperature. FT-IR and powder XRD were used to characterize the compounds, and the polymorphism in the two compounds was also studied [6]. They have also studied the electrochemical properties of Cu(II) in the polyoxotungstates [7].

In 2005, Yasuda et al synthesized tetra-n-heptyl ammonium and tetra-n-butyl ammonium salts of mono-copper substituted silicotungstate using the synthetic method reported by Tourne et al [5] and further used them for catalytic applications [2]. In 2009, Yang et al synthesized a one-dimensional mono Cu substituted phosphotungstates by hydrothermal technique using trivacant $Na_9[A\text{-}\alpha\text{-}PW_9O_{34}].7H_2O$, $CuCl_2.2H_2O$ and ethylene diamine, where Cu is incorporated into the Keggin unit and Cu (ethylene diamine) forms the counter-cation [8]. A year later, in 2010, Li et al synthesized the octadecyl trimethyl ammonium salt of mono-copper substituted phosphotungstate from the individual salts and used it as catalyst for the oxidation of benzothiophene [3]. In a similar manner, in 2017, mono-copper substituted phosphotungstate was synthesized by Xin et al and used for catalytic oxidation of cyclohexene with hydrogen peroxide as the oxidant [4].

It can, therefore, be seen that in all the above methods, the compounds are synthesized from the lacunary precursors. There are no reports on easy methods of synthesis like one-pot method or microwave technique. Use of microwave radiation is considered a more efficient source of heating as compared to conventional techniques. It saves reaction time by imparting energy directly to the reaction system rather than through the walls of reaction vessel. Also, it is cleaner and more eco-friendly compared to conventional techniques.

Herein, we report, for the first time, the synthesis of Cesium salt of mono copper substituted phosphotungstate from the parent 12-tungstophosphoric acid by two techniques (i) one-pot synthesis (designated as $RPW_{11}Cu$) and (ii) a novel microwave synthetic route (designated as $MPW_{11}Cu$). The materials 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, and both were found to be the same. This is followed by a detailed study to explore the catalytic activity of the synthesized complexes for the oxidation of styrene and cis-cyclooctene using tert-butyl hydroperoxide (TBHP) as the oxidant. Further, experiments for leaching and heterogeneity were carried out to confirm the heterogeneous nature of the catalyst. Finally, studies were carried out to compare the results of the catalytic activity of the complex synthesized by microwave technique with that of one-pot. For the first time, a detailed kinetic study and the activation energy has also been evaluated for the said reactions.

EXPERIMENTAL

Materials

All chemicals used were of A.R. grade. $H_3PW_{12}O_{40}.nH_2O$, $CuCl_2.2H_2O$, CsCl, styrene, dichloromethane and 70% TBHP were obtained from Merck. $NaHCO_3$ was obtained from SRL, Mumbai, while cis-cyclooctene was obtained from Spectrochem Pvt. Ltd. All chemicals were used as received.

One-pot synthesis of mono-copper substituted phosphotungstate

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 saturated $NaHCO_3$ 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 $RPW_{11}Cu$ (yield: 41.3%).

Microwave synthesis of mono-copper substituted phosphotungstate

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 saturated $NaHCO_3$ 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 microwaved at 90^{o}C for 30 seconds (Onida PC23 Black Beauty, power output – 800 W) with intervals after 10, 5, 5, 5 seconds. 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 $MPW_{11}Cu$ (yield: 39.3%).

Catalytic Evaluation

A typical oxidation reaction was carried out in a 50 mL batch reactor with a double walled air condenser, magnetic stirrer and a guard tube, in which 10 mmol of substrate was taken. TBHP was used as the oxidant and optimum amount of the catalyst was added. Owing to the fact that there was no aqueous medium, the catalyst remained heterogeneous. The conditions for maximum conversion and selectivity of cyclooctene oxide has been optimized by varying different reaction parameters like reaction time, catalyst amount, amount of TBHP and reaction temperature. The products obtained were extracted with dichloromethane by repeated extractions. The obtained products were analyzed on a gas chromatograph (Shimatzu-2014) using a capillary column (RTX-5) and were identified by comparison with the authentic samples.

Conversion and selectivity of each product was calculated as follows:

$$Conversion = \frac{(initial\ mol\%) - (final\ mol\%)}{(initial\ mol\%)}\ x\ 100$$

$$Selectivity = \frac{moles\ of\ product\ formed}{moles\ of\ substrate\ consumed}\ x\ 100$$

Further, Turn Over Number (TON) was calculated using the equation:

$$TON = \frac{moles\ of\ product}{moles\ of\ catalyst}$$

RESULTS AND DISCUSSION

Catalyst Characterization

Although we were not able to obtain good quality crystals suitable for single crystal X-ray analysis, we have provided enough evidence to show that Cu(II) is present in the lacuna of the phosphotungstate.

After the complexes $RPW_{11}Cu$ and $MPW_{11}Cu$ were isolated as their cesium salts, the remaining filtrate was analyzed gravimetrically for unreacted tungsten. It was found to be 1.21% and 1.20% for $RPW_{11}Cu$ and $MPW_{11}Cu$ respectively, corresponding to the loss of one equivalent of tungsten from both complexes (Theoretical – 1.22%).

The theoretical and experimental EDS values for $MPW_{11}Cu$ and $RPW_{11}Cu$ respectively are as follows. Calc. (%): Cs, 19.11; W, 58.16; P, 0.89; Cu, 1.83; O, 19.78. Found: $MPW_{11}Cu$ (%): Cs, 20.03; W, 57.42 (Gravimetry-57.2); P, 0.98; Cu, 1.8 (Volumetry-1.8); O, 19.76; $RPW_{11}Cu$ (%): Cs, 20.01; W, 57.43 (Gravimetry-57.1); P, 0.97: Cu, 1.8 (Volumetry-1.8); O, 19.78.

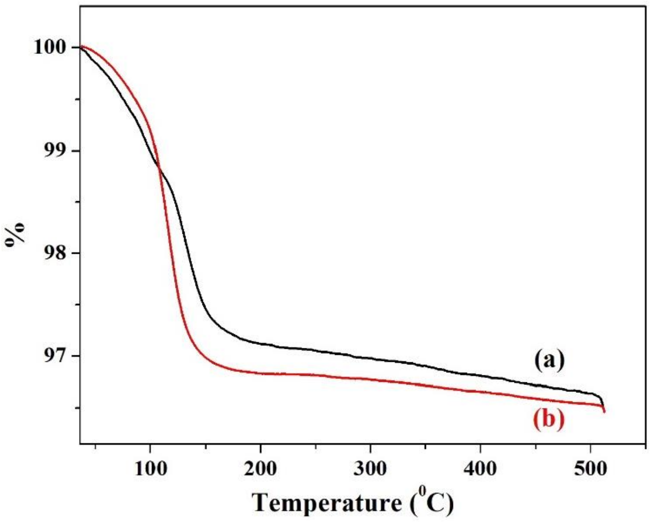

Figure 1. TGA of (a) $MPW_{11}Cu$ and (b) $RPW_{11}Cu$

The TGA curve shows total weight loss of 2.2% in case of $MPW_{11}Cu$ (Figure 1a), and 2.1% in case of $RPW_{11}Cu$ (Figure 1b) up to 510°C, corresponding to 5 H_2O

molecules. From the elemental as well as the thermal analysis, the chemical formula of the isolated complexes obtained is $Cs_5[PW_{11}Cu(H_2O)O_{39}].4H_2O$.

The FT-IR spectra for PW_{12}, PW_{11}, $MPW_{11}Cu$ and $RPW_{11}Cu$ are shown in figure 2. As seen in the figure, the spectrum of $PW_{11}Cu$ is very different from that of PW_{12} but similar to that of PW_{11}, indicating the presence of PW_{11} in the complex. The P–O vibration of the core phosphate group exhibits splitting in case of PW_{11}, when compared to that of PW_{12} and has bands at 1097 and 1041 cm^{-1}. In case of $MPW_{11}Cu$ and $RPW_{11}Cu$, splitting is observed at 1103 and 1061 cm^{-1} and 1103 and 1068 cm^{-1}, with Δv values of 42 cm^{-1} and 35 cm^{-1} respectively. These values are very close to the reported value of 40 cm^{-1} obtained by Rocchiccioli-Deltcheff and Thouvenot [9, 10].

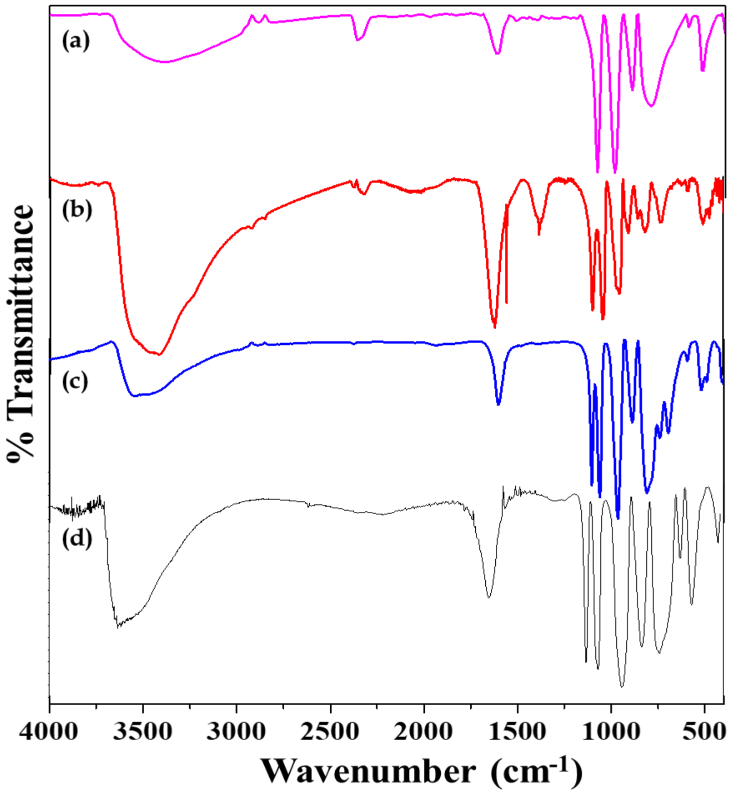

Figure 2. FT-IT spectra of (a) PW_{12}, (b) PW_{11}, (c) $RPW_{11}Cu$ and (d) $MPW_{11}Cu$

This clearly shows that Cu(II) is incorporated into the lacuna of the Keggin unit. Also, the difference in Δv values of $MPW_{11}Cu$ and $RPW_{11}Cu$ is lower compare to that of PW_{11}, which may be due to a pseudosymmetric environment that has resulted due to replacement of W with Cu [11]. The slight shift in the frequencies of $PW_{11}Cu$ compared to that of PW_{11} may be due to the incorporation of the Cu(II) in the lacuna. This also indicates that copper is not present as a counter-cation as in that case, no appreciable shifting would be expected. The presence of an additional band is also observed at 488 cm^{-1} and 489 cm^{-1} respectively for $RPW_{11}Cu$ and $MPW_{11}Cu$, which is attributed to Cu-O vibration, indicating the substitution of metal ion into the lacuna replacing one of the WO octahedral [12]. It is also observed that in case of $MPW_{11}Cu$, all the bands are sharper than those in case of $RPW_{11}Cu$. This may be attributed to different synthetic routes and indicates the superiority of microwave technique.

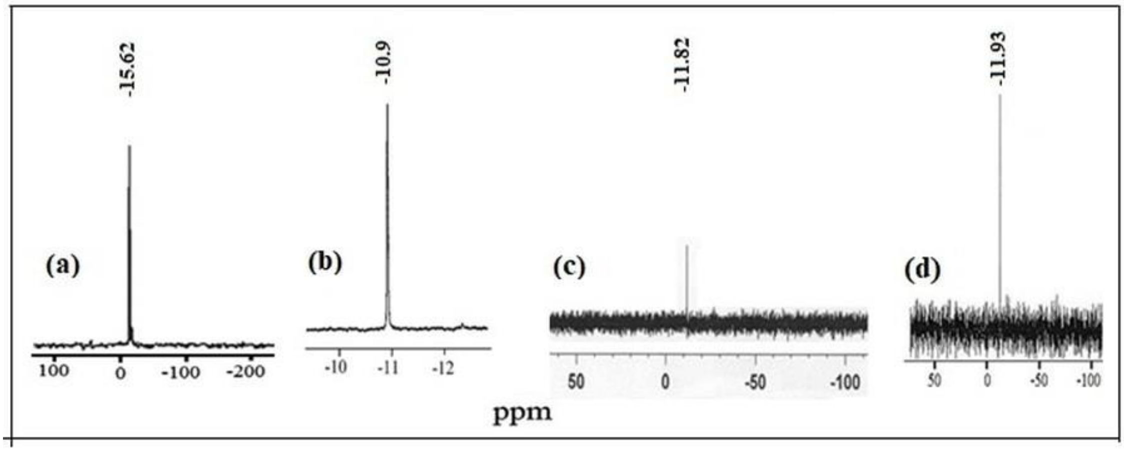

Figure 3. ^{31}P NMR spectra of (a) PW_{12} (b) PW_{11} (c) $MPW_{11}Cu$ and (d) $RPW_{11}Cu$.

The ^{31}P NMR spectra of PW_{12}, PW_{11}, $MPW_{11}Cu$ and $RPW_{11}Cu$ are shown in the Figure 3. The ^{31}PNMR for PW_{12} shows chemical shift at -15.62 ppm, while that of PW_{11} shows chemical shift at -10.89 ppm. The change in δ value by 4.73 ppm indicates the formation of $[PW_{11}O_{39}]^{7-}$ [13]. Both $MPW_{11}Cu$ and $RPW_{11}Cu$ show a single peak at -11.82 ppm and at -11.93 ppm respectively, confirming the presence of PW_{11} in the synthesized complex. However, the upfield shift may be attributed to the incorporation of paramagnetic Cu(II) ion into the lacuna of PW_{11}. The single peak also confirms the formation of a single product, thereby signifying that the drawback of multiple product formation is overcome in these synthetic routes.

The UV–Visible spectra of $RPW_{11}Cu$ and $MPW_{11}Cu$ are shown in Figure 4. In both the cases, the peak at 250 nm wavelength indicates presence of the PW_{11} moiety in the system. The obtained broad range peak from 700–1100 nm with λ_{max} values of 877 nm and 871 nm for $MPW_{11}Cu$ and $RPW_{11}Cu$ respectively, is due to the d-d transition of Cu(II) and indicates the presence of Cu(II) in the complexes.

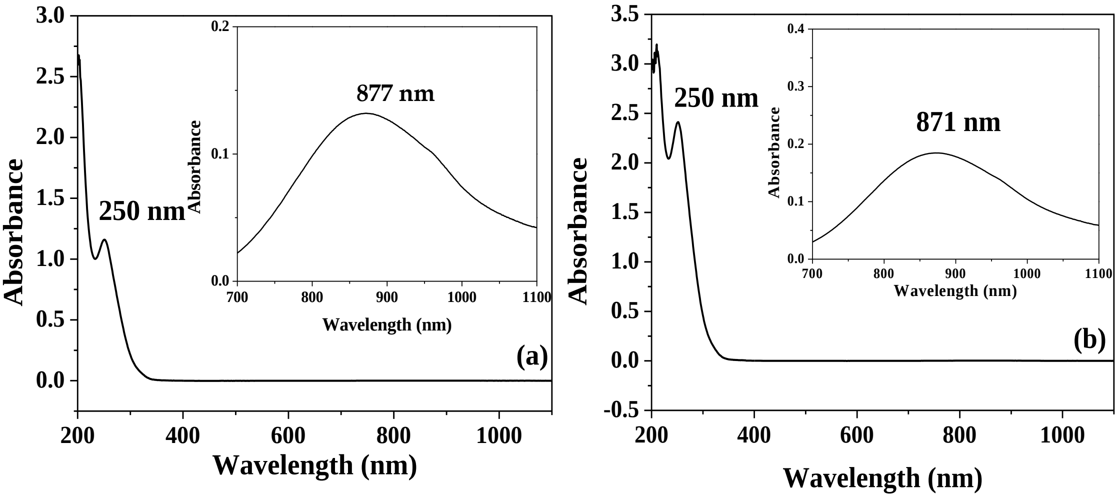

Figure 4. UV-Vis Spectra of (a) $MPW_{11}Cu$ and (b) $RPW_{11}Cu$

The full range X-band liquid nitrogen ESR spectra of both $MPW_{11}Cu$ and $RPW_{11}Cu$ given in figure 5, show a four line hyperfine spectrum, with $g_{\parallel} = 2.4031$ and $g_{\perp} = 2.0883$, which is typical of Cu(II). The four line hyperfine splitting along with the fact that $g_{\parallel} > g_{\perp}$ indicate that the Cu^{2+} is in a tetragonally distorted octahedral environment [4]. Thus, ESR confirms the incorporation of Cu(II) into the lacuna of the phosphotungstate.

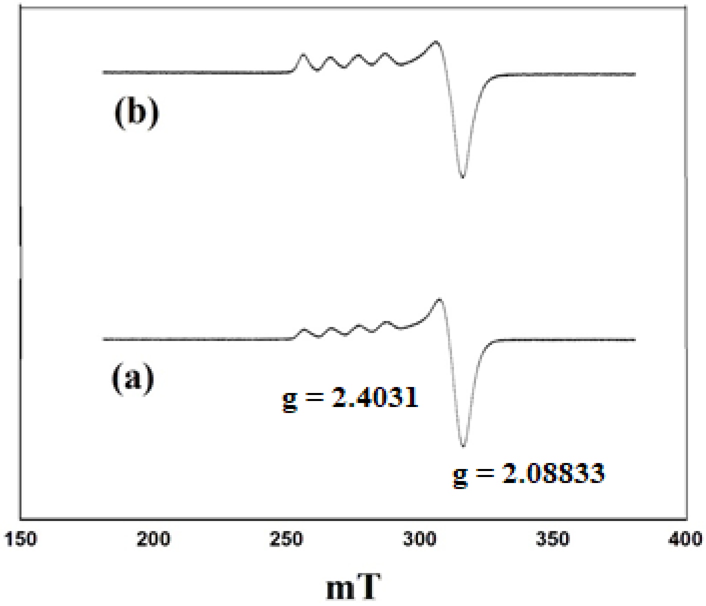

Figure 5. X-band LNT ESR spectra of (a) $MPW_{11}Cu$ and (b) $RPW_{11}Cu$

The powder XRD spectra of PW_{12}, PW_{11}, $MPW_{11}Cu$ and $RPW_{11}Cu$ are shown in the Figure 6. A typical powder XRD pattern for a Keggin type phosphotungstate shows peaks in the range of 15 to 30 degrees 2θ value as shown in the Figure 6. There is a distinct shift in case of the 2θ values of PW_{11}, to 25 to 35 degrees, indicating formation of lacuna. It can be seen that the peaks are retained in the spectra of both $MPW_{11}Cu$ and $RPW_{11}Cu$, which indicates presence of PW_{11} in the synthesized complexes. Further, additional peaks were also observed at 48 and 50 degrees 2θ for $MPW_{11}Cu$ and $RPW_{11}Cu$ respectively, confirming the presence of Cu(II) [14].

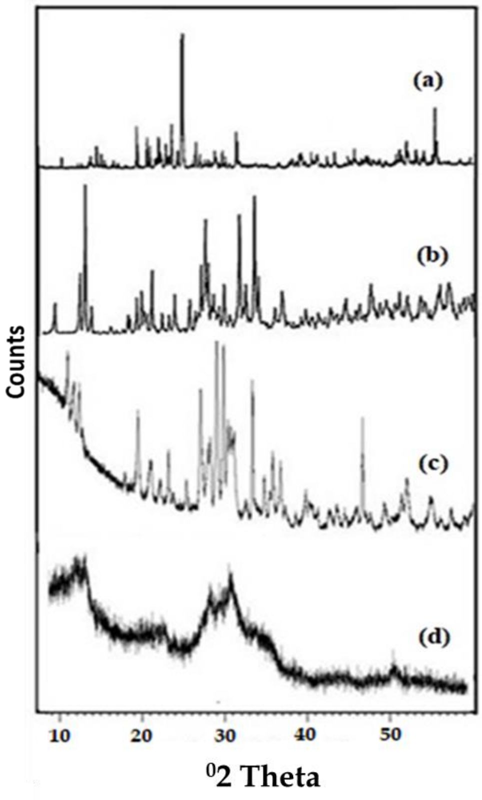

Figure 6. Powder XRD Spectra of (a) PW_{12}, (b) PW_{11}, (c) $MPW_{11}Cu$ and (d) $RPW_{11}Cu$.

Also, a comparison of the XRD patterns of $MPW_{11}Cu$ and $RPW_{11}Cu$ shows absence of sharp peaks in case of $RPW_{11}Cu$, suggesting that the complex synthesized by microwave technique shows better texture compared to that synthesized by reflux method.

Cyclic Voltammetry of 1 mM solution was recorded in buffer medium of pH 5 (acetate buffer) using glassy carbon electrode as working electrode, Ag/AgCl as reference electrode and Platinum wire as a counter electrode.

The Cyclic Voltammograms of PW_{11}, $MPW_{11}Cu$ and $RPW_{11}Cu$ are shown in figure 7. It has been reported in literature that lacunary anion with a formal charge of 7 shows one reversible redox process in aqueous buffer medium. Here too we see a single electron redox process with peak potentials at -0.7 V and -0.4 V, which is in good agreement with literature [15]. The slight shift in the peak potentials in this case may be due to change in the counter-cation.

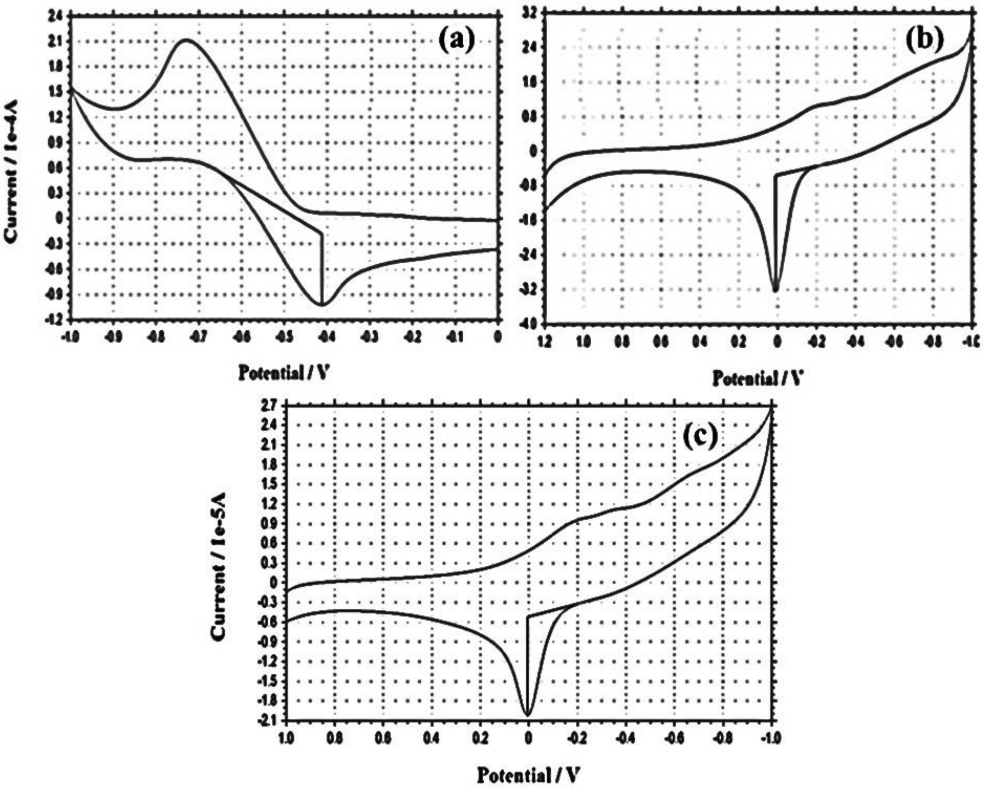

Figure 7. CV of (a) PW_{11}, (b) $MPW_{11}Cu$ and (c) $RPW_{11}Cu$.

(Working electrode: Glassy carbon, Reference electrode: Ag/AgCl, Counter electrode: Pt-wire)

In case of both MPW11Cu and RPW11Cu, the two peaks are seen at around -0.4 V and -0.45 V respectively, indicating the presence of lacunary structure. Along with this, there is a quasireversible wave with an anodic peak at 0.02 V confirming the presence of Cu(II).

Oxidation of styrene

Each experiment was carried out thrice and the results obtained were reproducible with an error of ±2%. Initially, a preliminary study was carried out using H_2O_2 as the oxidant and $MPW_{11}Cu$ as catalyst at 80 ^{0}C, but did not show a significant conversion. TBHP was then used as an initiator for H_2O_2 and the reaction was carried under the same conditions as above. 77% conversion was obtained with 50% selectivity for benzaldehyde. Despite high conversion, the drawback was excess polymerization of styrene. Hence, in the next attempt, H_2O_2 was discarded, TBHP played the role of the oxidant and 5 mL acetonitrile (ACN) was added as solvent. The reaction temperature was brought down to 60 ^{0}C, due to possible decomposition of TBHP at higher temperatures [16]. This gave 28% conversion with 68% selectivity for benzaldehyde and 23% styrene-oxide along with small quantities of acetophenone and benzoic acid, but did not show polymerization. This clarified that aqueous medium was responsible for over-oxidation and polymerization, and in further reactions, it was decided that aqueous media be completely avoided. Moreover, with increase in the amount of TBHP to 2 mL, subsequent increase in conversion (68%) as well as selectivity of styrene-oxide (29%) was obtained.

It is well known that oxidation using TBHP gives the by-product tert-butyl alcohol. Hence, instead of acetonitrile, tert-butyl alcohol was used as solvent, for which, similar results were obtained (Conversion: 60%; Benzaldehyde: 49% Styrene-oxide: 30%). This indicated that solvent may not play a role in the catalytic activity in the present case. Therefore, a reaction was carried out without addition of any solvent, which gave similar results. The results of the preliminary experiments are presented in table 1. Based on these preliminary results, the reaction optimization was carried out under solvent free conditions.

Table 1. Preliminary reactions

System	% conversion	% selectivity	
		Benzaldehyde	**Styrene Oxide**
Sty:H_2O_2 – 1:3; 25 mg; 20 h; 80 ^{0}C	–	–	–
Sty: H_2O_2 – 1:3; 15 mg; 20 h; 80 ^{0}C; 1 mL TBHP; 5 mL ACN	77.3	50.2	5.1
Sty – 1 mL; 15 mg; 20 h; 60 ^{0}C; 1 mL TBHP; 5 mL ACN; No H_2O_2	28.0	67.9	23.1
Sty – 1 mL; 15 mg; 20 h; 60 ^{0}C; 2 mL TBHP; 5 mL ACN; No H_2O_2	61	50.2	28.7
Sty – 1 mL; 15 mg; 20 h; 60 ^{0}C; 2 mL TBHP; 5 mL t-BuOH; No H_2O_2	60.2	49.1	30.2
Sty – 1 mL; 15 mg; 20 h; 60 ^{0}C; 2 mL TBHP; No t-BuOH; No H_2O_2	57.4	62.7	24.4

Similar reactions were also carried out using $RPW_{11}Cu$ as catalyst, which yielded similar results. Hence, for further optimizations, it was decided to use $MPW_{11}Cu$ as catalyst, as synthesis by microwave technique not only saves time, but is also greener compared to the conventional route.

i. Effect of time:

In order to study the effect of time, the reaction was carried out at different times, and the results are presented in Figure 8. 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.

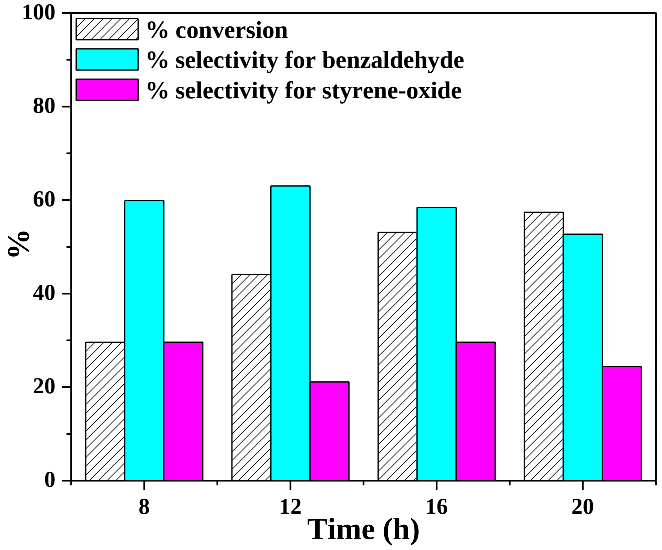

Figure 8. Effect of time (Catalyst amount – 15 mg; temp – 60 ^{0}C; TBHP – 2 mL)

ii. Effect of catalyst amount

The reaction was then carried out at different catalyst amounts and the results are presented in Figure 9. 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.

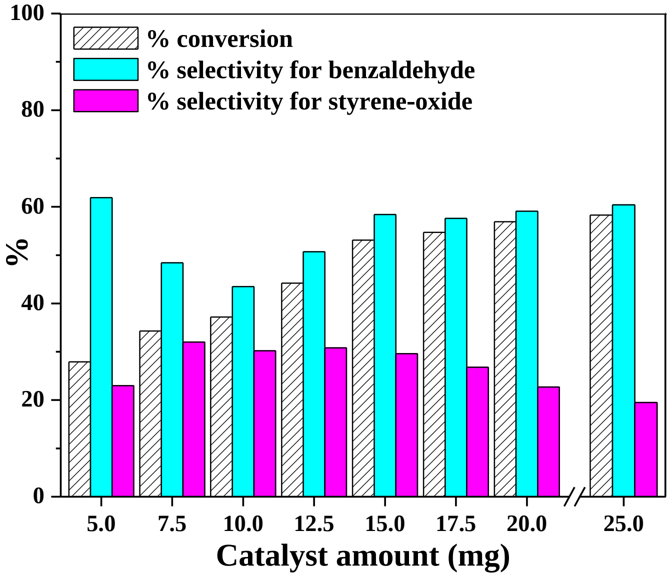

Figure 9. Effect of catalyst amount (Time – 16 h; temp – 60 ^{0}C; TBHP – 2 mL)

iii. Effect of amount of TBHP

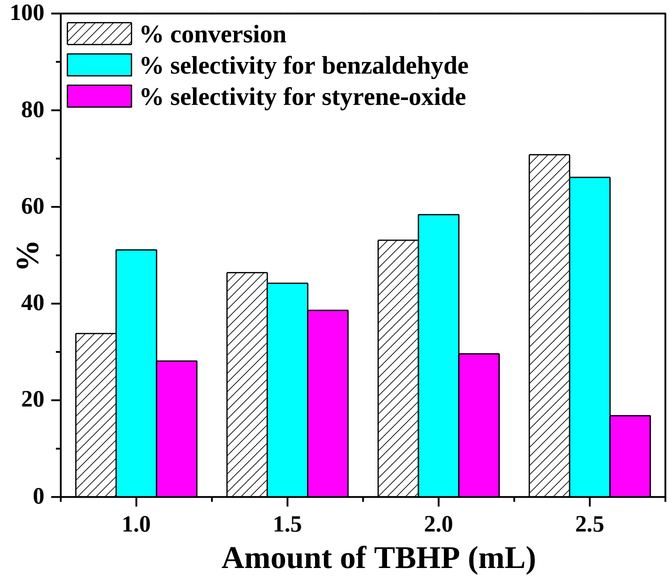

Figure 10. Effect of TBHP amount (catalyst amount – 15 mg; temp – 60 ^{0}C; time – 16 h)

The amount of TBHP was then varied to study the effect of oxidant and the results are presented in Figure 10. With increase in TBHP amount from 1 mL to 2.5 mL, there is an increase in 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.

iv. Effect of reaction temperature

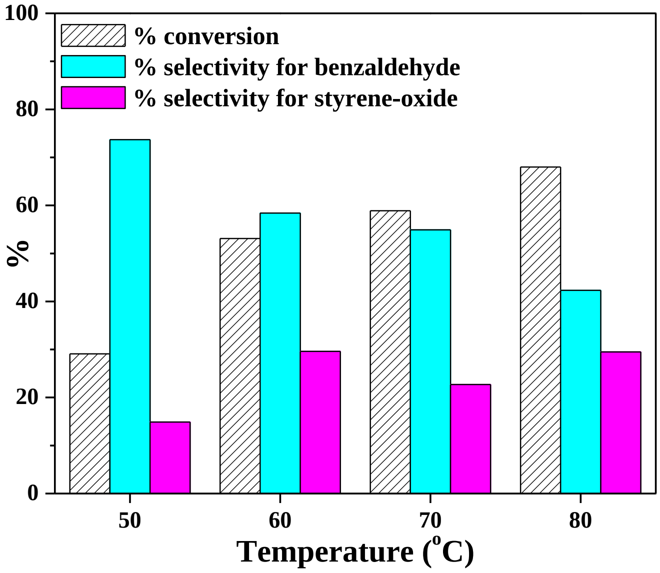

Figure 11. Effect of reaction temperature (catalyst amount – 15 mg; time – 16 h; TBHP – 2 mL)

Finally, the reaction was carried at different temperatures and the results are presented in figure 11. When the temperature was increased from 50 ^{0}C to 60 ^{0}C, there is an increase in conversion as well as selectivity of styrene-oxide. But on increasing temperature beyond 60 ^{0}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 ^{0}C.

The reaction conditions for oxidation of styrene over $PW_{11}Cu$ 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 ^{0}C.

Oxidation of cis-cyclooctene

Similarly, TBHP was used as the oxidant and optimization was carried out and the results are presented in figure 12. Cyclooctene-oxide was the major product, while cyclooctanone was the minor product. In all the experiments, small quantities of tert-butyl alcohol (3-4%) was obtained, which was as expected. An experiment without the catalyst was carried out in which there was no conversion, indicating that TBHP does not undergo auto-oxidation.

The effect of temperature shows that with increase in temperature from 60 ^{0}C to 65 ^{0}C, there was a significant rise in conversion of the substrate. But when the temperature was further increased to 70 ^{0}C, there was an increase in conversion, but the selectivity of epoxide decreases due to formation of unwanted byproducts. Thus, 65 ^{0}C was considered as optimum temperature.

There is significant increase in conversion of the substrate when catalyst amount is increased from 10 mg to 15 mg. But with further increase in catalyst amount, there is no substantial increase in the conversion. This may be attributed to blockage of catalytic sites. Hence, 15 mg catalyst was taken as optimum amount.

The reaction was then set at different hours, in order to understand effect of reaction time on the catalytic activity. With increase in the time from 12 h to 20 h, there is a steady increase in the conversion of substrate. But when increased further to 24 h, the increase in conversion is not very significant. Thus, 20 h was considered as optimum time required for the reaction.

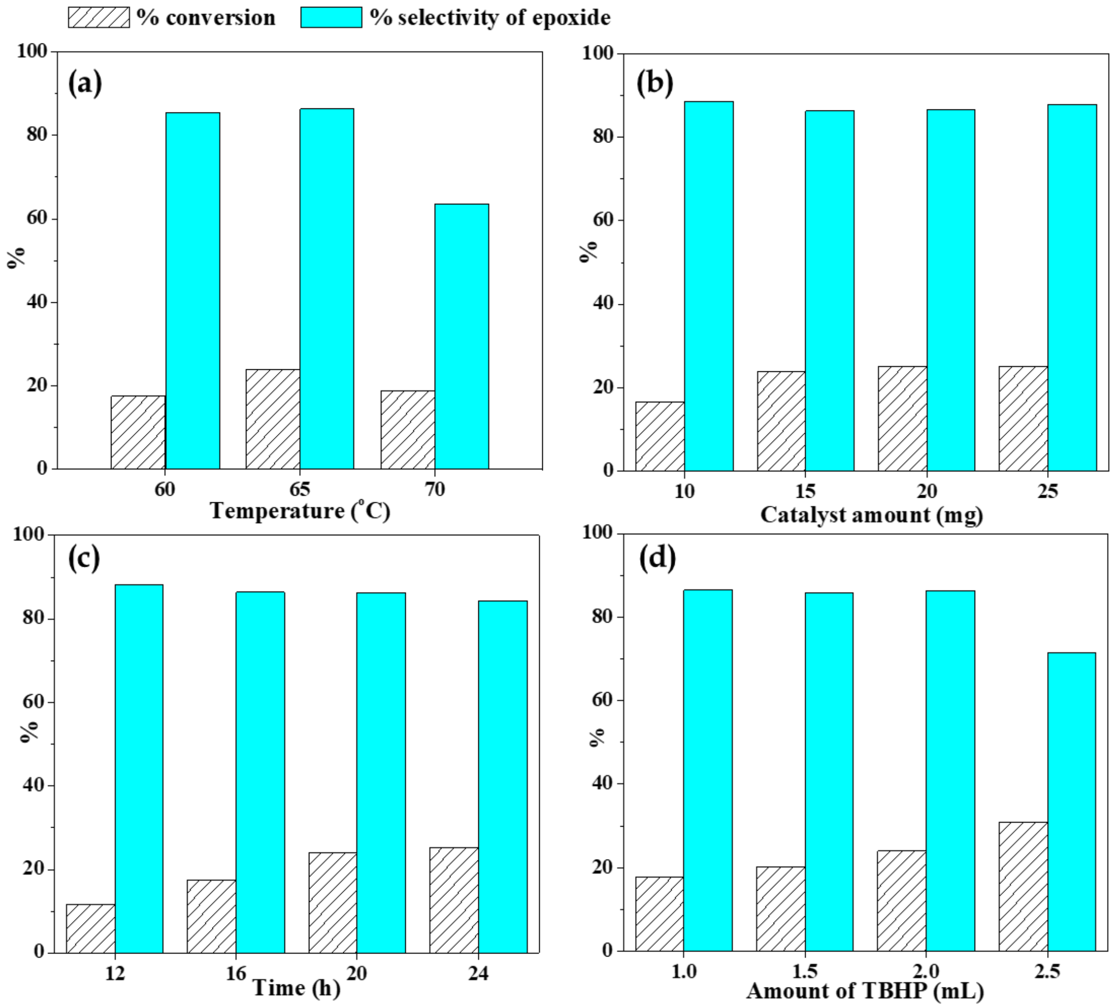

Figure 12. Optimization of parameters for oxidation of cis-cyclooctene over $MPW_{11}Cu$: (a) Effect of temperature (catalyst amount – 15 mg; time – 20h; TBHP – 2 mL), (b) Effect of catalyst amount (Time – 20h; temp – 65 ^{0}C; TBHP – 2 mL), (c) Effect of Time (Catalyst amount – 15 mg; temp – 65 ^{0}C; TBHP – 2 mL) (d) Effect of amount of TBHP (catalyst amount – 15 mg; temp – 65 ^{0}C; time – 20h)

Finally, the amount of TBHP was varied to know its effect. With increase in amount of TBHP from 1 mL to 1.5 mL and then to 2 mL, there is steady increase in conversion of cis-cyclooctene while the selectivity of the epoxide remains more or less constant. But with further increase in amount of TBHP to 2.5 mL, there is a decrease in selectivity of epoxide with formation of unwanted products. Thus, 2 mL TBHP was considered optimum for the reaction.

The optimized conditions for 24% conversion and 86.3% selectivity of the epoxide are: Temperature: 65 ^{0}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.

Role of TBHP

In order to obtain insight on the role of TBHP, the reaction was run under two different conditions as follows: (i) with catalyst i.e. substrate + TBHP + MPW$_{11}$Cu, and (ii) without the catalyst i.e. substrate + TBHP only. The reaction mixture was analyzed by GC at regular time intervals (0.5 h, 1 h, 2 h, 3 h, 4 h, 5 h, 6 h, 8 h, 10 h, 12 h and 16 h). In all the experiments, the analyses were carried out at fixed time intervals varying the amount of catalyst and temperature for the respective studies. The results are presented in Figure 13.

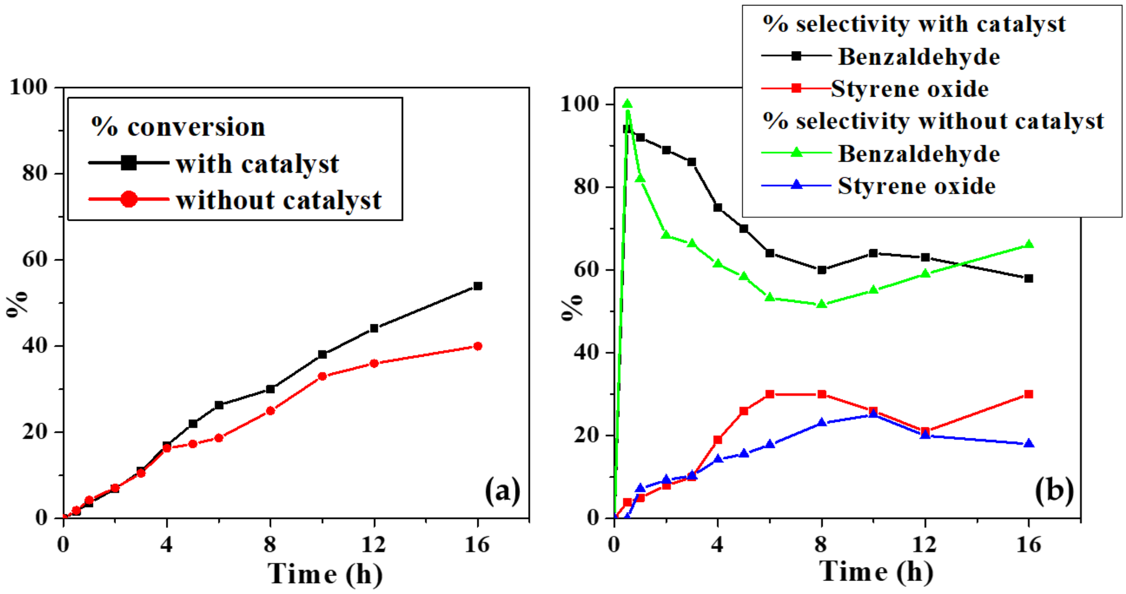

Figure 13. Role of TBHP in oxidation of styrene in the presence and absence of catalyst (a) conversion and (b) selectivity

As mentioned previously, in the absence of catalyst, the conversion of styrene is 40% after 16 h. The selectivity for benzaldehyde is very high (66%) while that of styrene oxide is low (18%). It is interesting to note that the trend in selectivity towards the products is exactly opposite in the presence of catalyst. This may be explained as follows. Due to the fact that TBHP undergoes self-disproportionation in absence of catalyst to form a highly unstable reactive intermediate species, it immediately reacts with styrene to form benzaldehyde. Hence, the selectivity of benzaldehyde is higher compared to the reaction with the catalyst. On the other hand, higher conversion in presence of catalyst indicates that catalyst is necessary for the reaction; which is also reflected in the selectivity of products. This further suggests that rate of the reaction depends on concentration of TBHP.

Similar experiments were carried out for cis-cyclooctene as well, and results obtained were analogous, further confirming the significance of the role played by TBHP in the reaction.

Leaching and Heterogeneity

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, $PW_{11}Cu$ was tested for 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, 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. Similar study was carried out in case of cyclooctene oxidation. No change in the conversion as well as selectivity of the products in both the cases (Table 2) indicates that the catalyst is truly heterogeneous in nature.

Table 2. Heterogeneity test

Substrate	Reaction time	% conversion	% selectivity	
			Epoxide	Aldehyde/Ketone
Styrene [a]	12 h	44	63	21
	16 h (Filtrate)	45	64	22
Cis-cyclooctene [b]	16 h	15.8	85	15
	20 h (Filtrate)	15.9	84	16

[a] Catalyst amount: 15 mg; Temp: 60 ^{0}C; TBHP: 2 mL

[b] Catalyst amount: 15 mg; Temp: 65 ^{0}C; TBHP: 2 mL

Control Experiments

Control experiments were carried out for both substrates 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 3. For styrene oxidation, in the absence of catalyst, 40% conversion was observed. This indicates that TBHP undergoes self-disproportionation to give reactive intermediate species, which further gives the products. In the presence of $CsPW_{11}$, there is no change in the % conversion and selectivity, indicating that the lacunary phosphotungstate does not play a role in the catalysis. 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.

In case of cis-cyclooctene, in presence of $CsPW_{11}$, no significant conversion was observed, indicating that disproportionation of TBHP is unable to oxidize cyclooctene. In case of $CuCl_2$, 24.7% conversion with good selectivity for the epoxide (74.6%) was observed indicating that copper plays a significant role in the oxidation of cis-cyclooctene. Both $MPW_{11}Cu$ and $RPW_{11}Cu$ also show similar conversion. **The advantages in case of the present catalysts lie in the higher conversion (for styrene) and better selectivity of epoxide, especially with excellent selectivity for cyclooctene-oxide. Also, they are heterogeneous in nature and can be easily recycled as well as reused.**

Table 3. Control experiments

Catalyst	^{i} Styrene oxidation % Conv. (Ald / Epo)	^{ii} Cis-cyclooctene oxidation % Conv. (Epo / Ket)	Turn Over Number (i/ii)
No Catalyst	40 (66 / 18)	4.6 (65.5 / 34.5)	-/-
$^{a}CsPW_{11}$	40 (68 / 17)	4.7 (70.6 / 29.4)	-/-
$^{b}CuCl_2$	51 (74 / 15)	24.7 (74 / 15)	-/-
$^{c}MPW_{11}Cu$	54 (59 / 30)	24 (86.3 / 13.7)	1102/560
$^{c}RPW_{11}Cu$	53 (60 / 30)	23.7 (86.5 / 13.5)	1102/552

i. Styrene oxidation. Catalyst amount - ^{a}13.16 mg; ^{b}0.72 mg (active amount of Cu-0.27 mg); ^{c}15 mg (active amount of Cu-0.27 mg); TBHP – 2 mL; Temp–60 ^{0}C; Time–16h.

ii. Cis-cyclooctene oxidation. Catalyst amount - ^{a}13.16 mg; ^{b}0.72 mg (active amount of Cu-0.27 mg); ^{c}15 mg (active amount of Cu-0.27 mg); Time: 20h; Temp: 65 ^{0}C; TBHP: 2 mL

It is also interested to note down that the catalytic activity of $MPW_{11}Cu$ and $RPW_{11}Cu$ is almost the same under the same reaction conditions for both substrates, indicating that both the synthetic routes give the same catalyst.

Chemical Kinetics

In order to gain a deeper understanding on the role of each reactant, i.e., substrate, TBHP as well as catalyst, a detailed kinetic study was carried out keeping in mind the effect of each component on the rate of reaction. All the reactions were carried out keeping at least one parameter constant. Each reaction was carried out thrice, and the results obtained is an average of all the three values.

Experiments were carried out with different initial concentrations of the substrates and TBHP, keeping the catalyst amount constant. Eqn (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/cyclooctene, '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 for both, styrene and cyclooctene (Figure 14), indicating that the reaction is first order with respect to both the substrates and TBHP, individually [16].

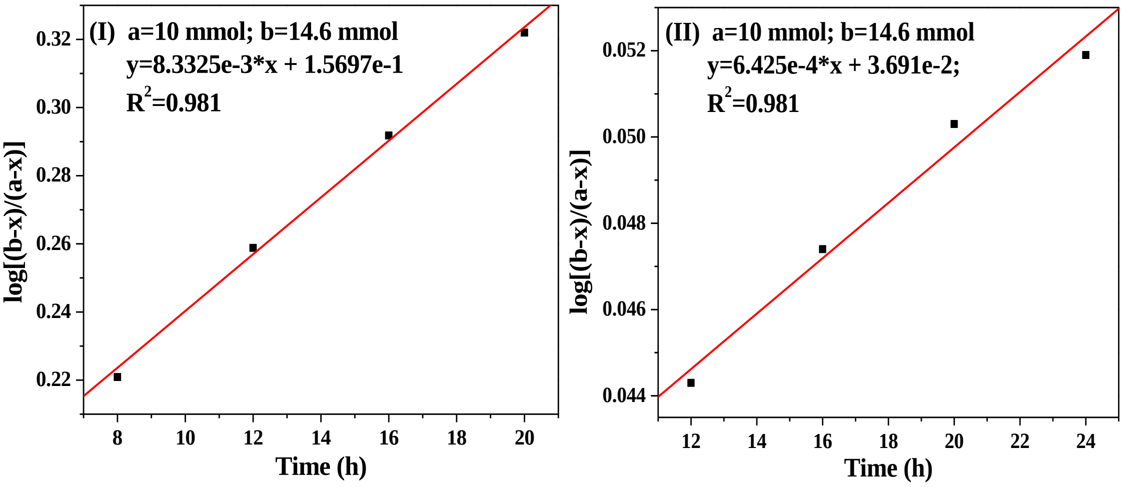

Figure 14. Plot of log[(b-x)/(a-x)] versus time for oxidation of (I) styrene and (II) cis-cyclooctene

Similarly, an experiment was then carried out keeping the initial concentration of the substrates as well as TBHP 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 substrate and TBHP and 'x' is the concentration at time t. As in the previous case, a plot of 1/(a-x) versus time shows a linear relationship for both substrates, (Figure 15) indicating that the reaction follows second order overall with respect to concentration of the substrates and TBHP [16].

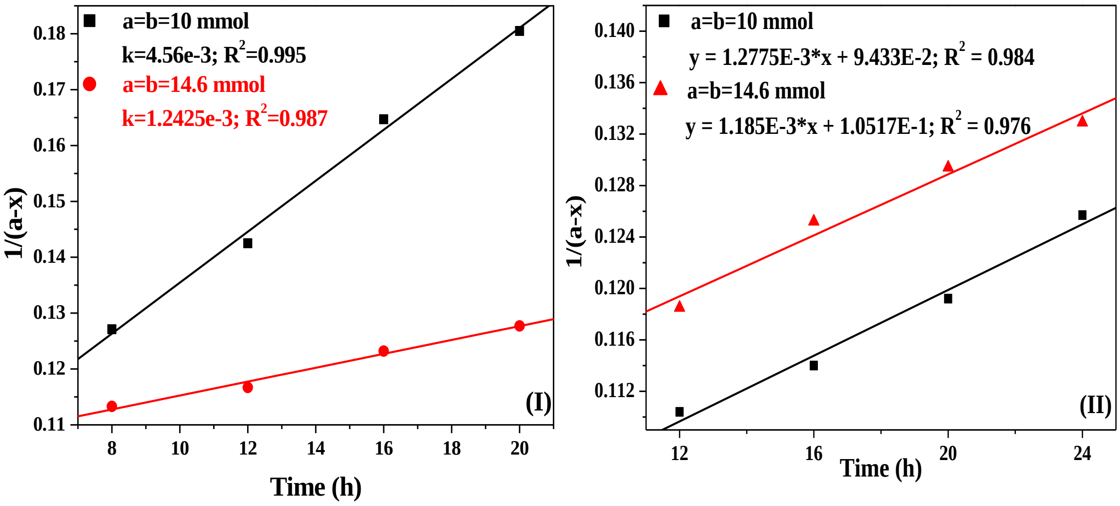

Figure 15. Plot of 1/(a-x) versus time for oxidation of (I) styrene and (II) cis-cyclooctene

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 16. In case of styrene oxidation, 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. Similarly for cis-cyclooctene oxidation, with increase in catalyst concentration from 1.43 x 10^{-3} mmol to 5.72 x 10^{-3} mmol, there is a steady increase in the rate constant (k), indicating that for both systems, the reaction follows first order kinetics with respect to catalyst concentration as well.

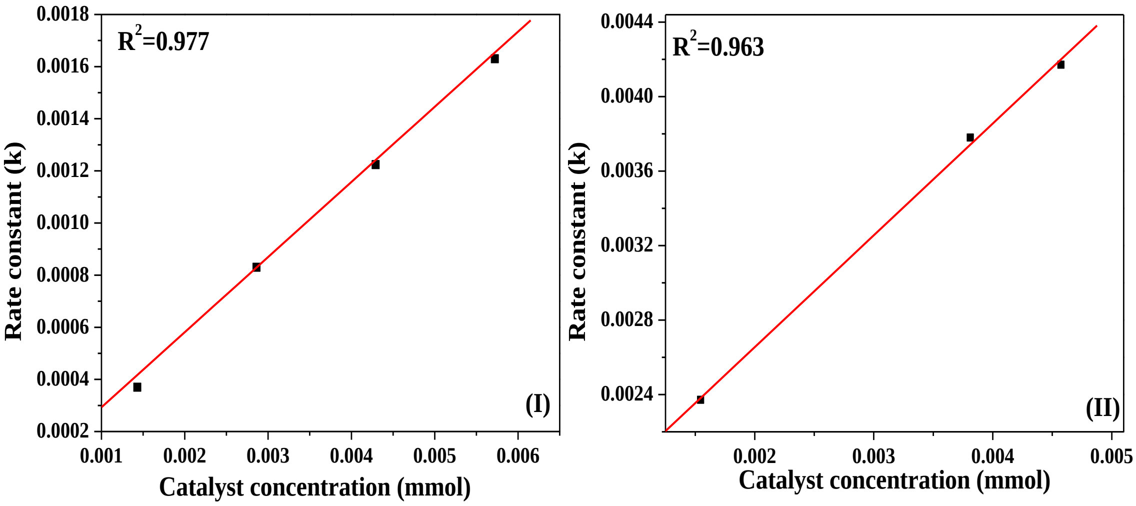

Figure 16. Plot of rate of reaction versus catalyst concentration for oxidation of (I) styrene and (II) cis-cyclooctene

Determination of Activation Energy

It is known that that in case of liquid phase reactions using heterogeneous catalyst, the reaction occurs in a two-phase system with the liquid substrate and oxidant and the solid catalyst. The basic reaction can be divided into five steps and any one of them can be the rate determining step: (i) reactants are transported to the catalyst; (ii) reactants are adsorbed on the catalyst; (iii) reaction occurs on the surface of the catalyst; (iv) products are desorbed from the catalyst and (v) products are transported away from the catalyst. Of these, the first and fifth steps do not involve any chemical change, and occur via simple mass transfer. The resistances due to mass transfer can easily alter the activity of the catalyst, and hence it is important to know that the reaction is not diffusion limited or mass transfer limited, but is truly governed by a chemical step. Hence it is necessary to know about the activation energy. Considering the importance of the same, in present case, energy of activation was calculated.

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 as well as cyclooctene is seen. Thus, 1/T shows a linear relationship with lnk (Figure 17), and the activation energy was evaluated using Arrhenius equation (Equation 3).

$$k = Ae^{\frac{-Ea}{RT}} \tag{3}$$

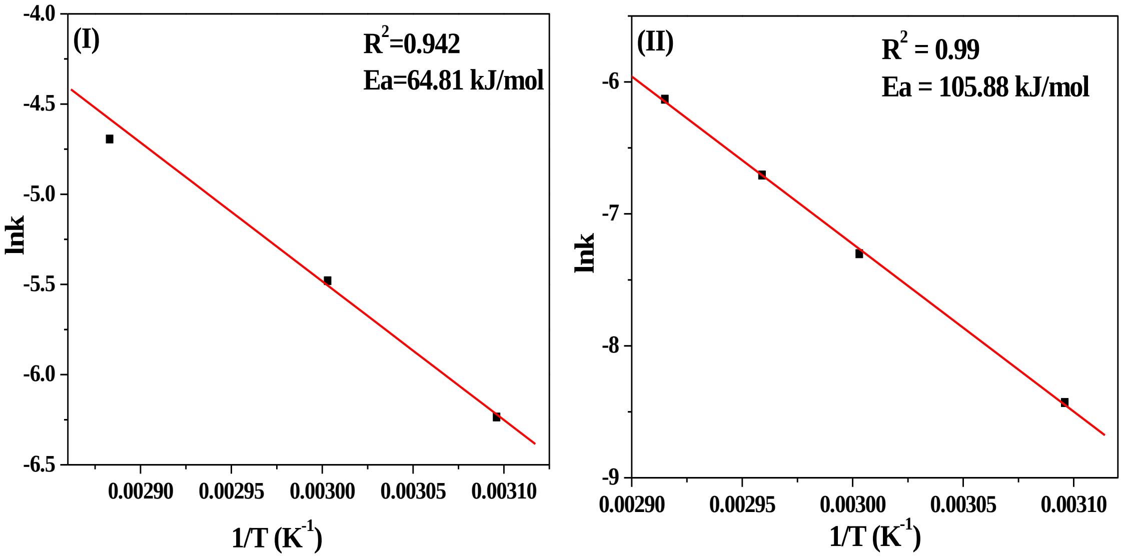

Figure 17. Plot for determination of activation energy for (I) styrene and (II) cis-cyclooctene

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 for styrene and 105.88 kJ/mol for cis-cyclooctene indicates that both the reactions are truly governed by a chemical step and also that the catalyst has been exploited to its maximum capacity.

Mechanistic Investigation

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 [17]. It is known that oxidation can proceed either by oxygen transfer or by one-electron transfer. It is also known that most of the metals, which catalyze oxygen transfer reactions, are also capable of catalyzing one-electron transfer processes with peroxides, and immobilization of the one-electron oxidants with molecular sieves will not influence the oxidation mechanism, as these oxidants will still catalyze the radical process even after incorporation in a solid matrix [18].

A detailed ESR study was carried out to determine the fate of the catalyst during the course of oxidation reaction of styrene as well as the type of reaction, whether oxygen transfer or electron transfer. The ESR spectra of the (a) fresh catalyst, (b) after 5h of the reaction, (c) 10h of the reaction and finally (d) recycled catalyst are shown in figure 18. The spectra after 5h of the reaction is ESR silent, indicating the formation of Cu(I) species, confirming that electron transfer takes place from the catalyst to the oxidant, thereby activating it. At a certain stage, the entire Cu(II) in the system is converted to Cu(I), and hence the silent spectrum. This may be due to the large POM unit, which is able to stabilize copper in its lower oxidation state, as mentioned earlier. Further, the ESR spectra after 10h shows a five-line hyperfine spectrum indicating the re-oxidation of Cu(I) to Cu(II) after completion of the reaction.

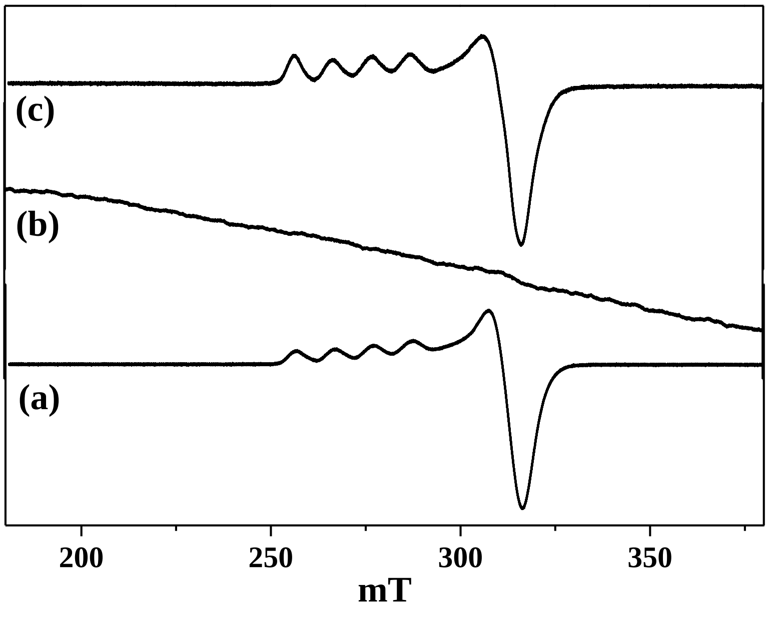

Figure 18. ESR spectra of $MPW_{11}Cu$ (a) Fresh, (b) after 5h and (c) after 10h

It has been reported that the oxidative cleavage of an alkene double bond by hydroperoxides generally proceeds by formation of a free radical. In order confirm the same, 2,6-di-tertbutyl-4-methyl phenol, a radical scavenger, was added to the system during the reaction**.** The radical scavenger was added **after** 12 h and then the reaction was allowed to proceed to completion (Table 4). No significant change in the conversion and selectivity indicates that the intermediate formed is a radical. The slight increase in conversion and selectivity of benzaldehyde may be due to presence of the intermediate after immediate addition of scavenger. This confirms that the reaction proceeds via radical mechanism [19].

Table 4. Inhibition experiment with 2,6-di-tert-butyl-4-methylphenol as radical scavenger for styrene oxidation

Condition	% conversion	% selectivity	
		Benzaldehyde	**Styrene-oxide**
After 12 h	44	63	21
After 16 h (after scavenger addition)	46	65	20

Catalyst amount: 15 mg; Temp: 60 ^{0}C; TBHP: 2 mL.

Based on the ESR and radical scavenger studies, a tentative reaction mechanism was proposed. In this case, the most important function of Cu(II) is to decompose the stable hydroperoxide, and initiate the radical mechanism [17]. It has been reported that metal ion decomposes TBHP into tert-butyl peroxyl radicals via one electron transfer, wherein Cu(II) gets reduced to Cu(I) and the electron that is released initiates the radical chain by reacting with TBHP to give tert-butyl peroxyl radicals [18]. Cu(II) is reduced to Cu(I) and electron transfer occurs to generate tert-butyl hydroperoxyl radical. The formed radical reacts with the olefin to give a radical intermediate, which further forms the **products** with the release of tert-butoxyl radical. Cu(I) is oxidised back to Cu(II) by the tert-butoxyl radical with the formation of tert-butyl alcohol as the by-product.

Similarly, addition of radical scavenger 2,6-di-tert-butyl-4-methylphenol after 16 h of the reaction inhibits further oxidation of cis-cyclooctene as well, indicating that the reaction follows radical mechanism, as in the previous case (Table 5).

Table 5. Inhibition experiment with 2,6-di-tert-butyl-4-methylphenol as radical scavenger for cyclooctene oxidation

Condition	**% conversion**	**% selectivity** **Cyclooctene-oxide**	 **Cyclooctanone**
After 16 h	13.9	88.5	11.5
After 20 h (after scavenger addition)	14.5	88	12

Catalyst amount: 15 mg; Time: 20h; temp: 65 ^{0}C; TBHP: 2 mL

Regeneration and recycling

The catalyst was centrifuged from the reaction mixture, washed with methanol and dried. The recovered catalyst was then used for the oxidation of the alkenes under the respective optimized conditions and the results are presented in table 6.

Table 6. Recycling of catalyst

Catalyst	**% conversion**	**% selectivity** **Epoxide**	 **Aldehyde/Ketone**
$PW_{11}Cu$	^{a}54/^{b}24	^{a}30/^{b}86.3	^{a}59/ ^{b}13.7
R_1- $PW_{11}Cu$	^{a}54/ ^{b}23.8	^{a}30/ ^{b}86.1	^{a}60/ ^{b}13.9
R_2- $PW_{11}Cu$	^{a}53/ ^{b}23.7	^{a}29/ ^{b}86	^{a}60/ ^{b}14
R_3- $PW_{11}Cu$	^{a}51/ ^{b}23.4	^{a}28/ ^{b}86.1	^{a}62/^{b}13.9

[a] **Styrene oxidation** - Catalyst amount: 15 mg; Time: 16 h; Temp: 60 ^{0}C; TBHP: 2 mL.

[b] **Cis-cyclooctene oxidation** - Catalyst amount: 15 mg; Time: 20h; Temp: 65 ^{0}C; TBHP: 2 mL

Same conversion and selectivity for the products are obtained even after multiple cycles indicating that the catalyst remains stable during the course of the reaction and that it can be reused for multiple times. A slight decrease in conversion in the third cycle may be due to loss of the catalyst during the recovery.

Characterization of regenerated catalyst

The regenerated catalyst was characterized by FT-IR, UV and ESR spectroscopy. The FT-IR spectrum of recycled $MPW_{11}Cu$ (Figure 19) 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 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.

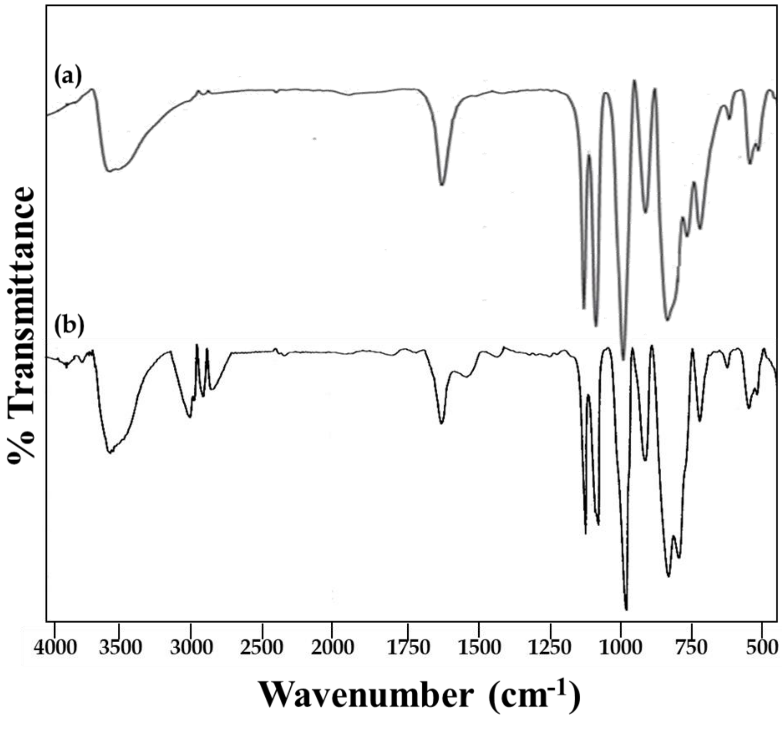

Figure 19. FT-IR spectra of (a) $MPW_{11}Cu$ and (b) Rec. $MPW_{11}Cu$

The ESR spectra of fresh and recycled $MPW_{11}Cu$ are shown in the Figure 20. 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.

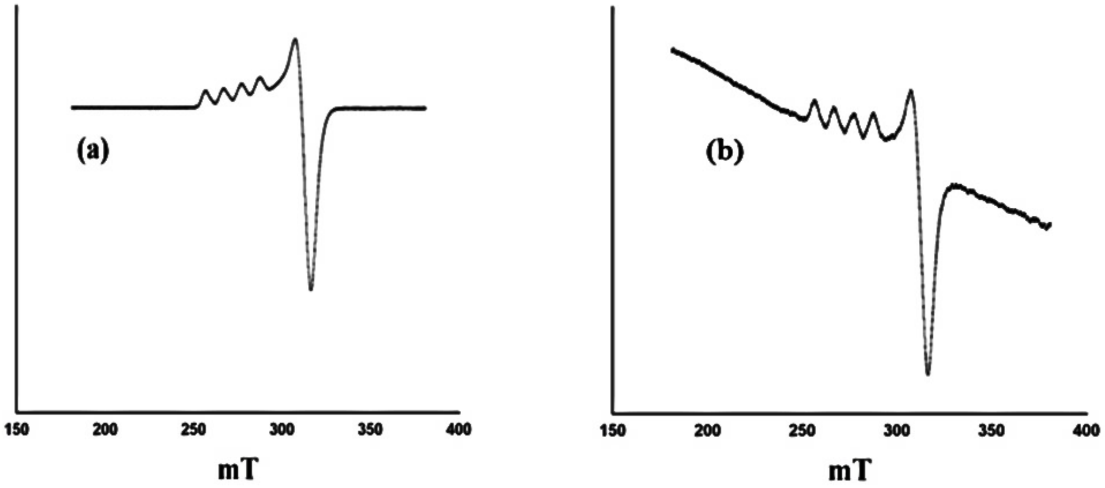

Figure 20. ESR spectra of (a) $MPW_{11}Cu$ and (b) recycled $MPW_{11}Cu$

The UV-Vis spectra (Figure 21) 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.

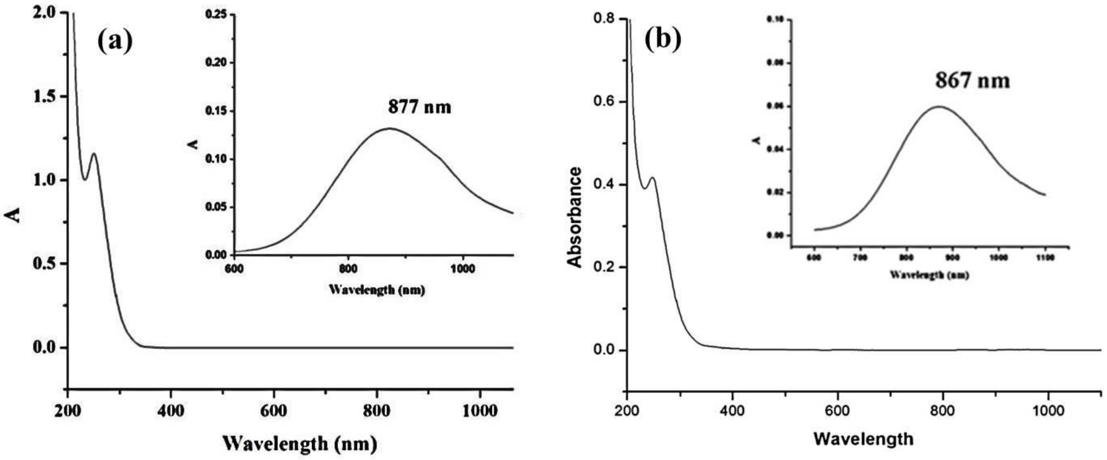

Figure 21. UV-Vis spectra of (a) $MPW_{11}Cu$ and (b) recycled $MPW_{11}Cu$

Comparison of substrates

Table 7. Comparison of substrates

Substrate	% conversion	% selectivity		Activation energy (Ea, kJ/mol)
		Epoxide	Aldehyde/Ketone	
Styrene	54	59	30 / -	64.81
Cis-cyclooctene	12	89	- / 11	105.88

Catalyst amount: 15 mg; Time: 12h; temp: 60 ^{0}C; TBHP: 2 mL

Table 7 shows the comparison of the results of oxidation reaction of the two substrates. It is clearly seen that styrene shows better reactivity compared to cis-cyclooctene which is as expected. This is attributed to the structural morphology of the two substrates. Styrene is a planar open chain alkene while cis-cyclooctene is a non-planar cyclic alkene. Also, because of its bulky and rigid nature, the double bond of cis-cyclooctene can not be broken easily. Hence, activation of the double bond in case of styrene is easier compared to that of cyclooctene.

Conclusion

- $Cs_5[PW_{11}Cu(H_2O)O_{39}].4H_2O$ by traditional one-pot technique as well as a green and sustainable microwave technique. Structure as well as similarity were confirmed by various spectral techniques.
- The synthesized catalysts displayed high selectivity for the respective epoxides, and Ea value 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.
- The catalyst was regenerated and reused thrice without any significant loss in % conversion as well as % selectivity and may be reused for further cycles.

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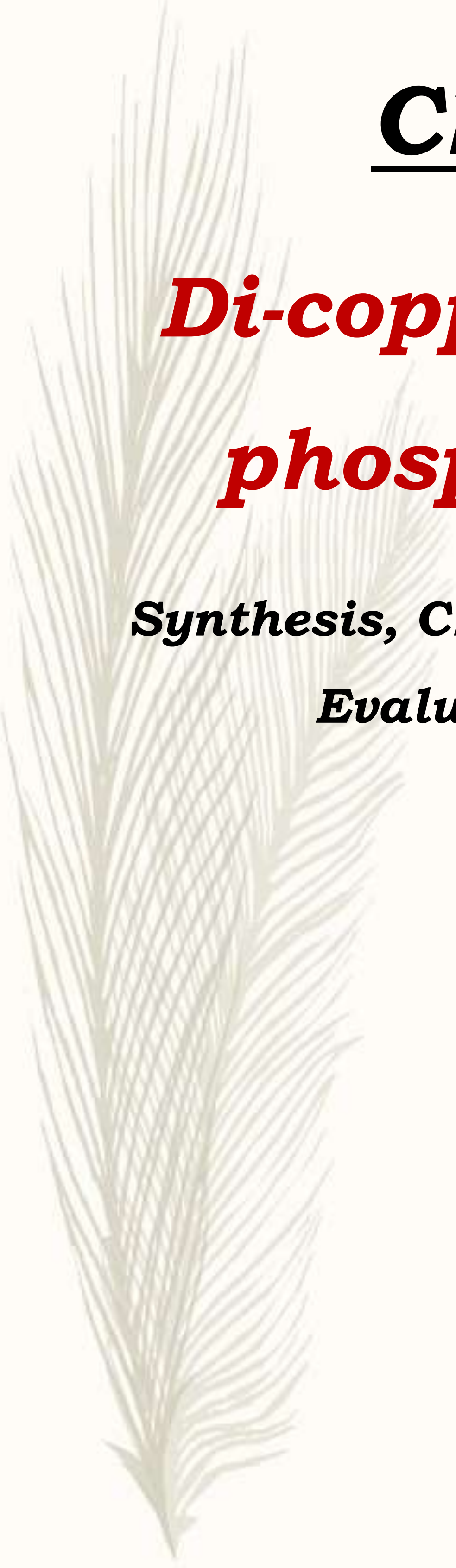
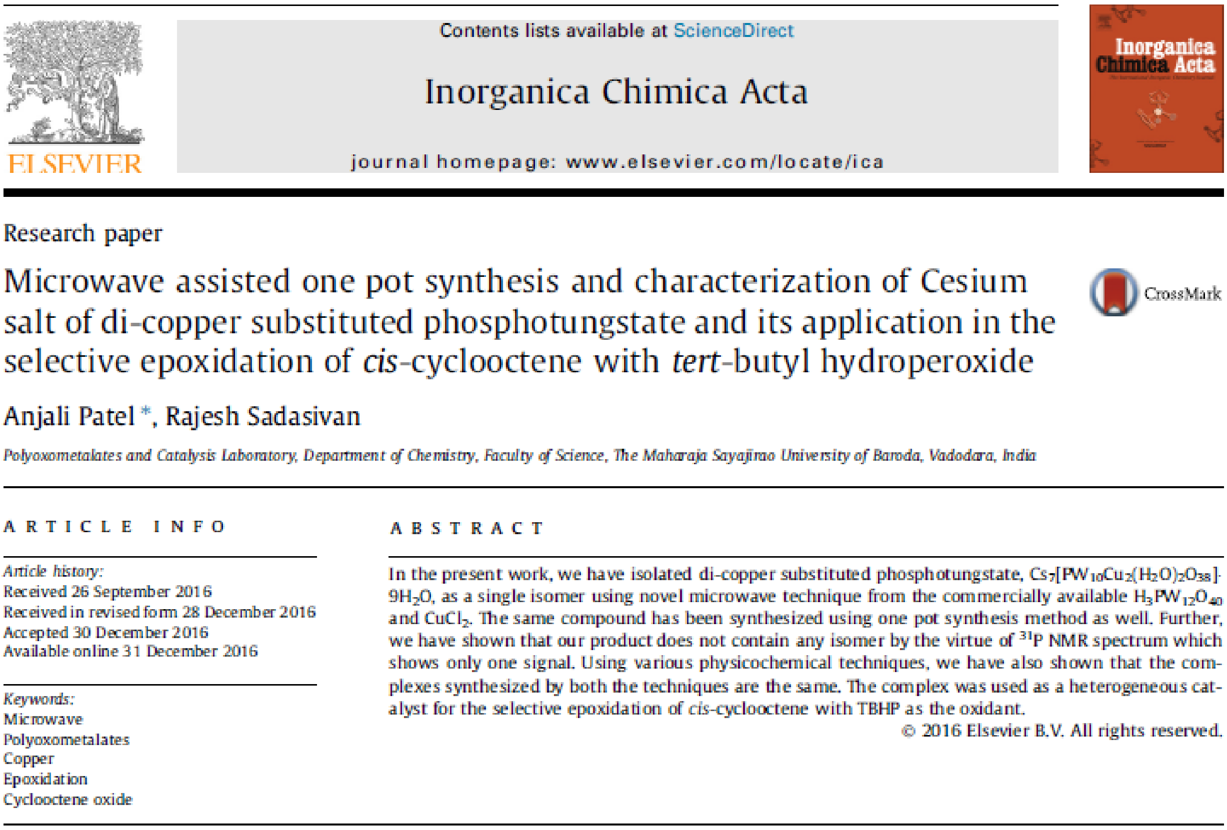


Chapter 2

Di-copper substituted phosphotungstate

Synthesis, Characterization, Catalytic Evaluation and Kinetics



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Research paper

Microwave assisted one pot synthesis and characterization of Cesium salt of di-copper substituted phosphotungstate and its application in the selective epoxidation of *cis*-cyclooctene with *tert*-butyl hydroperoxide

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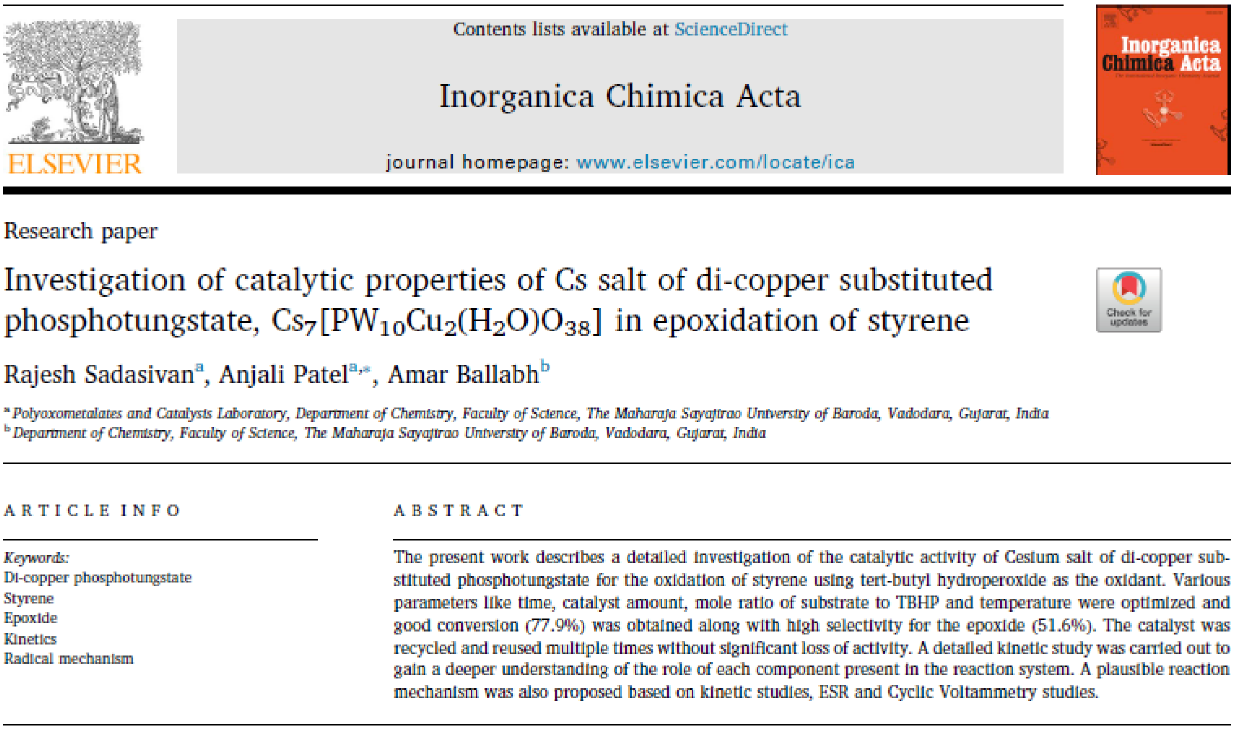
A B S T R A C T

In the present work, we have isolated di-copper substituted phosphotungstate, $Cs_7[PW_{10}Cu_2(H_2O)_2O_{38}]\cdot 9H_2O$, as a single isomer using novel microwave technique from the commercially available $H_3PW_{12}O_{40}$ and $CuCl_2$. The same compound has been synthesized using one pot synthesis method as well. Further, we have shown that our product does not contain any isomer by the virtue of ^{31}P NMR spectrum which shows only one signal. Using various physicochemical techniques, we have also shown that the complexes synthesized by both the techniques are the same. The complex was used as a heterogeneous catalyst for the selective epoxidation of *cis*-cyclooctene with TBHP as the oxidant.



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Research paper

Investigation of catalytic properties of Cs salt of di-copper substituted phosphotungstate, $Cs_7[PW_{10}Cu_2(H_2O)O_{38}]$ in epoxidation of styrene

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A R T I C L E I N F O

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A B S T R A C T

The present work describes a detailed investigation of the catalytic activity of Cesium salt of di-copper substituted phosphotungstate for the oxidation of styrene using tert-butyl hydroperoxide as the oxidant. Various parameters like time, catalyst amount, mole ratio of substrate to TBHP and temperature were optimized and good conversion (77.9%) was obtained along with high selectivity for the epoxide (51.6%). The catalyst was recycled and reused multiple times without significant loss of activity. A detailed kinetic study was carried out to gain a deeper understanding of the role of each component present in the reaction system. A plausible reaction mechanism was also proposed based on kinetic studies, ESR and Cyclic Voltammetry studies.

As discussed in the introduction, even though di-TMSPOMs are gaining significant importance as incorporation of two transition metals can drastically affect the properties and catalytic activity, work carried out on synthesis as well as catalytic applications of monomeric di-TMSPOMs is very scanty. Further, reports specifically on di-copper substituted phosphotungstates are negligible.

In 1987, Finke et al. reported the presence of an unidentified thermolysis product, by FT-IR, during the rational synthesis of $[Cu_4(H_2O)_2(PW_9O_{34})_2]^{10-}$ [1]. They also found that the type of the product obtained depends largely on the experimental conditions such as temperature and time. It was observed as a major product when crystallization was carried at 100 ^{0}C for a longer time. In 1993, Casan-Pastor et al. synthesized $K_{5.5}Na_{1.5}[PW_{10}Cu_2(H_2O)_2O_{38}].13H_2O$ from the trilacunary $Na_8HPW_9O_{34}.19H_2O$ and $CuCl_2$ followed by recrystallization for several weeks [2]. The obtained product was characterized by single crystal XRD analysis and the formula of the anion was proposed as $[PW_{10}Cu_2(H_2O)_2O_{38}]^{7-}$. The FT-IR of the synthesized product was found to be similar to that of Finke's thermolytic compound. From FT-IR, they concluded the presence of two types of distortions of the PO_4 group as a consequence of the presence of two different isomers. Further, they have identified the isomers, relative to the location of the pair of Cu^{2+} ions, by studying the magnetic susceptibility as well as ESR study.

By far, in the last two and a half decades, the above mentioned is the only report available on the di-copper substituted phosphotungstate, despite the distinct advantages of copper. A literature survey also shows that no catalytic study has been carried out for any of the di-substituted phosphotungstates. In this chapter, we describe the synthesis of di-copper substituted phosphotungstate by microwave as well as one-pot techniques. Both the products have been analyzed by various spectroscopic techniques such as FT-IR, ^{31}P NMR, ESR and CV. A comparison of the FT-IR, ESR, ^{31}P NMR and CV data of the products obtained by both the synthetic techniques showed that the products obtained in both the methods are the same. Further the synthesized material has been used for oxidation of alkenes with TBHP as the oxidant under mild reaction conditions. In addition, we report a detailed study of the kinetics for the oxidation of styrene. Based on the kinetics, ESR and CV studies, a mechanism is also proposed.

EXPERIMENTAL

Materials

All chemicals used were of A.R. grade. $H_3PW_{12}O_{40}.nH_2O$, $CuCl_2.2H_2O$, CsCl, dichloromethane, 70% tert-butyl hydroperoxide and NaOH were obtained from Merck. Cis-cyclooctene was obtained from Spectrochem Pvt. Ltd. All chemicals were used as received.

One pot synthesis of di-copper substituted phosphotungstate

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 6.4 using supersaturated $NaHCO_3$ solution. The solution was heated to 100 ^{0}C with stirring. To this hot solution, 0.32 g (2 mmol) of $CuCl_2.2H_2O$ dissolved in minimum amount of water, was added. The solution was refluxed for 2 h at 100 ^{0}C. 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 $RPW_{10}Cu_2$ (Yield-44.6%).

Microwave synthesis of di-copper substituted phosphotungstate

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 6.4 using supersaturated $NaHCO_3$ solution. The solution was heated to 90 ^{0}C with stirring. To this hot solution, 0.32 g (2 mmol) of $CuCl_2.2H_2O$ dissolved in minimum amount of water, was added. The solution was microwaved at 100 ^{0}C for 30 s (Onida PC23 Black Beauty, power output – 800 W) with 5 intervals of 10, 5, 5, 5 and 5 s. 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 $MPW_{10}Cu_2$ (Yield-43.8%).

Catalytic Evaluation

The oxidation reactions of styrene and cis-cyclooctene were carried out following the procedure mentioned in chapter 1.

RESULTS AND DISCUSSION

Catalyst Characterization

Although good quality crystals suitable for single crystal X-ray analysis were not obtained, we have been able to provide enough evidence to show that two Cu(II) centres are present in the lacuna of the phosphotungstate. Tungsten and copper were estimated by Inductive Coupling Plasma-Optical Emission Spectroscopy and Cesium was estimated by Energy Dispersive X-ray Spectroscopy. Their experimental and theoretical values were as follows: Theoretical: W, 49.33; Cu, 3.41; Cs, 24.97. Found ($RPW_{10}Cu_2$): W, 49.82, Cu, 3.64. Found ($MPW_{10}Cu_2$): W, 49.85; Cu, 3.62.

The TGA (Figure 1), shows total weight loss of 5.3% up to 495 ^{0}C, in case of $RPW_{10}Cu_2$ and 5.1% in case of $MPW_{10}Cu_2$, corresponding to 11 H_2O molecules. From the elemental as well as the thermal analysis, the chemical formulae of the isolated complexes obtained are $Cs_7[PW_{10}Cu_2(H_2O)_2O_{38}].9H_2O$.

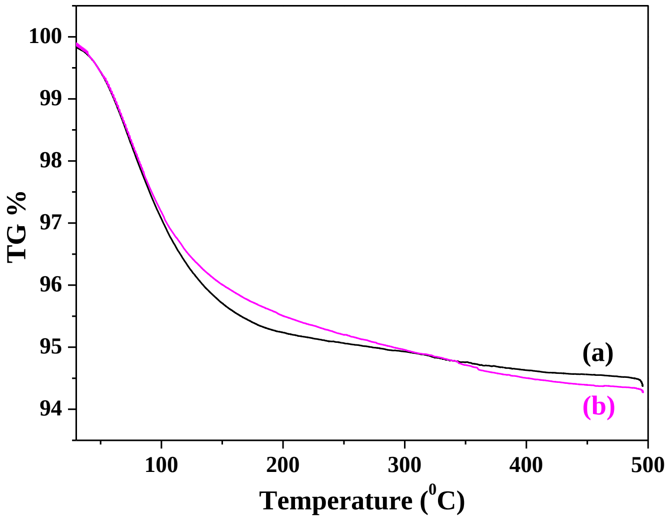


Figure 1. TGA of (a) $MPW_{10}Cu_2$ and (b) $RPW_{10}Cu_2$

It can be seen from Figure 2, that the FT-IR spectra of $RPW_{10}Cu_2$ and $MPW_{10}Cu_2$ are different from that of PW_{12}, but similar to that of PW_{10}. This confirms the presence of PW_{10} in the synthesized compounds. As the characteristic P–O vibration is clearly separated and distinct, the central PO_4 group can be a good probe for the determination of symmetry in a phosphotungstate [3]. The P–O band of PW_{12} splits into three bands in case of both $RPW_{10}Cu_2$ and $MPW_{10}Cu_2$, which is characteristic of PW_{10} [4, 5]. This indicates the presence of di-lacunary phosphotungstate in the compounds synthesized. The three bands also confirm retention of C_{2v} symmetry in the compounds. The shift in the P–O band vibrations compared to PW_{10} may be attributed to incorporation of Cu(II) in the lacuna.

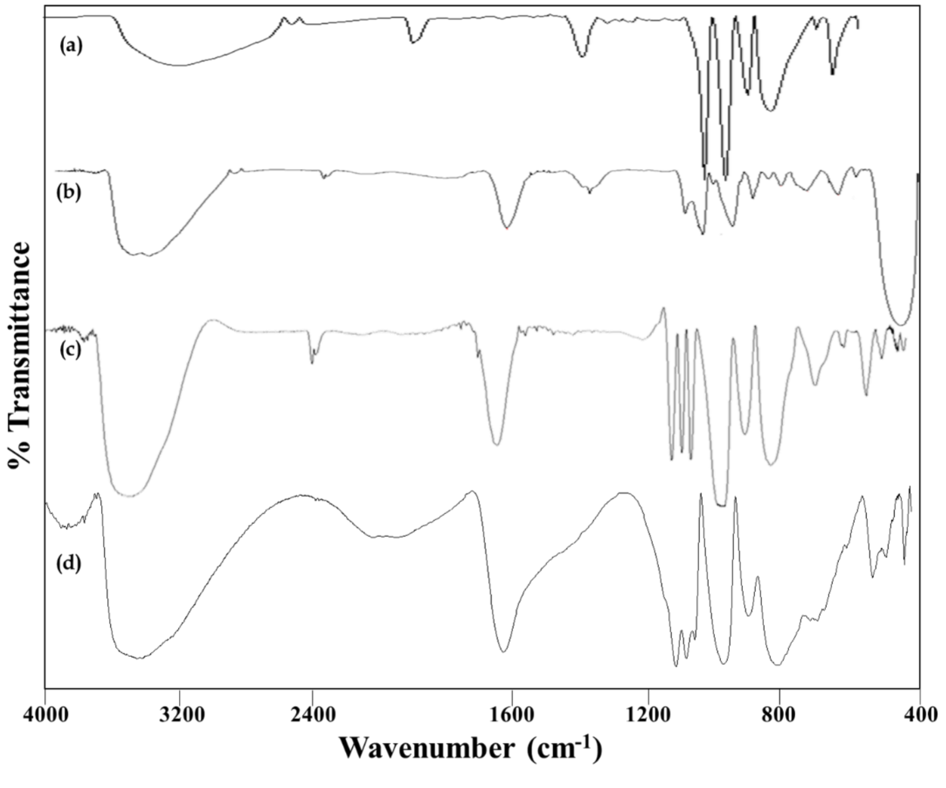


Figure 2. FT-IT spectra of (a) PW_{12}, (b) PW_{10} (c) $RPW_{10}Cu_2$ and (d) $MPW_{10}Cu_2$

Table 1 shows a comparison of the obtained FT-IR data to those reported by Finke et al [1] (1986) and Pastor et al [2] (1993). It can be seen that the FT-IR spectrum of the unidentified compound reported by Finke et al. and the FT-IR spectrum of $K_{5.5}Na_{1.5}[PW_{10}Cu_2(H_2O)_2O_{38}].13H_2O$, synthesized by Pastor et al. are almost similar to that obtained by us, except the fourth band (at about 1140 cm^{-1} in case of Finke and 1150 cm^{-1} in case of Pastor) which is in the form of a shoulder peak. In the present case, it is interesting to note that the compounds synthesized by both, the one pot technique and microwave technique, show only three bands. This indicates the presence of only one isomer, and is in good agreement with Pastor's conclusions [2]. Thus, the FT-IR clearly suggests that we have been able to successfully isolate the unidentified product as a single isomer. This has further been confirmed by ^{31}P NMR.

Table 1. Comparison of P–O bands with reported works.

Band	**FT-IR Wavenumbers (cm^{-1})**			
	Finke et al	**Pastor et al**	**$RPW_{10}Cu_2$**	**$MPW_{10}Cu_2$**
P–O	1140 (sh.) 1110 1060 1040	1150 (sh.) 1105 1070 1030	1102 1072 1044	1101 1072 1044

The ^{31}P NMR spectra of PW_{10}, $RPW_{10}Cu_2$ and $MPW_{10}Cu_2$ are shown in Figure 3. The ^{31}P NMR for PW_{10} shows a chemical shift value at -10.88 ppm which indicates the formation of $[PW_{10}O_{36}]^{7-}$. Apart from this, one more low intensity peak at 1.37 ppm indicates the formation of another species, $[PW_{10}O_{37}]^{7-}$ [3]. Incorporation of two coppers into the lacuna of PW_{10} results in an upfield shift of the peak.

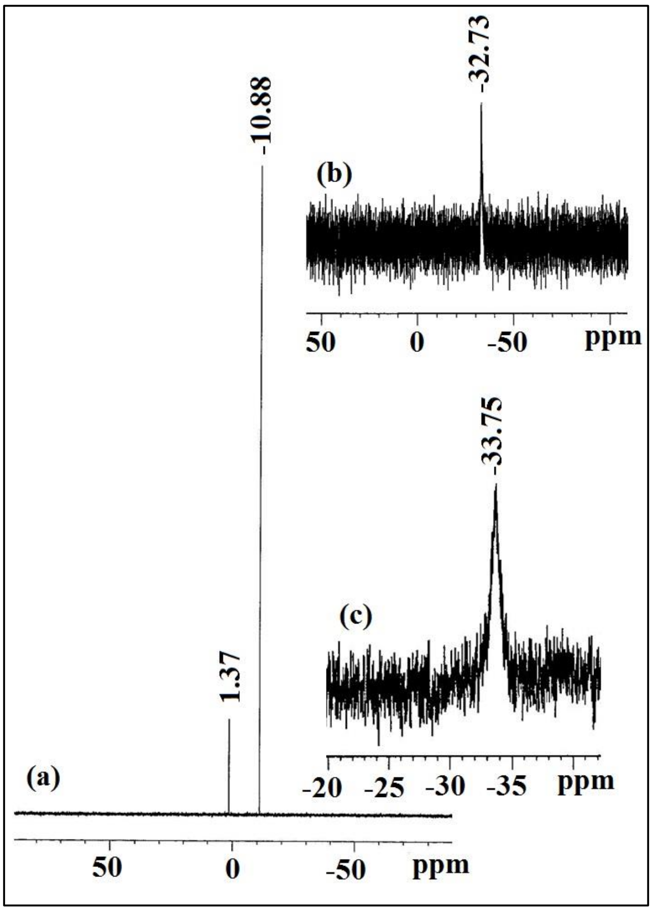


Figure 3. ^{31}P NMR spectra of (a) PW_{10} (b) $RPW_{10}Cu_2$ and (c) $MPW_{10}Cu_2$

A single peak at -32.73 and -33.75 ppm are observed in case of $RPW_{10}Cu_2$ and $MPW_{10}Cu_2$ respectively. The upfield shift and peak broadening in both the cases may be due to paramagnetic d^9 Cu(II) species [6]. Thus, both the synthetic procedures overcome the disadvantage of multiple products that may be formed during the synthesis of desired compound. Further, both $MPW_{10}Cu_2$ and $RPW_{10}Cu_{-}$ give only a single peak confirming the presence of a single isomer.

The UV–Visible spectra of $RPW_{10}Cu_2$ and $MPW_{10}Cu_2$ are shown in figure 4. The peak at 250 nm wavelength indicates presence of the Keggin moiety in the system. In both the cases, the weak broad range peak from 700 to 1100 nm with λ_{max} at around 800 nm was obtained, indicating tetragonal distortion for octahedral Cu (II) in the complex [7].

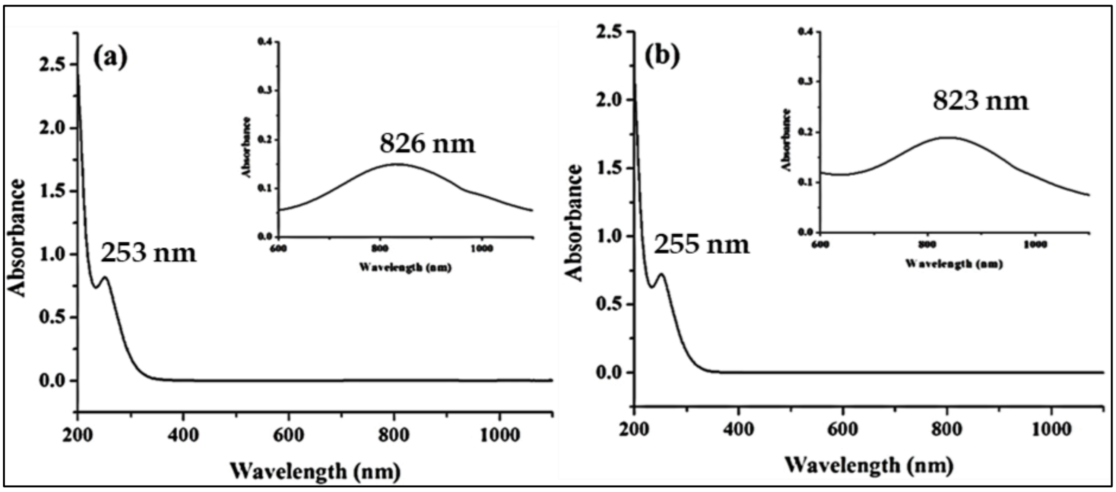


Figure 4. UV-Vis spectra of (a) $MPW_{10}Cu_2$ and (b) $RPW_{10}Cu_2$

Absence of band around 600 nm, typical of tetrahedral Cu(II), shows that Cu(II) exhibits a tetragonally distorted octahedral geometry. This is further confirmed by ESR.

The ESR spectrum of $RPW_{10}Cu_2$ and $MPW_{10}Cu_2$ are shown in the Figure 5. The first important observation is the presence of a half-field signal at about 1500G in both the cases indicating the presence of two copper centres in the same lacuna [8].

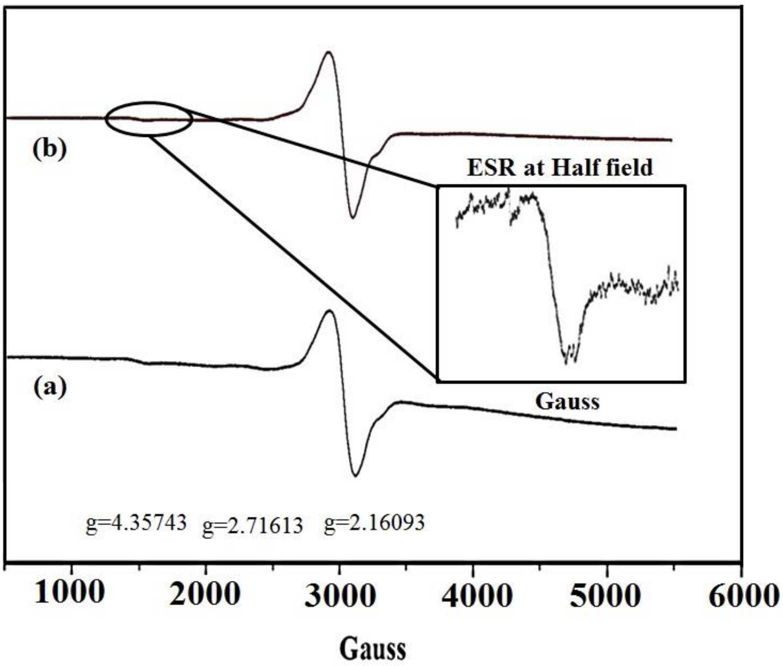


Figure 5. ESR spectra of (a) $MPW_{10}Cu_2$ and (b) $RPW_{10}Cu_2$

Further, the obtained unresolved hyperfine spectra confirms the presence of Cu in a sixfold tetragonal elongated oxygen coordination, as after the incorporation of Cu(II), the rigid and heavy heteropoly anion is unable to govern the actual geometry surrounding the Cu^{2+} ion, also reported by Gudrun Scholez in 1991 [9]. The observed g-values, $g_{\parallel}$ (2.716) > $g_{\perp}$ (2.161) > 2 also proves the existence of Cu^{2+} in a tetrahedrally elongated octahedral environment [10]. The higher value of g, i.e., g > 4 is an indication of strong dipole-dipole contribution than exchange coupling interactions [2]. It also suggests that the local tetragonal axis is aligned parallel or slightly misaligned and consistent with $d_{xy}{}^2$ ground state [11]. In the present case, the calculated value of G is greater than 4 (4.614), indicating that spin-exchange interaction is negligible [2, 12] because of misalignment of the local tetragonal axis.

The powder XRD for PW_{12}, PW_{10}, $RPW_{10}Cu_2$ and $MPW_{10}Cu_2$ are shown in the figure 6. It can be seen, that the powder XRD spectra of $RPW_{10}Cu_2$ and $MPW_{10}Cu_2$ are similar to that of PW_{10} and not PW_{12}, indicating the formation of PW_{10} moiety. Thus, though the starting material used for the synthesis is PW_{12}, formation of PW_{10} species is confirmed. The slight variation in peak intensity may be attributed to the incorporation of Cu into the system. It can be seen that $MPW_{10}Cu_2$ shows crystalline nature, while $RPW_{10}Cu_2$ does not. This also indicates that the product formed by microwave technique may be better when compared to that synthesized by the reflux technique.

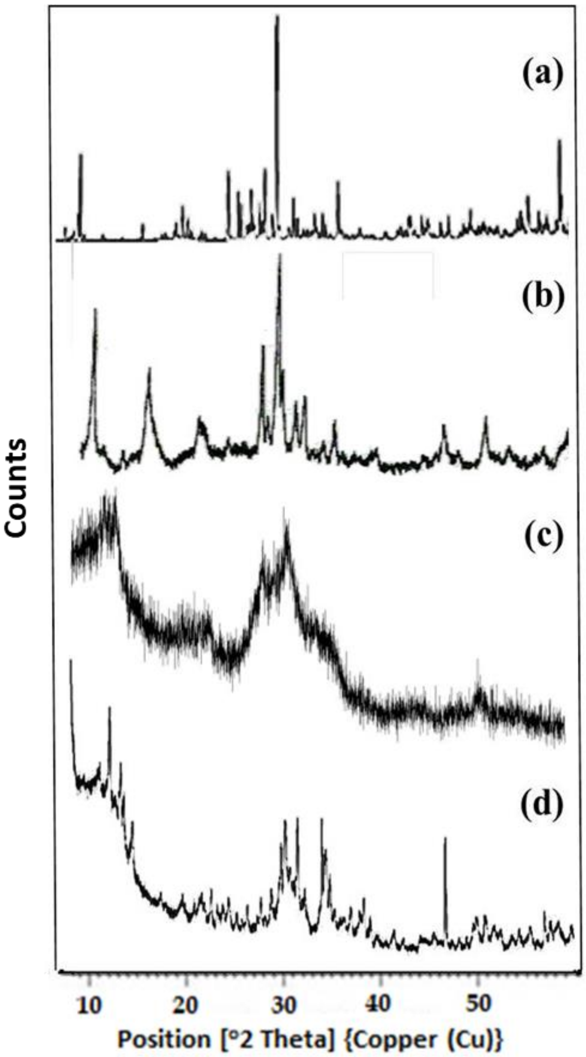


Figure 6. Powder XRD of (a) PW_{12} (b) PW_{10} (c) $RPW_{10}Cu_2$ and (d) $MPW_{10}Cu_2$

The Cyclic Voltammograms of PW_{10}, $RPW_{10}Cu_2$ and $MPW_{10}Cu_2$ are shown in the figure 7. PW_{10} shows reversible redox process with E_{pa} and E_{pc} peaks at -0.65 V and -0.6 V respectively. In case of both $RPW_{10}Cu_2$ and $MPW_{10}Cu_2$, show reversible redox couples at approximately -0.7 V. This indicates presence of PW_{10} moiety.

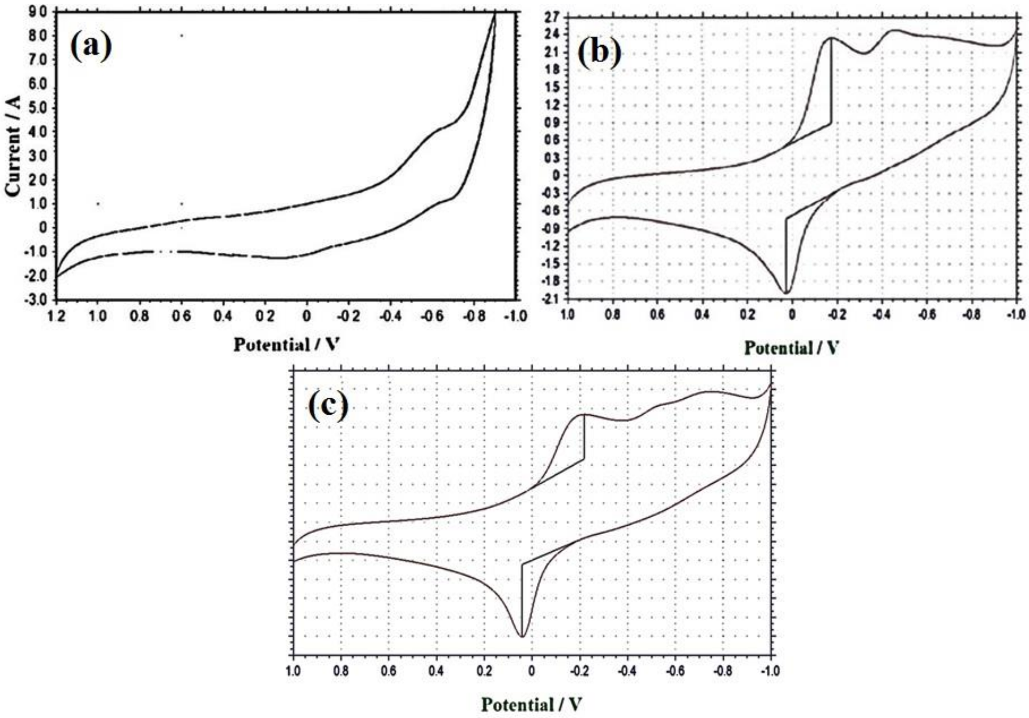


Figure 7. CV of (a) PW_{10}, (b) $MPW_{10}Cu_2$ and (c) $RPW_{10}Cu_2$. Working electrode: Glassy carbon, Reference electrode: Ag/AgCl, Counter electrode: Pt-wire)

The shift may be due to incorporation of Cu(II) in the lacuna. The incorporation of Cu(II) is further confirmed by a quasireversible wave with an anodic peak at 0.03V and a cathodic peak at -0.2 V and an irreversible process at -0.5 V.

Oxidation of styrene

A detailed study on the oxidation of styrene was carried out similar to chapter 1. First, the reaction was monitored at different reaction time (Table 2) and with increase in time from 5 h to 8 h, there is a steady increase in the conversion as well as selectivity of styrene-oxide, but a decrease in the selectivity of benzaldehyde. With further increase in time, the % conversion becomes constant with slight change in epoxide selectivity. This may be attributed to the fact that with increase in time, the reaction tends to proceed towards complete oxidation, thereby forming benzaldehyde and further, benzoic acid. Hence, the reaction time was optimized at 8 h.

Table 2. Effect of time (Catalyst amount – 15 mg; TBHP – 2 mL; Temp – 60 ^{0}C)

Time	% conversion	% selectivity	
		Benzaldehyde	Styrene-oxide
5h	52.2	30.7	56.1
6h	62.3	38.6	51.9
7h	63.9	33.7	51.7
8h	77.9	28.9	51.6
10h	82.8	30.2	34.9
12h	82.8	34.4	32.8
20h	82.9	34.2	32.9

Catalyst amount – 15 mg; Styrene:TBHP – 1:1.5; temp – 60 ^{0}C

Next, the reaction was carried out at different catalyst amounts and the results are shown in figure 8. There is increase in conversion when catalyst amount is increased from 10 mg to 15 mg. but after that, there is a significant decrease in conversion of styrene as well as selectivity of epoxide. Hence, the amount of catalyst was optimized to 15 mg.

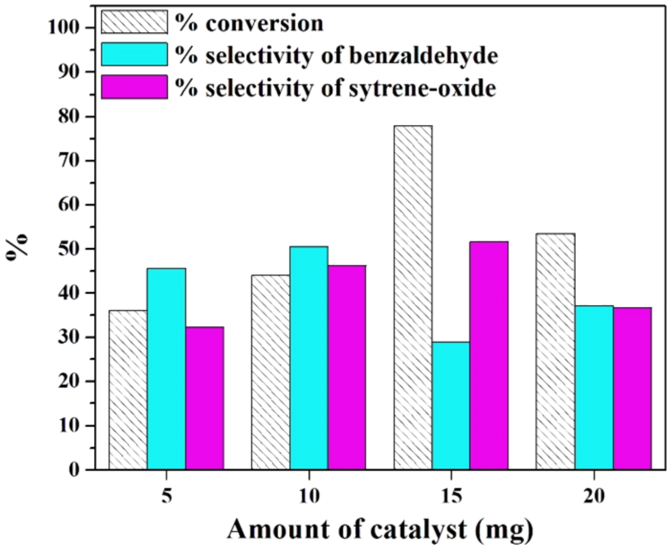


Figure 8. Effect of catalyst amount (Time–8h; temp–60 ^{0}C; Styrene:TBHP–1:1.5)

The effect of amount of TBHP was determined by varying the mole ratio of styrene to TBHP (1:1.5 to 1:3). There is an increase in conversion of styrene with increase in TBHP amount. However, there is also a decrease in the selectivity of the desired products. As mentioned in Chapter 1, excess TBHP implies higher concentration of oxygen source, thereby resulting in complete oxidation of epoxide to benzaldehyde and further to benzoic acid. From this view point, mole ratio of 1:1.5 was considered as optimum, which corresponded to 2 mL of TBHP (Figure 9).

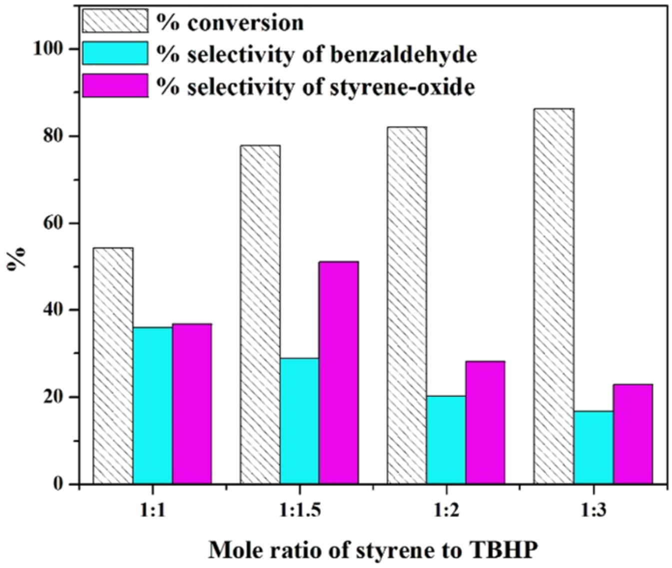


Figure 9. Effect of mole ratio (catalyst amount – 15 mg; temp – 60 ^{0}C; time – 8h)

Finally, the reaction temperature was optimized (Figure 10) and with increase in the temperature from 50 °C to 60 °C, there is an increase in conversion as well as selectivity of styrene-oxide. But on increasing temperature from 60 ^{0}C to 80 ^{0}C, there is a significant decrease in the selectivity of benzaldehyde as well as styrene-oxide. Hence, temperature was optimized at 60 ^{0}C.

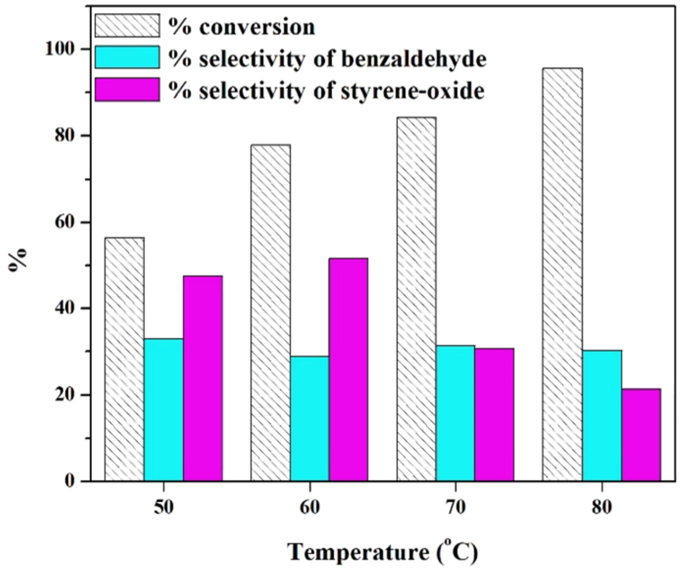


Figure 10. Effect of temperature (catalyst amount – 15 mg; time – 8h; Styrene:TBHP – 1:1.5)

The optimized conditions are as follows: catalyst amount – 15 mg (Active amount of Cu – 0.51 mg); reaction time – 8 h; TBHP – 2 mL; reaction temperature – 60 ^{0}C

Oxidation of cis-cyclooctene

A detailed study of oxidation of cis-cyclooctene was carried out using $MPW_{10}Cu_2$ as catalyst and TBHP as the oxidant, similar to chapter 1.

The effect of reaction time was studied by varying the time and keeping all other parameters constant. With increase in time from 14 h to 20 h, there is a steady increase in conversion and selectivity of the epoxide. With increase in time to 24 h, the conversion increases, but selectivity of epoxide decreases (Figure 11a). Hence, time was optimized at 20 h.

Next, with increase in catalyst amount from 10 mg to 15 mg, there is increase in conversion and selectivity. But, with further increase, there is a decrease in selectivity of the epoxide (Figure 11b). Hence 15 mg catalyst was taken as optimum.

The ratio of the substrate to oxidant was varied keeping all other parameters constant. It was found that with increase in the ratio from 1:1.5 to 1:3, an increase in conversion of cyclooctene is seen, but there in a decrease in the selectivity of epoxide (Figure 11c). Hence, 1:1.5 was taken as the optimum ratio.

To know the effect of temperature on catalytic activity, the reaction was carried out at three different temperatures. From 60 ^{0}C to 80 ^{0}C, there is a linear increase in conversion, but a decrease in the selectivity of cyclooctene oxide with an increase in unwanted products (Figure 11d). Hence, 60 ^{0}C was chosen to be the optimum temperature for the reaction.

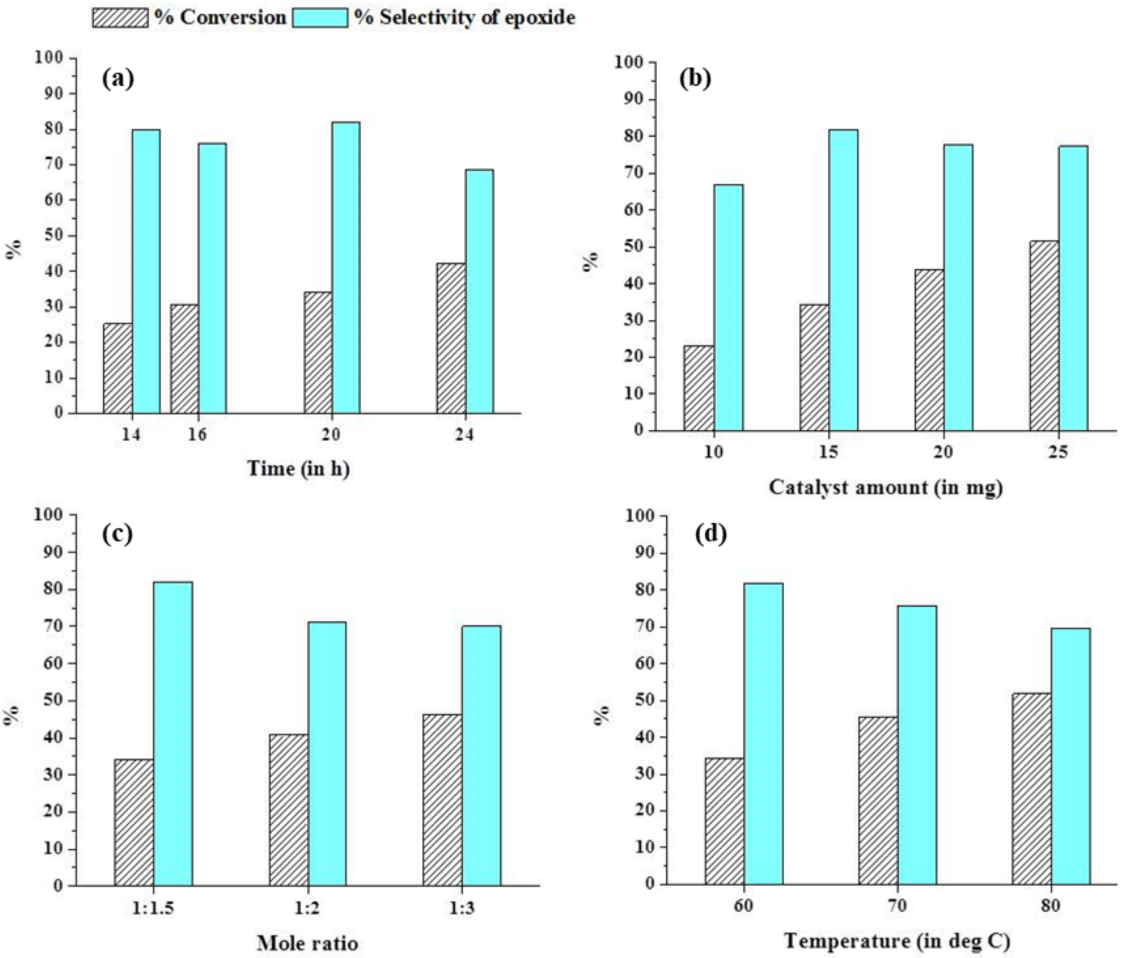


Figure 11. Optimization of parameters for oxidation of cis-cyclooctene (a) Effect of time: mole ratio (cis-cyclooctene to TBHP) (1:1.5), amount of Catalyst (15 mg), temp. (60 ^{0}C); (b) Effect of Catalyst amount: mole ratio (1:1.5), temp. (60 ^{0}C), time (20 h); (c) Effect of mole ratio: amount of Catalyst (15 mg), temp. (60 ^{0}C), time (20 h); (d) Effect of temperature: mole ratio (1:1.5), amount of Catalyst (15 mg), time (20 h).

The optimized conditions are as follows: catalyst amount – 15 mg (Active amount of Cu – 0.51 mg); reaction time – 20 h; TBHP – 2 mL; reaction temperature – 60 ^{0}C

Role of TBHP

Experiments similar to those described in chapter 1 were performed to understand the role of TBHP in the present system (Figure 12). Results obtained are similar to those of $PW_{11}Cu$, indicating that both TBHP as well as the catalyst are essential for the higher selectivity of epoxide. It is interesting to note that selectivity of epoxide with $PW_{10}Cu_2$ catalyst is double that of $PW_{11}Cu$, further confirming that Cu(II) is the active species in the catalyst. Also, the rate of reaction shows direct dependence on concentration of TBHP.

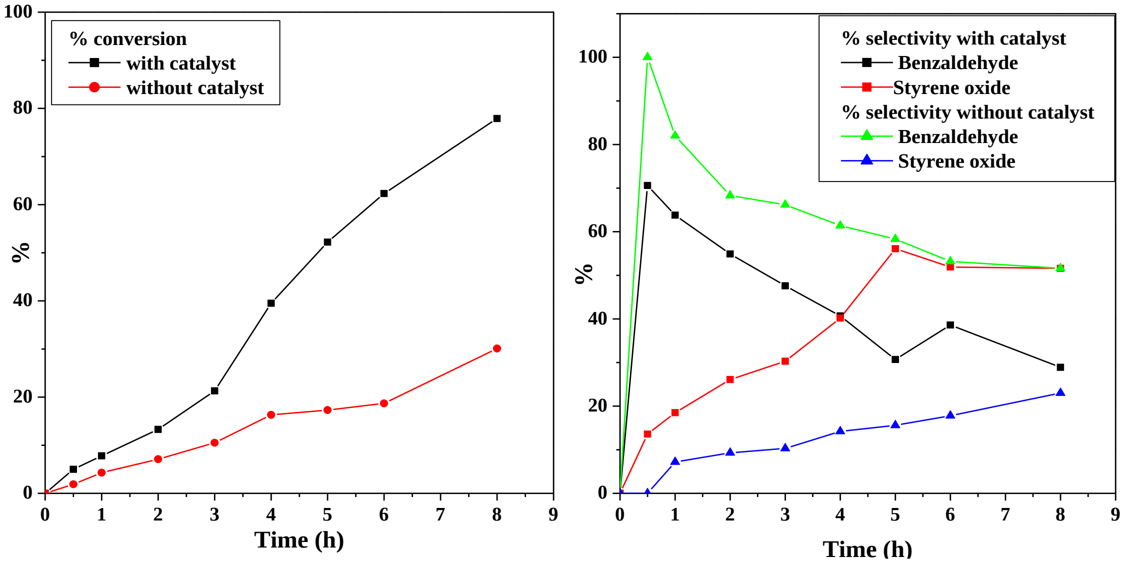


Figure 12. Role of TBHP in oxidation of styrene in the presence and absence of catalyst (a) conversion and (b) selectivity

Similar experiments were carried out for cis-cyclooctene, and the results obtained were also similar to those of styrene, confirming the significance of the role that TBHP plays in the reaction.

Leaching and Heterogeneity

Like $PW_{11}Cu$, in the present case too, UV Visible spectra of the reaction mixture showed absence of characteristic Cu absorption peaks indicating that Cu does not leach out of the catalyst during the course of the reaction.

Table 3. Heterogeneity test

Substrate	Reaction time	% conversion	% selectivity	
			Epoxide	Aldehyde/Ketone
Styrene [a]	5 h	52	31	56
	8 h (Filtrate)	53	30	56
Cis-cyclooctene [b]	14 h	25.2	80.0	20.0
	16 h (Filtrate)	25.7	80.6	19.4

[a] Catalyst amount: 15 mg; Time: 8h; temp: 60 ^{0}C; TBHP: 2 mL.
[b] Catalyst amount-15 mg; Mole ratio 1:1.5; Temperature–60 ^{0}C

Heterogeneity test was carried out as mentioned in chapter 1. No change in the conversion as well as selectivity of the products (Table 3) after removal of catalyst indicates that the catalyst is truly heterogeneous in nature for both the reactions.

Control experiments

A set of control experiments for oxidation of styrene with $CsPW_{10}$, $CuCl_2$ and $MPW_{10}Cu_2$ were carried out and the results are presented in table 4. On using the metal salt $CuCl_2$ as catalyst, 53% conversion and 55% selectivity for benzaldehyde was observed, indicating that copper plays a major role in the catalysis. The present catalyst, $MPW_{10}Cu_2$, gave 78% conversion with 52% selectivity for epoxide. The higher conversion, higher selectivity of epoxide as well as the higher turnover number may be due to synergic effect between Cu ion and PW_{10}. In addition, $MPW_{10}Cu_2$ is a better catalyst as compared to the metal salt for the following reasons: (i) it is heterogeneous in nature and can be regenerated and reused multiple times and (ii) it gives higher conversion with higher selectivity for the epoxide.

Similar experiments were carried out for the oxidation of cis-cyclooctene. The conversion in case of $CuCl_2$ may also be due to the fact that the electron withdrawing nature of chloride stabilizes the reduction of Cu(II), thus facilitating oxidation of the reactant [13].

Although $MPW_{10}Cu_2$ and $CuCl_2$ give comparable results, the present catalyst exhibits better selectivity for the epoxide as well as is heterogeneous in nature, hence can be recovered easily.

Table 4. Control experiments

Catalyst	[i] Styrene oxidation % Conv. (Ald / Epo)	[ii] Cis-cyclooctene oxidation % Conv. (Epo / Ket)	Turn Over Number (i/ii)
No catalyst	30 (59 / 22)	N.A.	-/-
$CsPW_{10}$[a]	31 (56 / 22)	4.3 (78 / 22)	-/-
$CuCl_2$ [b]	53 (55 / 28)	34 (71 / 12)	653/414
$MPW_{10}Cu_2$ [c]	78 (29 / 52)	34 (81 / 19)	1952/851
$RPW_{10}Cu_2$ [c]	78 (29 / 51)	34 (82 / 18)	1952/851

i. Styrene oxidation. Catalyst amount: [a] 13.16 mg; [b] 1.37 mg (active amount of Cu: 0.51 mg); [c] 15 mg (active amount of Cu: 0.51 mg); Time: 8h; temp: 60 ^{0}C; TBHP: 2 mL.

ii. Cis-cyclooctene oxidation. Catalyst amount: [a] 13.16 mg; [b] 1.37 mg (active amount of Cu: 0.51 mg); [c] 15 mg (active amount of Cu: 0.51 mg); Temp – 60 ^{0}C; Time – 20h; TBHP – 2 mL

Kinetic studies

As in chapter 1, a detailed kinetic study was carried out keeping in mind the effect of each component on the rate of reaction. Experiments were carried out with different initial concentrations of the substrates and TBHP, keeping the catalyst amount constant. A relation was obtained between the individual concentration of reactants and time using the equation 1 (Chapter 1) [14]. A plot of log[(b-x)/(a-x)] versus time shows a straight line (Figure 13), indicating that the reaction is first order with respect to both the substrates and TBHP, individually.

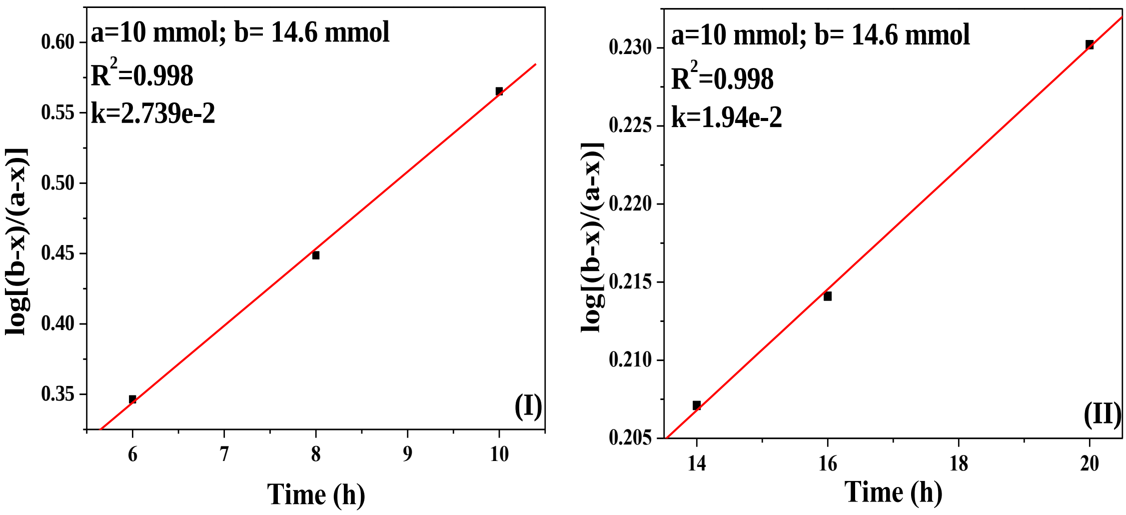


Figure 13. Plot of log[(b-x)/(a-x)] versus time for oxidation of (I) styrene and (II) cis-cyclooctene

A similar experiment was then carried out where concentration of the substrates as well as TBHP concentration were the same. A relationship between the concentration and time was obtained using the equation 2 (Chapter 1) [14].

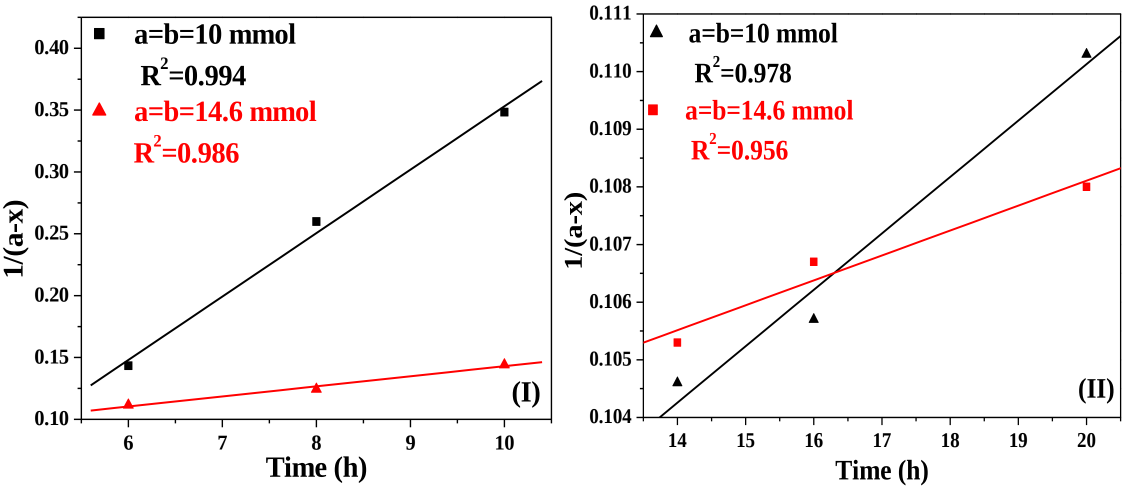


Figure 14. Plot of 1/(a-x) versus time for oxidation of (I) styrene and (II) cis-cyclooctene

Here too, 1/(a-x) shows a linear relationship with time (Figure 14), indicating that the reaction follows second order overall with respect to concentration of the substrates and TBHP.

The effect of reaction rate with respect to catalyst concentration was studied and is shown in figure 15. When the concentration is increased, there is a linear increase in rate of the reaction. This confirms that the reaction follows first order kinetics with respect to catalyst concentration as well.

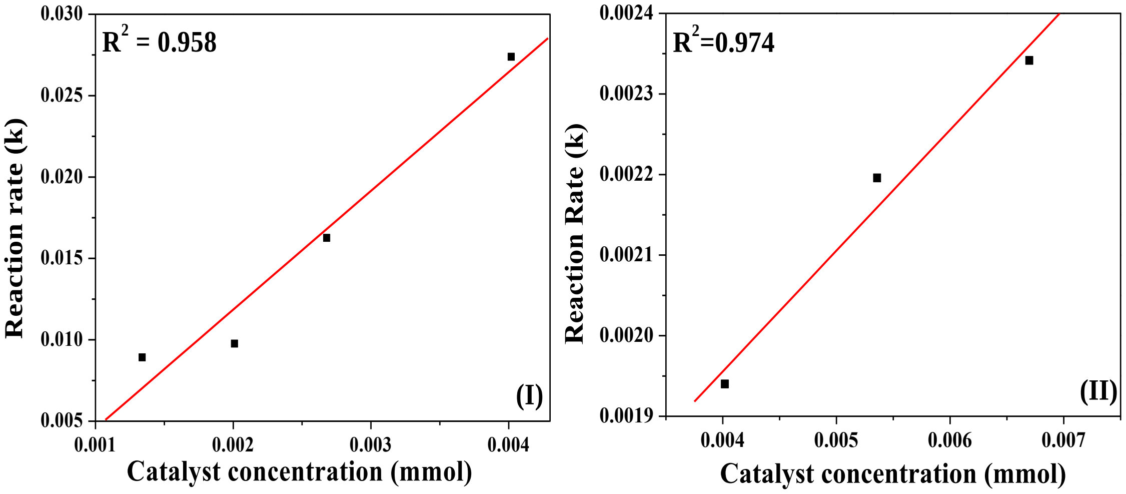


Figure 15. Plot of rate of reaction versus catalyst concentration for oxidation of (I) styrene and (II) cis-cyclooctene

Determination of Activation Energy

Experiments were carried out at different temperatures and a gradual increase in conversion of both substrates is seen with increase in temperature from 323K to 353K. Thus, a plot of 1/T versus lnk shows linear relationship (Figure 16), and the activation energy was evaluated using the Arrhenius equation. Significantly higher activation energies of 57.64 kJ/mol for styrene oxidation and 82.57 kJ/mol for cyclooctene oxidation indicate that the reaction is truly governed by a chemical step in both the case and also that the catalyst has been exploited to its maximum capacity.

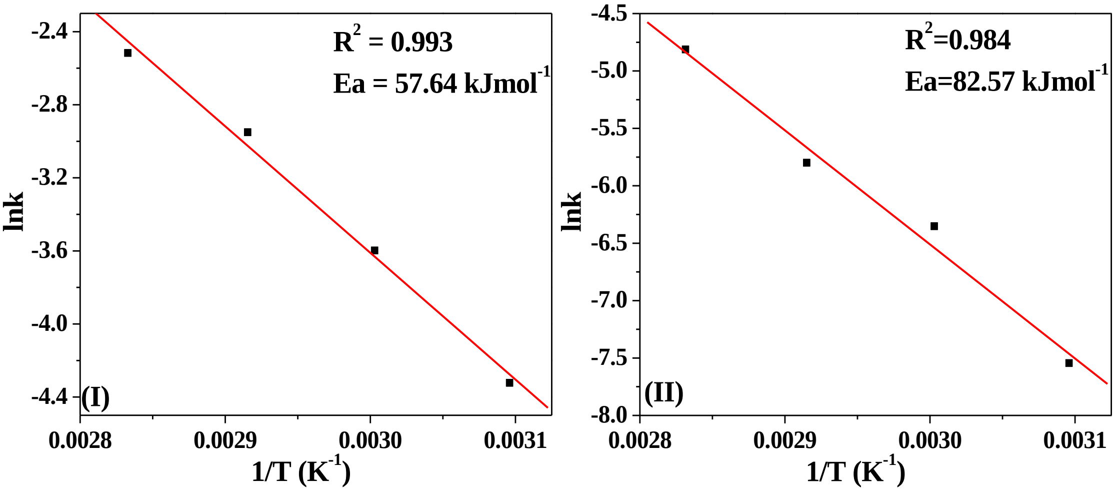


Figure 16. Plot for determination of activation energy for oxidation of (I) styrene and (II) cis-cyclooctene

Mechanistic study

Like in chapter 1, detailed ESR studies were carried out in order to confirm whether the reaction involves oxygen transfer or electron transfer. Figure 17 shows, (a) ESR of fresh catalyst (b) ESR spectra of the catalyst after 5h of the reaction, (c) ESR spectra of the catalyst after 8h of the reaction, (d) ESR spectra of the catalyst after 20h of the reaction and (e) ESR spectra of the regenerated catalyst. In the first three cases, the catalyst was taken from the reaction mixture, dried and directly analysed without washing. The regenerated catalyst was washed with methanol, dried and then analysed.

Figure 17b gives a hyperfine five line splitting which is well known for a species containing a single Cu(II) [8]. This indicates that one of the two Cu(II) in the complex has reduced to Cu(I), thereby becoming ESR inactive. Thus, only one of the two coppers in the catalyst takes part in the epoxidation reaction.

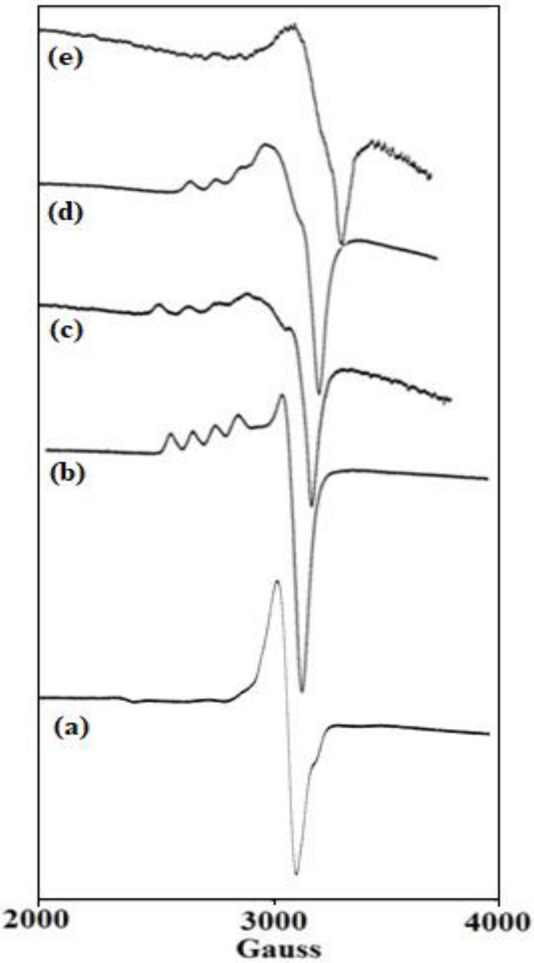


Figure 17. ESR spectra of $MPW_{10}Cu_2$ (a) fresh (b) after 5h (c) after 8h (d) after 20h and (e) regenerated catalyst

Figures 17c and 17d show the ESR of the catalyst after 8h and 20h of the reaction respectively. In these cases, the five line splitting is seen, but the hyperfine structure is lost. This is attributed to the fact that there is a formation of a mixed valent Cu(II)–Cu(I) species. The unpaired electron present in the copper not taking part in the reaction gets delocalized between the two coppers in the system. Further, the copper in its lower oxidation state, Cu(I), is stabilized by the large POM unit. This may be the reason for the higher stability of the intermediate species, thereby resulting in higher conversion of styrene and selectivity of epoxide. Finally, figure 16e shows the ESR spectrum of recycled catalyst. Here we see that the unresolved hyperfine structure of $MPW_{10}Cu_2$ is obtained back, indicating the regeneration of the original catalyst.

These results have further been supported by Cyclic Voltammetry. Though cyclic voltammetry is unable to confirm the number of copper ions in the system, it confirms that at least one copper ion exists in the Cu(II) state, thereby proving the fact that only one copper takes part in the reaction. The cyclic voltammogram of the catalyst after 5h (Figure 18a) of the reaction shows a two-step one electron reduction from Cu(II) to Cu(I) and then from Cu(I) to Cu(0) followed by a one-step two electron oxidation from Cu(0) to Cu(II). This indicates that one of the two Cu(II) remains in the 2+ oxidation state. Similar results are obtained in case of the catalyst taken 10h after the reaction (Figure 18b) and the recycled catalyst (Figure 18c).

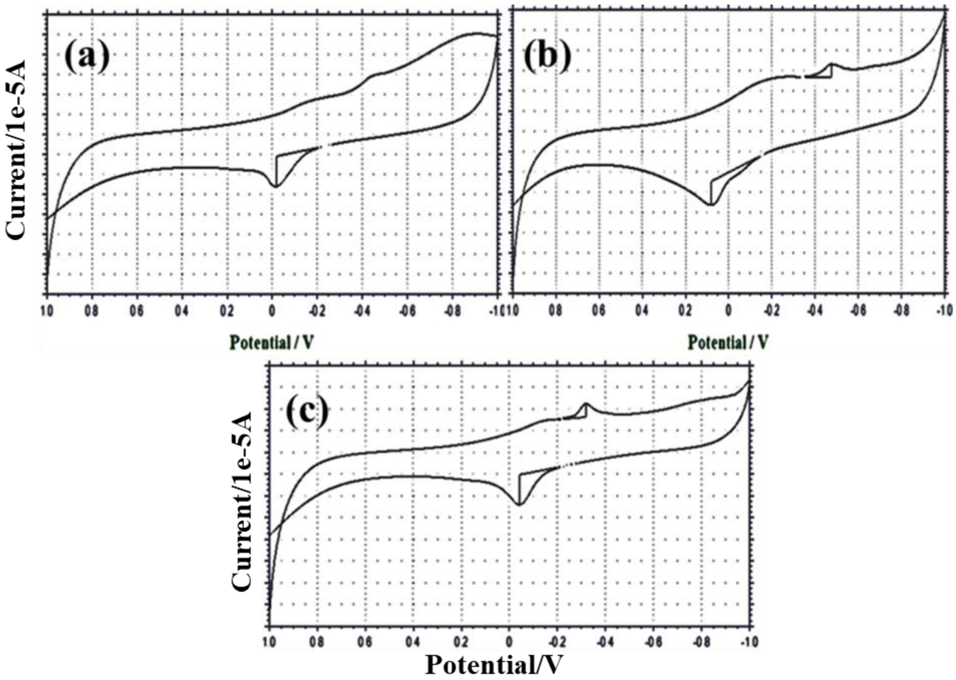


Figure 18. Cyclic Voltammogram of $MPW_{10}Cu_2$ (a) after 5h (b) after 10h and (c) recycled catalyst

To confirm the presence of Cu(I), copper was estimated in the fresh catalyst as well as after 5h of the reaction by iodometric titrations. It can be seen from table 5, that the experimental value for the amount of Cu(II) in the fresh catalyst is 0.50 mg, almost the same as that of theoretical value. After 5h of the reaction, the amount of Cu(II) is 0.21 mg. This further supports the conclusion obtained from

ESR and CV. At this stage, it is not possible to comment on the exact amount of Cu(I). However, we believe that almost half of the Cu(II) may be reduced to Cu(I).

Table 5. Estimation of Cu(II) by iodometric titration

System	Theoretical value	Calculated value
Fresh Catalyst	0.51 mg	0.50 mg
After 5h of the reaction	0.25 mg	0.21 mg

2,6-di-tert-butyl-4-methylphenol was added as radical scavenger after 5h of the reaction after which the reaction was allowed to run for further 3h and the results are presented in table 6. No significant increase in the conversion of styrene indicated that the reaction proceeds via formation of a radical intermediate.

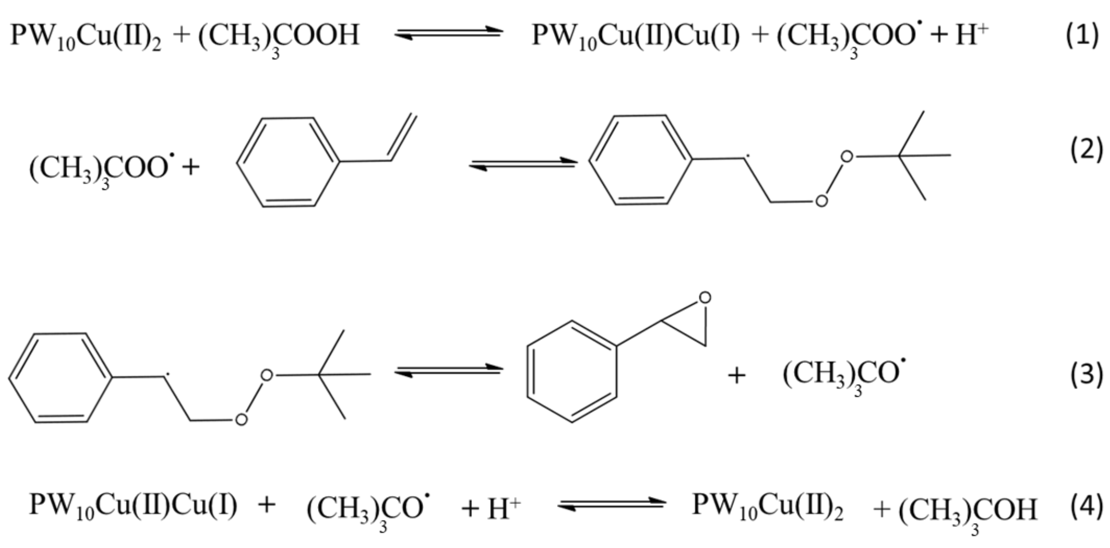
Table 6. Inhibition Experiment with 2,6-di-tert-butyl-4-methylphenol as radical scavenger

Condition	% conversion	% selectivity	
		Benzaldehyde	Styrene-oxide
After 5 h	52.2	30.7	56.1
After 8 h (after scavenger addition)	52.5	33.5	50.2

Catalyst amount: 15 mg; temp: 60 ^{0}C; TBHP: 2 mL

In the present case, as in chapter 1, we believe the formation of radical occurs via reduction of Cu(II) to Cu(I). The radical reacts with styrene to give a radical intermediate, which then rearranges to give styrene-oxide and tert-butoxyl radical. This then oxidizes Cu(I) back to Cu(II) and forms tert-butyl alcohol, which is released as by-product.

The proposed mechanism is presented in scheme 1. The valence state of the metal was maintained at Cu(II) and Cu(I) as shown by the ESR and CV studies. Though, we propose that the reduction of Cu(II) to Cu(I) in the catalyst leads to the radical initiation process, we cannot ignore the fact that tungsten helps in stabilizing the intermediate, and is indirectly involved in the reaction mechanism.



Scheme 1. Proposed mechanism for oxidation of styrene using TBHP

Radical scavenger experiment was carried out for oxidation of cis-cyclooctene and similar results indicated that the reaction follows radical mechanism, as expected (Table 7).

Table 7. Inhibition Experiment with 2,6-di-tert-butyl-4-methylphenol as radical scavenger for oxidation of cis-cyclooctene

Condition	% conversion	% selectivity	
		Cyclooctene-oxide	Cyclooctanone
After 16 h	31	76	24
After 20 h (after scavenger addition)	32	75	25

Catalyst amount: 15 mg; temp: 60 ^{0}C; TBHP: 2 mL

Regeneration and recycling

Regeneration of catalyst was carried out as mentioned in chapter 1 and the results are presented in table 8. Negligible change in conversion as well as selectivity of desired product in both the cases indicates the catalyst can be reused for multiple times.

Table 8. Recycle study

Catalyst	% conversion	% selectivity	
		Epoxide	Aldehyde/Ketone
$MPW_{10}Cu_2$	[a]78/[b]34	[a]52/[b]81.9	[a]29/ [b]18.1
R_1- $MPW_{10}Cu_2$	[a]78/ [b]32	[a]52/ [b]81	[a]29/ [b]19
R_2- $MPW_{10}Cu_2$	[a]78/ [b]32	[a]51/ [b]80	[a]29/ [b]20
R_3- $MPW_{10}Cu_2$	[a]77/ [b]31	[a]50/ [b]79.7	[a]31/[b]20.3

[a] Catalyst amount: 15 mg; Time: 8h; Temp: 60 ^{0}C; TBHP: 2 mL.

[b] Catalyst amount-15 mg; Mole ratio 1:1.5; Temperature–60 ^{0}C; Time–20h

Characterization of regenerated catalyst

The regenerated catalyst was characterized by ESR, FT-IR and CV. The ESR spectrum of recycled catalyst shows an unresolved hyperfine spectrum, indicating the regeneration of the original material (Figure 19).

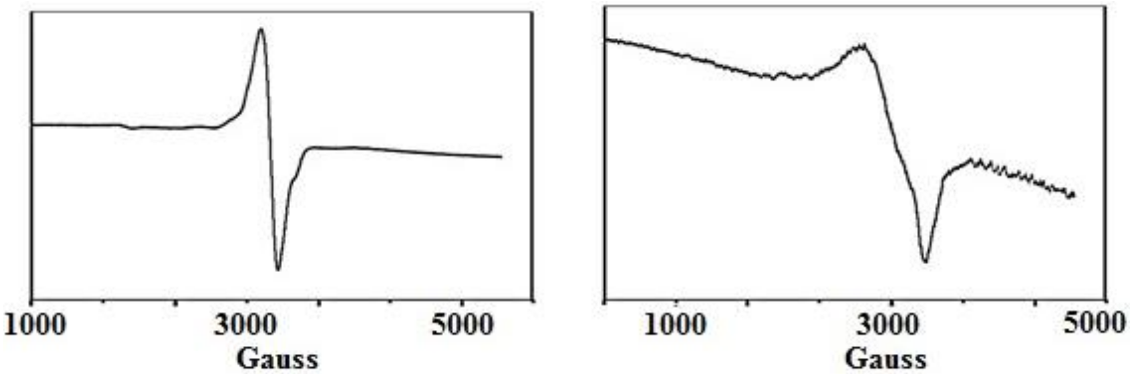


Figure 19. ESR spectra of (a) Fresh $MPW_{10}Cu_2$ and (b) Recycled $MPW_{10}Cu_2$

The FT-IR spectra of regenerated catalyst (Figure 20) shows characteristic bands at 1103, 1072, 1049 cm^{-1} corresponding to P-O bond, 956 cm^{-1} corresponding to W=O bond, 879, 802 cm^{-1} corresponding to W-O-W bonds and 516 cm^{-1} corresponding to the Cu-O bond. No significant shift in the wavelengths indicate that there is no change in the structural morphology of the catalyst and the catalyst does not degrade during the course of the reaction.

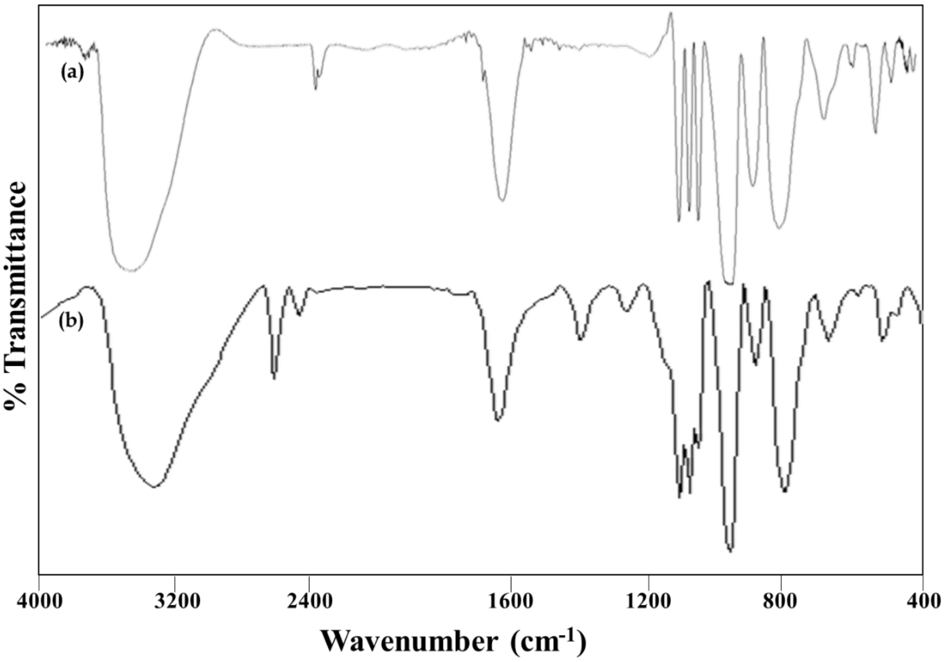


Figure 20. FT – IR spectra of $MPW_{10}Cu_2$ (a) Fresh and (b) Recycled

The cyclic voltammograms of both fresh and recycled $MPW_{10}Cu_2$ are similar, as seen in figure 21. We can clearly interpret that the quasireversible peak is retained in the recycled complex, thereby confirming that the catalyst is regenerated after the reaction.

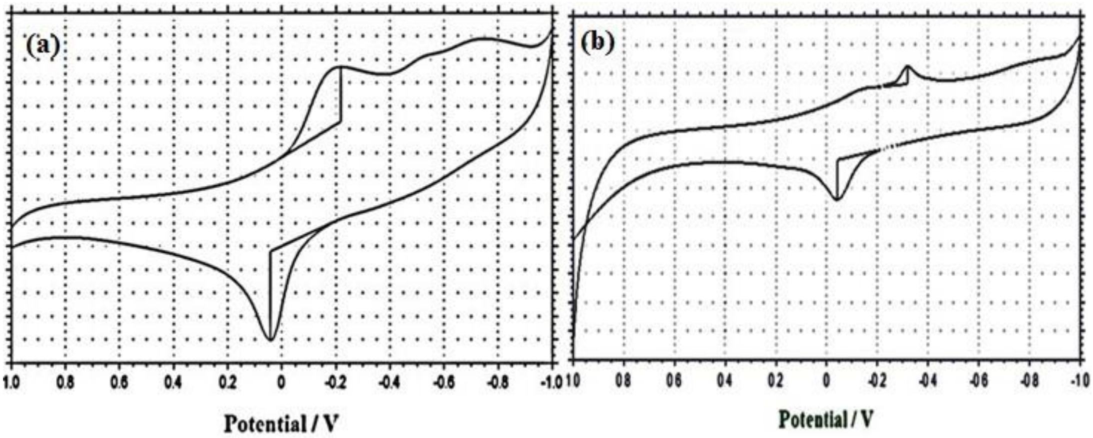


Figure 21. CV of (a) Fresh $MPW_{10}Cu_2$ and (b) Recycled $MPW_{10}Cu_2$

Comparison of substrates

Table 9. Comparison of substrates

Substrate	% conversion	% selectivity		Activation energy (Ea, kJ/mol)
		Epoxide	**Aldehyde/Ketone**	
Styrene	78	52	29	57.64
Cis-cyclooctene	16	73	26	82.57

Catalyst amount: 15 mg; Time: 8h; temp: 60 ^{0}C; TBHP: 2 mL

Table 9 shows the comparison of the results of oxidation reaction of the two substrates. Like in case of $PW_{11}Cu$, styrene shows better reactivity compared to cis-cyclooctene as expected. Due to the difference in structural morphology of the two substrates as well as the bulkiness and regidity of the cyclic alkene, activation of the double bond in case of styrene is easier compared to that of cyclooctene.

Conclusion

- $Cs_7[PW_{10}O_{38}Cu_2(H_2O)_2].9H_2O$ was successfully synthesized from commercially available 12-tungstophosphoric acid by one-pot as well as microwave techniques.
- Spectral characterizations confirmed incorporation of two Cu(II) units into the two lacuna and also established that the materials synthesized from both techniques are the same.
- Catalytic evaluation of the materials showed high selectivity of the respective epoxides and high Ea values indicated that the reactions are truly chemically driven and not limited to mass transfer/diffusion.
- Multiple recycle studies showed that the catalyst can be reused without significant loss in activity and characterization of recycled catalyst confirmed that the material remained intact during the reaction.

Comparison of mono- and di-substituted catalysts – effect of Cu(II) centre

Oxidation of styrene

Oxidation of styrene over $MPW_{11}Cu$ as well as $MPW_{10}Cu_2$ was carried out under same reaction conditions and the results are presented in table 10. $MPW_{10}Cu_2$ gives almost double conversion compared to $MPW_{11}Cu$ with lower activation energy, indicating that Cu(II) is the active catalytic site. Further, it is interesting to note the higher selectivity for epoxide in case of $MPW_{10}Cu_2$, in contrast to that of $MPW_{11}Cu$. This is explained as follows.

Selectivity of epoxide largely depends on the stability of Cu(I) intermediate. As already mentioned, POMs have ability to stabilize transition metals in their lower oxidation states. In case of $MPW_{10}Cu_2$, along with POM, the formation of Cu(II)-Cu(I) mixed valent species further stabilizes the intermediate. Hence, it shows higher selectivity for styrene-oxide.

Table 10. Oxidation of styrene over $MPW_{11}Cu$ as well as $MPW_{10}Cu_2$

Catalyst	% conversion	% selectivity		Activation energy (Ea)
		Benzaldehyde	Styrene oxide	
$MPW_{11}Cu$	44	63	21	64.81 $kJmol^{-1}$
$MPW_{10}Cu_2$	83	35	33	57.64 $kJmol^{-1}$

Catalyst amount: 15 mg; Time: 12 h; temp: 60 ^0C; TBHP: 2 mL.

Oxidation of cis-cyclooctene

Similarly, oxidation of cis-cyclooctene over $MPW_{11}Cu$ as well as $MPW_{10}Cu_2$ was carried out under same reaction conditions and the results are presented in table 11. Double the conversion and extremely low activation energy in case of $MPW_{10}Cu_2$ indicates that Cu(II) is the active catalytic site for this reaction as well.

Table 11. Oxidation of cis-cyclooctene over $MPW_{11}Cu$ as well as $MPW_{10}Cu_2$

Catalyst	**% conversion**	**% selectivity**		**Activation energy (Ea, kJmol^{-1})**
		Cyclooctene-oxide	**Cyclooctanone**	
$MPW_{11}Cu$	18	85	15	105.88
$MPW_{10}Cu_2$	34	81	19	82.57

Catalyst amount: 15 mg; Time: 20 h; temp: 60 ^{0}C; TBHP: 2 mL.

In both the cases, since Cu(II) ion is the catalytic site, one would expect that there would be a doubling of activity with two Cu(II) ions. But, this is not equivalent of using twice the amount of $PW_{11}Cu$. As mentioned earlier, with increase in catalyst amount beyond 15 mg, the % conversion of both the alkenes does not increase substantially. This is attributed to blocking of catalytic sites, and also ageing of catalyst, i.e., due to higher quantity of solid catalyst and lesser quantity of liquid substrate, the rate of rotation (~700 rpm) is insufficient. It must, however, be noted that the reactions in both the systems are carried out in identical experimental conditions. Therefore, under different conditions, the results may vary.

NOTE: The following chapters describe various modifications such as supporting and functionalization. Though both, $PW_{11}Cu$ and $PW_{10}Cu_2$ can be modified, in the present study, we are focusing on $PW_{11}Cu$ alone, for the following reasons: (I) Further modifications of $PW_{11}Cu$ itself are scanty in literature and (II) it is very difficult to confirm the occurrence of the mentioned modifications in case of $PW_{10}Cu_2$ due to presence of two Cu centres.

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