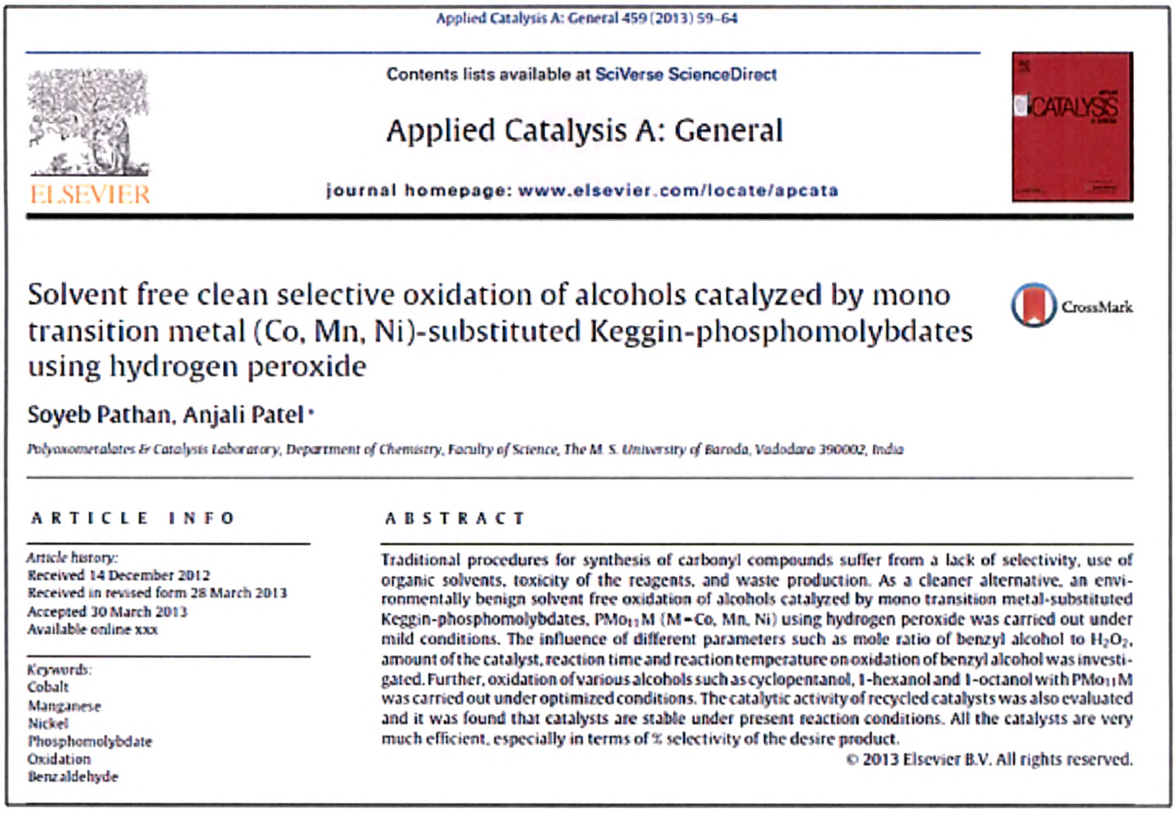
Chapter
6

Transition Metal (Co, Mn, Ni)-Substituted Phosphomolybdates as Sustainable catalysts



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Solvent free clean selective oxidation of alcohols catalyzed by mono transition metal (Co, Mn, Ni)-substituted Keggin-phosphomolybdates using hydrogen peroxide

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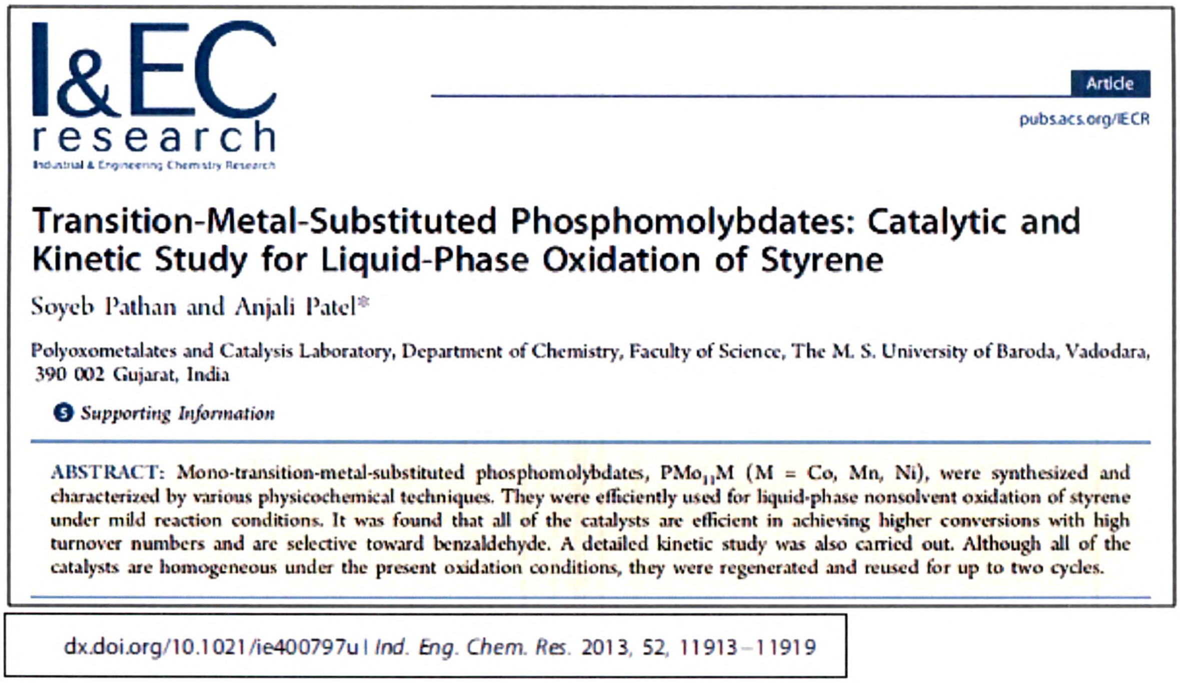
Traditional procedures for synthesis of carbonyl compounds suffer from a lack of selectivity, use of organic solvents, toxicity of the reagents, and waste production. As a cleaner alternative, an environmentally benign solvent free oxidation of alcohols catalyzed by mono transition metal-substituted Keggin-phosphomolybdates, $PMo_{11}M$ (M = Co, Mn, Ni) using hydrogen peroxide was carried out under mild conditions. The influence of different parameters such as mole ratio of benzyl alcohol to H_2O_2, amount of the catalyst, reaction time and reaction temperature on oxidation of benzyl alcohol was investigated. Further, oxidation of various alcohols such as cyclopentanol, 1-hexanol and 1-octanol with $PMo_{11}M$ was carried out under optimized conditions. The catalytic activity of recycled catalysts was also evaluated and it was found that catalysts are stable under present reaction conditions. All the catalysts are very much efficient, especially in terms of % selectivity of the desire product.



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Transition-Metal-Substituted Phosphomolybdates: Catalytic and Kinetic Study for Liquid-Phase Oxidation of Styrene

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Supporting Information

ABSTRACT: Mono-transition-metal-substituted phosphomolybdates, $PMo_{11}M$ (M = Co, Mn, Ni), were synthesized and characterized by various physicochemical techniques. They were efficiently used for liquid-phase nonsolvent oxidation of styrene under mild reaction conditions. It was found that all of the catalysts are efficient in achieving higher conversions with high turnover numbers and are selective toward benzaldehyde. A detailed kinetic study was also carried out. Although all of the catalysts are homogeneous under the present oxidation conditions, they were regenerated and reused for up to two cycles.

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Keggin type transition metal substituted phosphomolybdates: heterogeneous catalysts for selective aerobic oxidation of alcohols and alkenes under solvent free condition†

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Environmentally benign oxidation of alcohols and alkenes over transition metal substituted phosphomolybdates with molecular oxygen as an oxidant and TBHP as an initiator was carried out. The influence of different parameters on the conversion as well as the selectivity was investigated. All the catalysts showed good catalytic activity with excellent selectivity for the desired products as well as a higher TON. The system not only catalyzes the reaction but also avoids the use of organic solvents as it was carried out under solvent free conditions. Moreover, the catalysts could be recovered and reused four times without a significant loss in their activity and selectivity. A probable reaction mechanism was also proposed for the oxidation of alcohols and alkenes.

It has been well established that oxidation reactions play a significant role in industries as well as laboratories and much attention has been paid to the development of efficient catalytic oxidation systems [1-5]. Traditionally, oxidation reactions have been carried out with inorganic oxidants such as PCC, MnO_2, $Na_2Cr_2O_7$, $NaClO_4$, $KMnO_4$, organic solvents and at high temperature. These mentioned procedures have drawbacks such as use of relatively expensive oxidizing agents, lack of selectivity, metal waste generation and use of non-green halogenated solvents, which are economically and environmentally undesirable.

In Chapter 3, we have already described industrial importance of carbonyl compounds especially benzaldehyde as well as environmental importance of O_2 and H_2O_2 as oxidants. The advantages of use of O_2 and H_2O_2 as oxidants over traditional oxidants encourage researchers to develop new catalytic systems based on the same. A detail study on H_2O_2-mediated oxidation of various organic compounds using tungstate based catalyst and a phase-transfer catalyst (PTC) has been reported by Noyori et al. [6]. Apart from these, reports are available on transition metal complexes catalyzed aerobic oxidation reactions [7-14]. These catalytic systems suffer from the recycling of complexes due to the difficult separation and rapid loss of activity.

The search for active, green, and recyclable catalysts to activate O_2 and H_2O_2 for the oxidation of organic compounds is the focus of many researchers in both academia and industry. POMs meet both activity and stability criteria. Also, the use of POMs as catalysts is important in the so-called clean technologies because objections to environmental pollution and corrosion of the traditional technologies are avoided [9, 15-17].

Among POMs, TMSPOMs $[XM_{11}M'O_{39}]^{(n-m)-}$ (central atom X = P, Si, B; addenda atom M = W, Mo), have generated substantial interest as oxidative catalysts. This is because they have available open coordination sites on the transition metals and their redox properties could be controlled at the atomic/molecular levels by changing addenda atoms without affecting the Keggin type primary structure [18,19]. It has been reported that addition of transition metals are expected to influence redox properties considerably, particularly when they are incorporated in the primary structure of the Keggin ion [20,21].

A literature survey shows that many reports on oxidation reactions catalyzed by transition metal substituted polyoxotungstates with H_2O_2 [22-24] and O_2 [25-30]. Even though, phosphomolybdates are known to be better catalysts for oxidation reactions than their tungstate counterparts [18], reports on catalytic activity are comparatively less.

As described in **Chapter 4**, among transition metal substituted phosphomolybdates, numbers of reports are available on oxidation reaction catalyzed by transition metal substituted phosphomolybdates. However, in most of applied protocols, catalytic oxidation requires harsh conditions of temperature and use of relatively expensive transition metals (V, Ru) as well as use of organic solvent.

Few reports on use of other redox active and inexpensive transition metals (Co, Ni and Mn) substituted phosphomolybdates as catalysts are also available. Neumann et al reported use of $[PXMo_{11}O_{39}]^{q-}$ (X=Co, Mn) as bifunctional catalysts for the aerobic oxidation of cumene to hydroperoxo/peroxo intermediate followed by oxygen transfer to an alkene to yield epoxide in acetonitrile [31]. Burns et al. reported homogeneous oxidation of isobutyraldehyde catalyzed by $[PZ(II)(Br)Mo_{11}O_{39}]^{6-}$, (Z= Mn(II), Co(II), Ni(II), Cu(II) and Zn(II)) using H_2O_2 as an oxidant in acetonitrile at 50 °C [32]. Rabia et al. investigated use of ammonium salt of $PMo_{11}MO_{40}$ (M= Co, Ni) for oxidation of propane with molecular oxygen at temperature 380 - 420 °C [33]. Use of TBA salt of $PMo_{11}MO_{40}$ (M= Co, Mn) as catalysts for oxidation of phenol in acetonitrile has been explored by karcz et al [34]. Cavaleiro et al reported homogeneous catalytic oxidation of olefins with hydrogen peroxide catalyzed by $TBA_4H[PMo_{11}Mn(H_2O)O_{39}].2H_2O$ in acetonitrile [35].

A literature survey shows that all the reported oxidation reactions have been carried out either using solvent or at higher temperature. The current goal of basic research is the development of sustainable i.e. environmentally friendly and inexpensive catalysts that can effectively activate the clean oxidants (or substrates under ambient conditions) and transfer the active oxygen species to various substrates with high efficiency and selectivity.

So, looking at the importance of oxidation reactions as well as considering the economic and ecological aspects, it was thought of interest to develop a sustainable catalytic system for oxidation of alkenes and alcohols based on (relatively inexpensive) transition metal substituted phosphomolybdates with O_2 and H_2O_2 under solvent free conditions.

In this context, transition metal (Co, Mn, Ni)- substituted phosphomolybdates are expected to be efficient candidates for selective oxidation of various organic substrates due to their redox active nature. At the same time the POM framework is robust under extreme oxidation conditions and hence is expected to play a significant role for the same.

The present chapter deals with evaluation catalytic activity of $Cs_5[PM(H_2O)Mo_{11}O_{39}]6H_2O$; $PMo_{11}M$ (M= Co, Mn, Ni) for non solvent liquid phase oxidation of alcohols and alkenes with environmentally friendly and economical oxidants viz. molecular oxygen (O_2) and H_2O_2. In order to optimize the conditions detailed study was carried on oxidation of benzyl alcohol (for alcohols) and styrene (for alkenes) by varying different parameters such as mole ratio of substrate to H_2O_2, reaction temperature, catalyst amount and reaction time. In order to see viability of these catalysts, we explore use of the same as sustainable catalysts for solvent free oxidation of alcohols and alkenes with O_2 and H_2O_2. Further, the heterogeneity test was also performed for aerobic oxidation, to confirm the absence of leaching of the transition metals. The catalysts were also regenerated and reused. Mechanism for aerobic oxidation reactions was proposed. A detailed kinetic study was also performed for oxidation of styrene using H_2O_2.

EXPERIMENTAL

Materials

All the chemicals used were of A. R. grade. Styrene, α-methyl styrene, benzyl alcohol, cyclopentanol, cyclohexanol, 1- hexanol, 1- octanol, tertiary butylhydroperoxide (70% aq. TBHP) and dichloromethane were obtained from Merck and used as received.

Catalytic Reaction

Oxidation with molecular oxygen

The catalytic activity was evaluated for oxidation of alcohols using molecular oxygen as an oxidant and TBHP as an initiator. Oxidation reaction was carried out in a batch type reactor operated under atmospheric pressure. In a typical reaction, measured amount of catalyst was added to a three necked flask containing alcohol at 90 °C. The reaction was started by bubbling O_2 into the liquid. Similar procedure was followed for alkenes oxidation with reaction temperature 80 °C. The reactions were carried out by varying different parameters such as effect of, reaction temperature, catalyst amount and reaction time.

Oxidation with H_2O_2

The oxidation reaction was carried out in a borosilicate glass reactor equipped with a double walled condenser. The desired catalyst, alcohol, and H_2O_2 mixtures were intensively stirred in the reactor at 90 °C temperature for the whole duration of reactions. A similar procedure was followed for alkenes oxidation at 80 °C. The reaction was carried out by varying different parameters such as effect of molar ratio of substrate to H_2O_2, reaction temperature, amount of catalyst and reaction time.

After completion of the reaction, catalyst was removed and the product was extracted with dichloromethane. The product was dried with magnesium sulphate and analyzed on Gas Chromatograph (Nucon 5700 model) using BP-1 capillary column (30m, 0.25mm id). Gas Chromatograph programming parameters were Injector temperature= 220 °C, Detector temperature= 250 °C, Column temperature= 80- 220 °C with rate 10 °C/min. Product was identified by comparison with the authentic samples and finally by Gas Chromatography-Mass Spectroscopy (GC-MS).

The conversion, selectivity as well as TON was calculated using the same formula as shown in Chapter 3.

RESULTS AND DISCUSSION

Oxidation reactions with O_2 as an oxidant

Oxidation of alcohols with O_2

A detail study was carried out on oxidation of benzyl alcohol to optimize the conditions. To ensure the catalytic activity, all reactions were carried out without catalyst and no oxidation takes place. The reaction was carried out with 20 mg of catalysts for 24 h at 90 °C. Generally, benzyl alcohol on oxidation gives benzaldehyde and benzoic acid. However, benzaldehyde was obtained as the major oxidation product in the present case.

Effect of temperature

In order to determine the optimum temperature the reaction was investigated at three different temperatures 70, 90 and 110 °C, keeping other parameters fixed (20mg catalyst amount, reaction time 24h). The results for the same are presented in Figure 1.

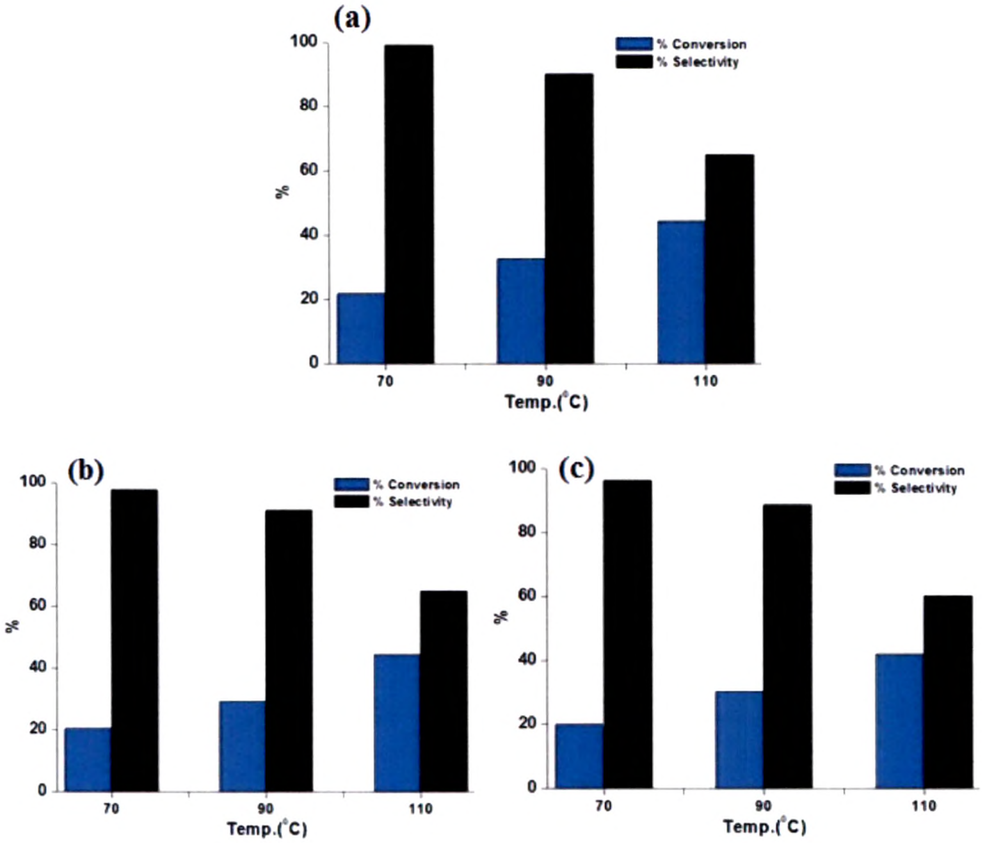


Figure 1. % conversion is based on benzyl alcohol; benzyl alcohol = 100mmol, TBHP= 0.2%, Time= 24h, amount of catalyst= 20 mg; (a) $PMo_{11}Co$, (b) $PMo_{11}Mn$ and (c) $PMo_{11}Ni$

The results show that conversion increased with increasing temperature from 70 to 110 °C for all catalysts. At the same time, on increasing temperature from 90 to 110 °C, drastic decrease in selectivity of benzaldehyde was observed. This is due to over oxidation of benzaldehyde to benzoic acid at elevated temperature. So the temperature of 90 °C was found optimized for further studies.

Effect of catalyst amount

The effect of amount of the catalyst on the conversion was studied and the obtained results are shown in Figure 2.

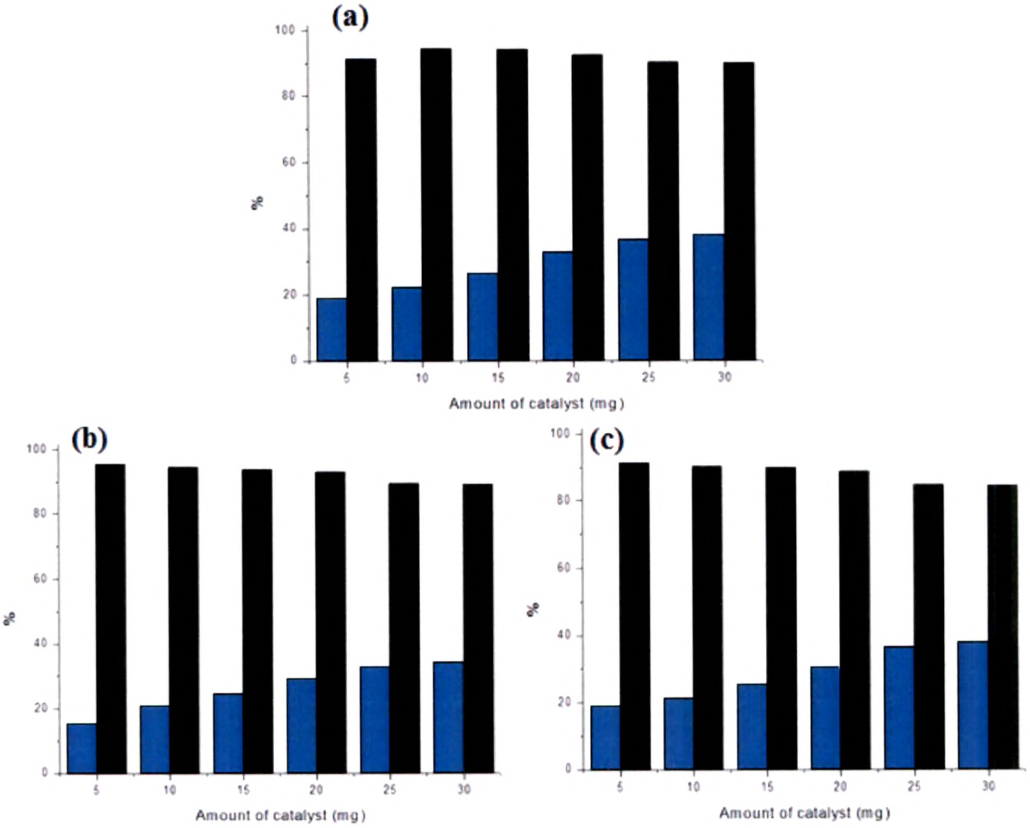


Figure 2. % conversion is based on benzyl alcohol; benzyl alcohol = 100mmol, TBHP= 0.2%, Time= 24h, Temp= 90 ° C; (a) $PMo_{11}Co$, (b) $PMo_{11}Mn$ and (c) $PMo_{11}Ni$

With increases in the amount of catalysts i.e. concentration of metal contains, % conversion also increases. This suggests that transition metal functions as active sites for oxidation. It is very interesting to observe the difference in the selectivity of the products with increase in the concentration of the catalyst. It is observed from Figure 2 that with lower amount of catalysts, >96% selectivity of benzaldehyde is obtained. On increasing amount of catalysts (more than 20 mg), selectivity for benzaldehyde decreases. This may be due the fact that with increase in the amount of the active species the reaction becomes fast which favours the conversion of the formed benzaldehyde to benzoic acid. Thus, amount of catalysts was optimized to 20 mg for optimum conversion and selectivity.

Effect of reaction time

The percentage of conversion was monitored at different reaction times and result is presented in Figure 3.

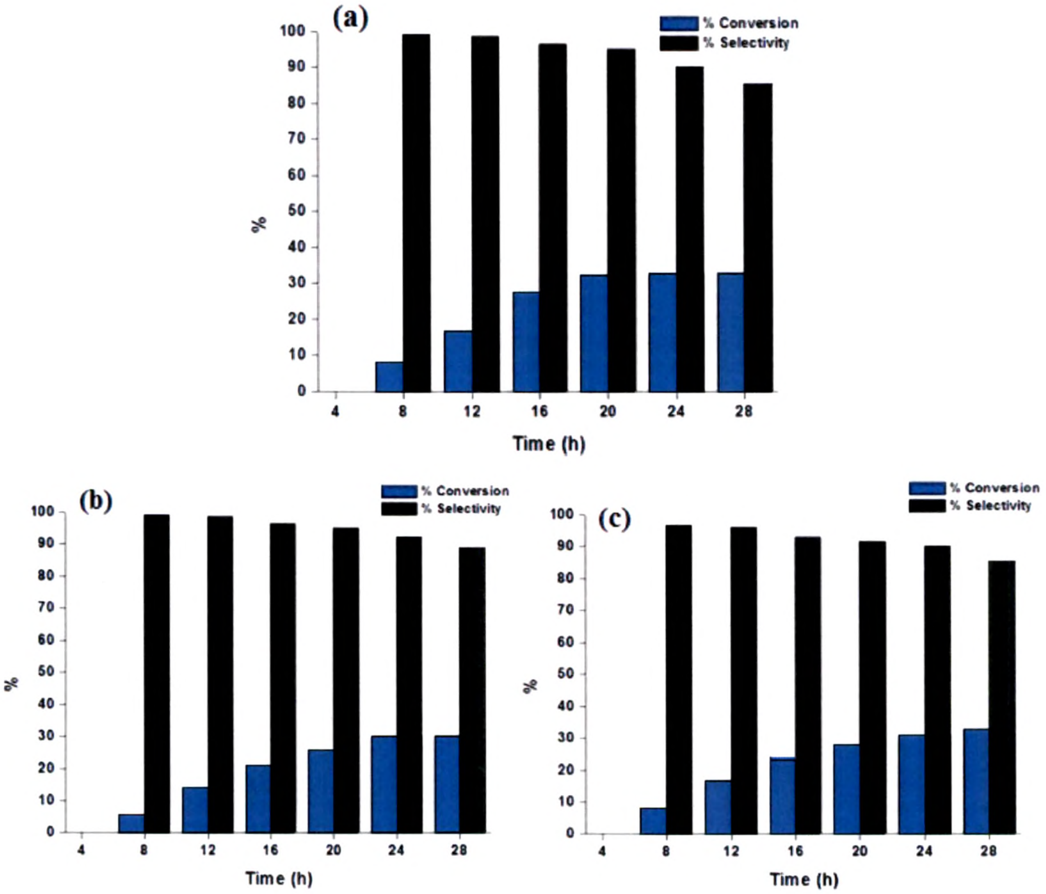


Figure 3. % conversion is based on benzyl alcohol; benzyl alcohol = 100mmol, TBHP= 0.2%, amount of catalyst= 20 mg, Temp= 90 ° C; (a) $PMo_{11}Co$, (b) $PMo_{11}Mn$ and (c) $PMo_{11}Ni$

It is seen from Figure 3, that with increase in reaction time, the % conversion also increases. Initial conversion of benzyl alcohol increased with the reaction time. This is due to the reason that more time is required for the formation of reactive intermediate (substrate + catalyst) which is finally converted into the products. For, $PMo_{11}Co$, It is seen that 32.6 % conversion of benzyl alcohol with 92.3% selectivity of benzaldehyde was observed at 24 h. When the reaction was allowed to continue after 24 h, no significant change in conversion was observed, but selectivity of benzaldehyde was decreased. This is because of over oxidation of benzaldehyde to benzoic acid. Similar trend in activity was observed for $PMo_{11}M$ (M=Mn, Ni). So, reaction time was optimized as 24 h.

The optimum conditions for optimum conversion of benzyl alcohol and selectivity of benzaldehyde over $PMo_{11}M$ (M=Co, Mn, Ni) are; 20 mg of catalyst, 24 h reaction time, reaction temperature 90 °C.

Comparison of $PMo_{11}M$ (M= Co, Mn, Ni) for aerobic oxidation of alcohols

In order to see the effect of substitution of metal in PMo_{11} as well as to explore scope and limitations of present catalytic system, oxidation of different alcohols was also carried out using $PMo_{11}M$ (M=Co, Mn, Ni) under optimized conditions and results are presented in Table 1.

Table 1 Oxidation of alcohols with O_2 using $PMo_{11}M$ (M= Co, Mn, Ni)

Catalyst	Alcohols	% Conv.	Products (%Selectivity)	TON
$PMo_{11}Co$	Benzyl alcohol	32.6	Benzaldehyde(92.3)	4281
	Cyclopentanol	29.8	Cyclopentanone(100)	3913
	Cyclohexanol	29.2	Cyclohexanone (100)	3834
	1-Hexanol	20.6	1-Hexanal (100)	2705
	1- Octanol	NC	-	-
$PMo_{11}Mn$	Benzyl alcohol	28.3	Benzaldehyde(93.6)	3628
	Cyclopentanol	24.3	Cyclopentanone(100)	3115
	Cyclohexanol	23.7	Cyclohexanone (100)	3038
	1-Hexanol	15.9	1-Hexanal (100)	2038
	1- Octanol	NC	-	-
$PMo_{11}Ni$	Benzyl alcohol	31.9	Benzaldehyde(92.3)	4075
	Cyclopentanol	27.6	Cyclopentanone(100)	3526
	Cyclohexanol	24.1	Cyclohexanone (100)	3078
	1-Hexanol	17.7	1-Hexanal (100)	2261
	1- Octanol	NC	-	-

Conversion is based on Alcohols; alcohol = 100mmol, TBHP= 0.2%, Time= 24h, amount of catalyst= 20 mg, Temp= 90 °C

It is seen from Table 1 that, the order of activity of catalysts for oxidation of benzyl alcohol is $PMo_{11}Co \approx PMo_{11}Ni > PMo_{11}Mn$. These results indicate that the activity of catalyst is governed by reduction potential of metals used for substitution. The values for reduction potential for Co, Ni and Mn are -0.28 V, -0.27 V and -1.18 V respectively. Among all the catalysts, $PMo_{11}Mn$ shows lowest conversion of benzyl alcohol and H_2O_2, as compare to other $PMo_{11}M$ (M = Co, Ni). $PMo_{11}Co$ and $PMo_{11}Ni$ show almost same conversion of benzyl alcohol. It is well known that, more negative the reduction potential, the poorer its oxidizing ability. From the reduction potential value it is clear that, catalyst consisting Mn is expected to be least active as compare to Co and Ni. Also, because of same reduction potential of catalysts consisting Co and Ni, similar activity is expected for oxidation reaction. So, results are as expected.

As seen from Table 1 that, as benzyl alcohol oxidation, similar trend in activity of $PMo_{11}M$ (M = Co, Ni, Mn) was observed for oxidation of other alcohols such as cyclopentanol, 1-hexanol and 1-octanol i.e. $PMo_{11}Co$ shows better activity as compare to $PMo_{11}Mn$ and $PMo_{11}Ni$. It was observed from Table 1 that, oxidation of secondary alcohol is easier as compare to primary alcohols. The observed trend is in good agreement with reported in art [36]. It is also observed that, in all cases, very good selectivity of desired product with high TON is obtained. It is known that, oxidation of long chain alcohols (C8 and onwards) is still challenging task because of lower reactivity [37] and thus present catalytic system is also not applicable to less reactive long chain primary alcohol such as 1-octanol. For the present catalytic system, the reactivity of the alcohols was found in the order primary < cyclic secondary < aromatic.

Oxidation alkenes with O_2

A detail study was carried out on oxidation of styrene to optimize the conditions. To ensure the catalytic activity, all reactions were carried out without catalyst and no oxidation takes place. The reaction was carried out with 20 mg of catalysts for 8 h at 80 °C. Generally, styrene on oxidation gives styrene oxide, benzaldehyde, and benzoic acid. However, in the present reaction conditions, the major oxidation product obtained was benzaldehyde.

Effect of temperature

In order to determine the optimum temperature the reaction was investigated at four different temperatures 60, 80 and 100 °C, using both the catalysts keeping other parameters fixed. The results for the same are presented in Figure 4.

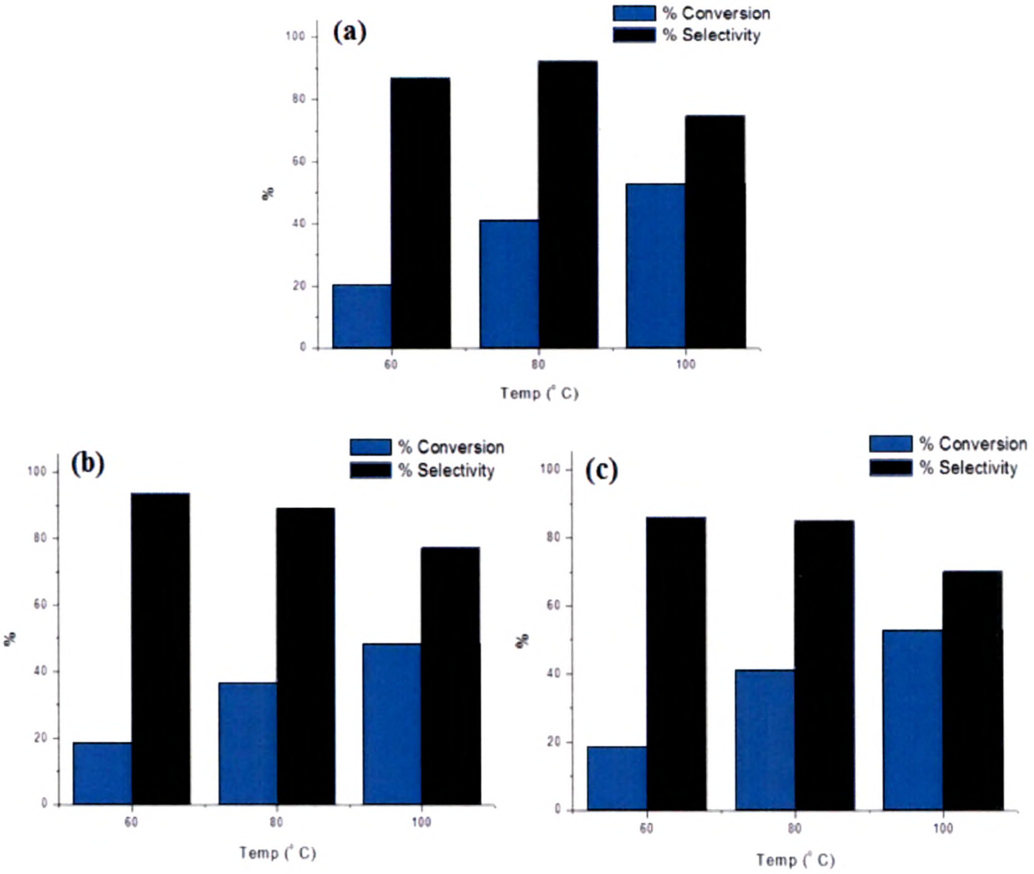


Figure 4. % conversion is based on styrene; styrene = 100mmol, TBHP= 0.2%, Time= 8h, amount of catalyst= 20 mg, (a) PMo$_{11}$Co, (b) PMo$_{11}$Mn and (c) PMo$_{11}$Ni

The results show that conversion increased with increasing temperature. However, on increasing temperature from 80 to 100 °C, selectivity of benzaldehyde decreases. So the temperature of 80 °C was found optimal for the maximum conversion of styrene as well selectivity of benzaldehyde.

Effect of catalyst amount

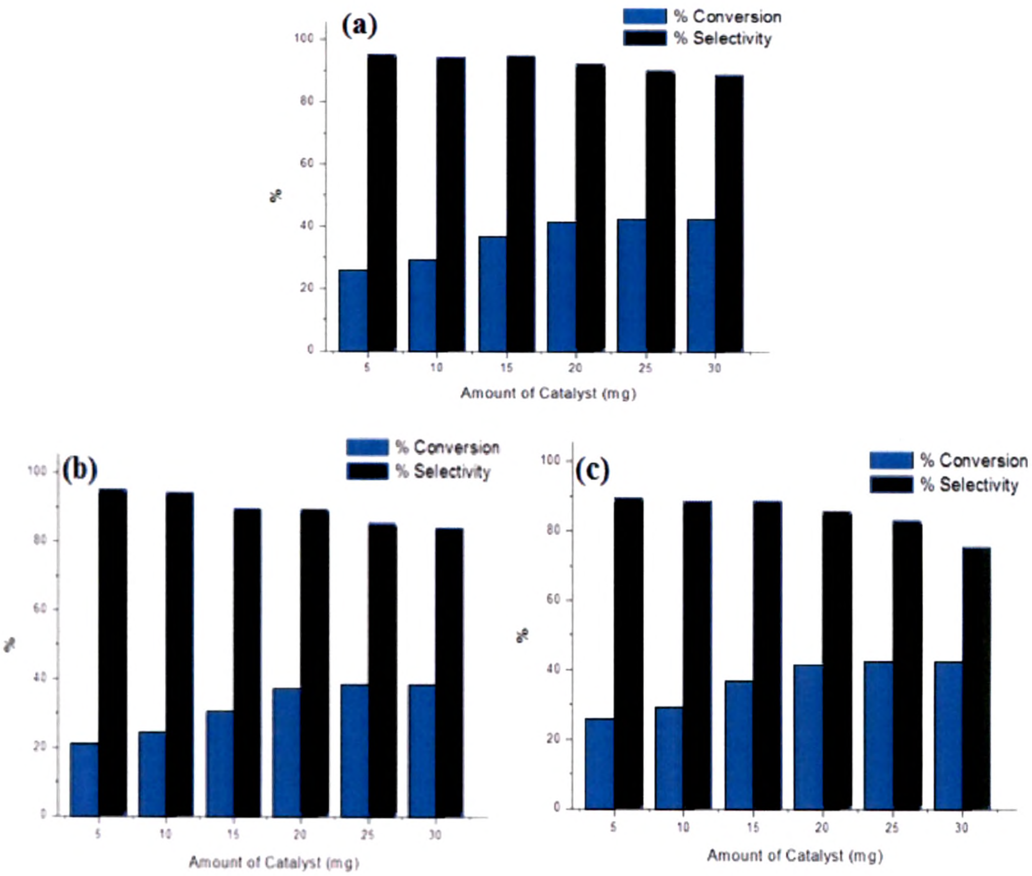


Figure 5. % conversion is based on styrene; styrene = 100mmol, TBHP= 0.2%, Time= 8h, Temp= 80 ° C; (a) $PMo_{11}Co$, (b) $PMo_{11}Mn$ and (c) $PMo_{11}Ni$

The effect of amount of catalysts on the conversion was studied and the obtained results are shown in Figure 5. With increase in the amount of catalysts % conversion also increases. It is also seen that with increase in the amount catalyst from 20 mg to 30 mg, no significant change in the conversion was observed. At the same time selectivity of benzaldehyde decreases. Thus, amount of catalysts was optimized to 20 mg for optimum conversion and selectivity.

Effect of reaction time

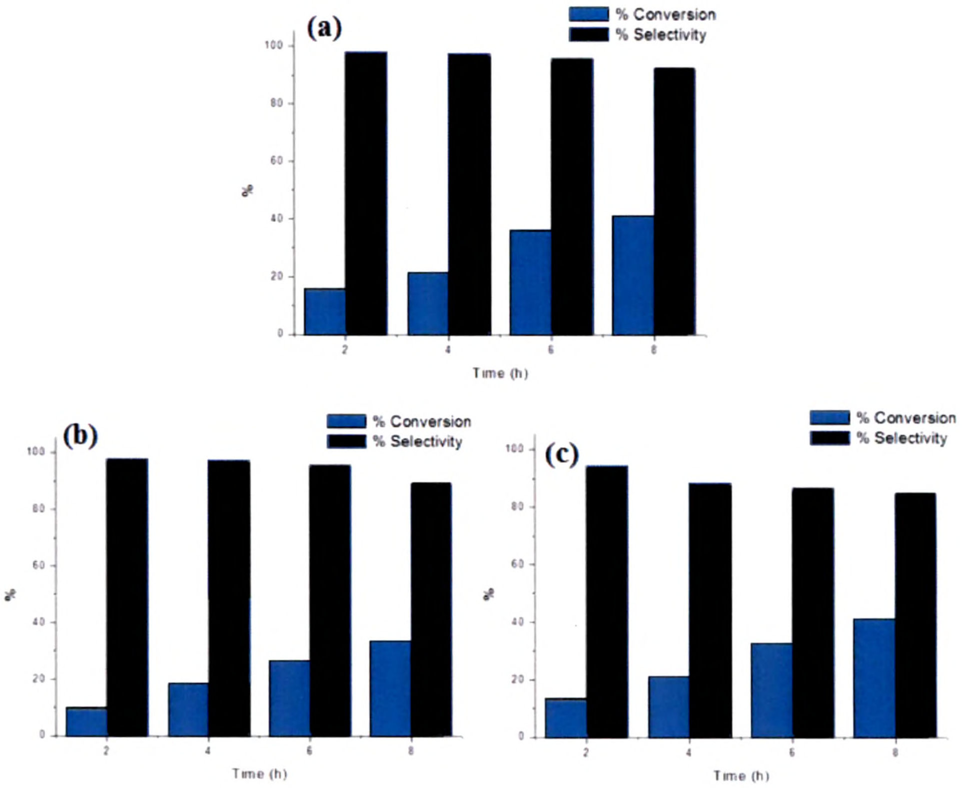


Figure 6. % conversion is based on styrene; styrene = 100mmol, TBHP= 0.2%, amount of catalyst= 20 mg, Temp= 80 ° C; (a) $PMo_{11}Co$, (b) $PMo_{11}Mn$ and (c) $PMo_{11}Ni$

The percentage of conversion was monitored at different reaction times and result is presented in Figure 6. It is seen from Figure 6, that with increase in reaction time, the % conversion also increases. This is due to the reason that more time is required for the formation of reactive intermediate (substrate + catalyst) which is finally converted into the products. After 8 h, polymerization of styrene was observed. Thus, reaction time was optimized for 8 h.

The optimum conditions for maximum % conversion of styrene and selectivity of benzaldehyde for $PMo_{11}M$ are; 20 mg of catalyst, 8 h reaction time, reaction temperature 80 °C.

Comparison of $PMo_{11}M$ (M= Co, Mn, Ni) for aerobic oxidation of alkenes

In order to see the effect of substitution of metal in PMo_{11} as well as to explore scope and limitations of present catalytic system, aerobic oxidation of different alkenes was also carried out using $PMo_{11}M$ (M=Co, Mn, Ni) under optimized conditions and results are presented in Table 2.

Table 2 Oxidation of alkenes with O_2 using $PMo_{11}M$ (M= Co, Mn, Ni)

Catalyst	Alkenes	%Conv	Products (%Selectivity)	TON
$PMo_{11}Co$	Styrene	41.1	Benzaldehyde (92.2)	5253
	α- Methyl styrene	36.2	Acetophenone (93.1	4627
	^{a}cyclohexene	NC	-	-
$PMo_{11}Mn$	Styrene	35.9	Benzaldehyde (90.7)	4602
	α- Methyl styrene	30.3	Acetophenone (91.1)	3885
	^{a}cyclohexene	NC	-	-
$PMo_{11}Ni$	Styrene	39.9	Benzaldehyde (87.2)	5074
	α- Methyl styrene	34.3	Acetophenone (87.1)	4362
	^{a}cyclohexene	NC	-	-

% conversion is based on styrene; styrene = 100mmol, TBHP= 0.2%, Time= 8h, amount of catalyst= 20 mg, Temp= 80 °C, ^{a}60°C; (a) $PMo_{11}Co$, (b) $PMo_{11}Mn$ and (c) $PMo_{11}Ni$

From the results it is clear that, similar to alcohol oxidation, styrene and substituted styrene was efficiently oxidised to desired product by $PMo_{11}M$ (M= Co, Mn, Ni) and the order of activity for oxidation is $PMo_{11}Co$ > $PMo_{11}Ni$ > $PMo_{11}Mn$. Generally, oxidation of styrene gives styrene oxide, benzaldehyde, diol, benzoic acid and acetophenone. However, in the present case C=C cleaved carbonyl compound was characterized as a major product. It is well known that, stable product benzaldehyde was observed as major product via i) direct oxidative cleavage of C=C of styrene and ii) fast conversion of styrene oxide to benzaldehyde. It has been reported by Vancheesan et al.[38] that use of TBHP with transition metal based catalysts activates the metal centre. The inter-conversion of the two oxidation states for the metal complexes, corresponding to an oxidative addition and reductive elimination, are responsible for effective catalysis. Hence, the activated catalysts, attack the C = C site in case of styrene and preferentially follow an oxidative cleavage rather than epoxide formation [39].

Thus, the obtained results are in good agreement with the reported explanation. In all cases, excellent selectivity (88-93%) of desired product with very high TON is obtained. As the present catalytic system followed oxidative cleavage rather than epoxide formation, cyclic olefins does not undergo epoxidation. Also, C = C bond cleavage in cyclic olefins is difficult task and therefore no ring opening product was obtained. Thus, present catalytic system is not applicable for oxidation of cyclic olefins.

Controlled experiment

A controlled experiment for oxidation of benzyl alcohol and styrene with $CsPMo_{11}$ and $CsPMo_{12}$, and $PMo_{11}M$ (M = Co, Mn, Ni) was carried out under optimized conditions and results are presented in Table 3.

Table 3 Controlled experiment for oxidation of benzyl alcohol and styrene with $CsPMo_{11}$, $CsPMo_{12}$, $PMo_{11}M$ (M=Co, Mn, Ni), under optimized conditions.

Entry	Catalyst	% Conversion	% Selectivity	
			Benzaldehyde	other
1	$CsPMo_{11}$	$13.4^a/16.5^b$	91.2^a / 90.1^b	$8.8^a/9.9^b$
2	$CsPMo_{12}$	$6.2^a/11.3^b$	$87.2^a/82.2^b$	$12.8^a/17.8^b$
3	$PMo_{11}M$	$28\text{-}33^a/39\text{-}41^b$	$92\text{-}93^a/87\text{-}92^b$	$7\text{-}8^a/8\text{-}13^b$

% Conversion is based on substrate (^{a}benzyl alcohol, ^{b}styrene); substrate = 100mmol, O_2, TBHP= 0.2%, Temp= ^{a}90, ^{b}80°C, Time= ^{1}24h, ^{2}8h, amount of catalyst= 25 mg ($PMo_{11}M$), 18mg ($CsPMo_{12}$), 27 mg PMo_{11}.

It is seen from Table 3 that in $CsPMo_{11}$ and $CsPMo_{12}$ catalyzed oxidation reactions, very low conversion of substrates and with 80-90% selectivity of benzaldehyde was obtained Whereas, $PMo_{11}M$, show good conversion i.e. >18 % more conversion as well as excellent selectivity for benzaldehyde was observed. Controlled experiment shows that $PMo_{11}M$ (M = Co, Mn, Ni) are better catalysts as compare to their parent ($CsPMo_{12}$) and lacunary counter-part ($CsPMo_{11}$). From experiment it will be also concluded that although transition metal can act as active centre for oxidation, possibility of involvement of the Mo species cannot be ruled out.

Heterogeneity Test

Heterogeneity test was carried out for the oxidation of benzyl alcohol (Figure 7a) and styrene (Figure 7b) over $PMo_{11}Co$ as examples. For the rigorous proof of heterogeneity, a test [40] was carried out by filtering catalyst from the reaction mixture at 90 °C after 12 h (for styrene; 80 °C after 4 h) and the filtrate was allowed to react up to 28 h (for styrene; 8 h).

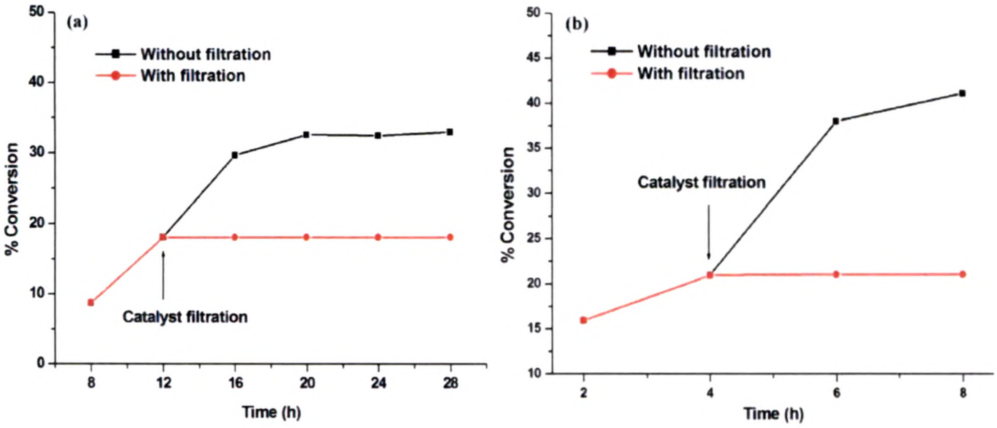


Figure 7. % Conversion is based on substrate (^{a}benzyl alcohol /^{b}styrene); amount of $PMo_{11}Co$ =20 mg; molar ratio of substrate (100 mmol), O_2, TBHP= 0.2%, temperature ^{a}90 °C, ^{b}80 °C

The reaction mixture of 12 h and the filtrate were analyzed by gas chromatography. Similar test was carried for $PMo_{11}M$ (M= Mn, Ni). No change in the % conversion as well as % selectivity was found indicating the present catalysts fall into category C [40] i.e., active species does not leach and the observed catalysis is truly heterogeneous in nature.

Regeneration and Recycling of Catalysts

Catalytic activity of regenerated catalysts

The catalyst was recycled in order to test for its activity as well as its stability. The catalysts remain insoluble under the present reaction conditions. The decomposition or leaching of metal contain from $PMo_{11}M$ was con-firmed by carrying out an analysis of the used catalyst (EDX) as well as the product mixtures (AAS). For all catalysts, the analysis of the used catalyst did not show appreciable loss in the metal content as compared to the fresh catalyst. Analysis of the product mixtures shows that if any metal was present it was below the detection limit, which corresponded to less than 1 ppm. These observations strongly suggest that the present catalyst is truly heterogeneous in nature.

Catalysts were separated easily by simple filtration followed by washing with dichloromethane and dried at 100°C. Oxidation reaction was carried out with the regenerated catalysts, under the optimized conditions. The data for the catalytic activity is represented in Table 4.

Table 4 Oxidation of benzyl alcohol and styrene with fresh and regenerated catalysts

Substrate	Cycle	Conversion (%)	Selectivity (%)
			Benzaldehyde
^{1}Benzyl alcohol	Fresh	$32.6^{a}/28.3^{b}/31.9^{c}$	$92.3^{a}/93.6^{b}/92.3^{c}$
	1	$32.6^{a}/28.3^{b}/31.9^{c}$	$92.0^{a}/93.4^{b}/92.2^{c}$
	2	$32.6^{a}/28.1^{b}/31.8^{c}$	$92.2^{a}/93.4^{b}/92.0^{c}$
	3	$32.4^{a}/28.1^{b}/31.8^{c}$	$92.2^{a}/93.4^{b}/92.1^{c}$
	4	$32.3^{a}/28.0^{b}/31.7^{c}$	$92.1^{a}/93.3^{b}/92.1^{c}$
^{2}Styrene	Fresh	$41.1^{a}/35.9^{b}/39.9^{c}$	$92.2^{a}/90.7^{b}/87.2^{c}$
	1	$41.1^{a}/35.7^{b}/39.9^{c}$	$92.2^{a}/90.5^{b}/87.1^{c}$
	2	$41.0^{a}/35.6^{b}/39.7^{c}$	$92.1^{a}/90.4^{b}/87.4^{c}$
	3	$41.0^{a}/35.6^{b}/39.7^{c}$	$92.0^{a}/90.4^{b}/87.0^{c}$
	4	$41.0^{a}/35.6^{b}/39.5^{c}$	$92.0^{a}/90.5^{b}/86.9^{c}$

% Conversion is based on substrate; substrate = 100mmol, TBHP= 0.2%, Temp= ^{1}90, ^{2}80°C, Time= ^{1}24h, ^{2}8h amount of catalyst= 20 mg, (a) $PMo_{11}Co$, (b) $PMo_{11}Mn$ and (c) $PMo_{11}Ni$

It is seen from the table that there was no significant change in conversion as well as selectivity. This shows that the catalysts are stable, regenerated and reused successfully up to 4 cycles.

Characterization of Regenerated Catalysts

The separated catalysts were washed with dichloromethane and then water and dried at 100 °C. The obtained recycled catalysts were characterized for FT-IR. The FT-IR spectra for the fresh as well as the regenerated catalysts are represented in Figure 8.

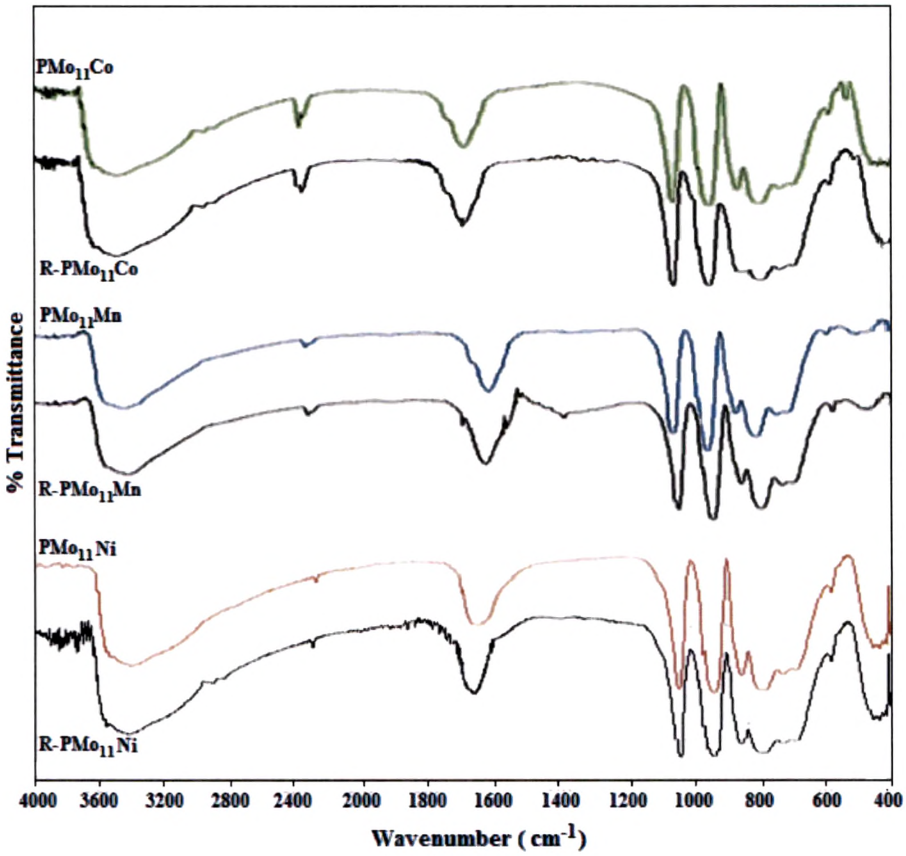


Figure 8. FT-IR spectra of fresh and recycled catalysts

No appreciable shift in the FT-IR band position of all regenerated catalysts compare to fresh $PMo_{11}M$ indicates the retention of Keggin-type structure of $PMo_{11}M$ i.e. $PMo_{11}M$ are stable under present reaction condition and can be re-used upto four cycles.

Probable reaction mechanism

In order to study the reaction mechanism the same sets of reactions were carried under two different conditions; (i) styrene + oxidant + TBHP and (ii) styrene + oxidant + $PMo_{11}M$. In both the cases the reaction did not progress significantly. These observations indicate that the liberation of O_2 from TBHP was not sufficient to proceed the reaction as well as activation of M^{2+} to M^{3+} being necessary for provoking the reaction under the optimized conditions. Hence it may be concluded that in present study TBHP acts as a radical initiator only.

In order to confirm radical mechanism, an experiment was carried out by the use of excess *i*-PrOH as radical terminator and result is presented in Figure 9.

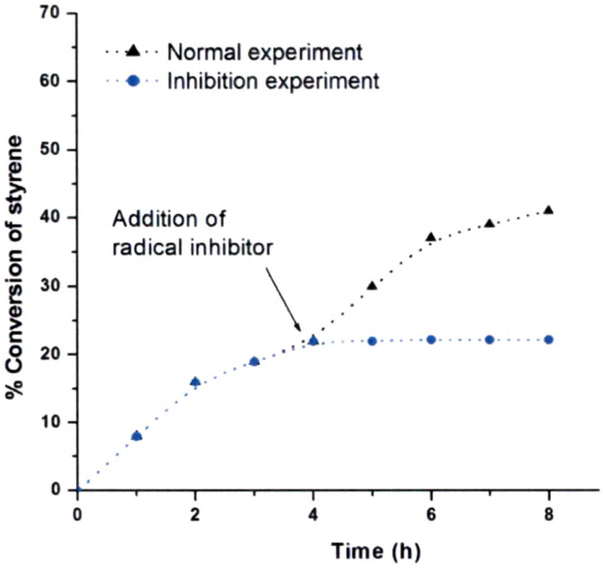
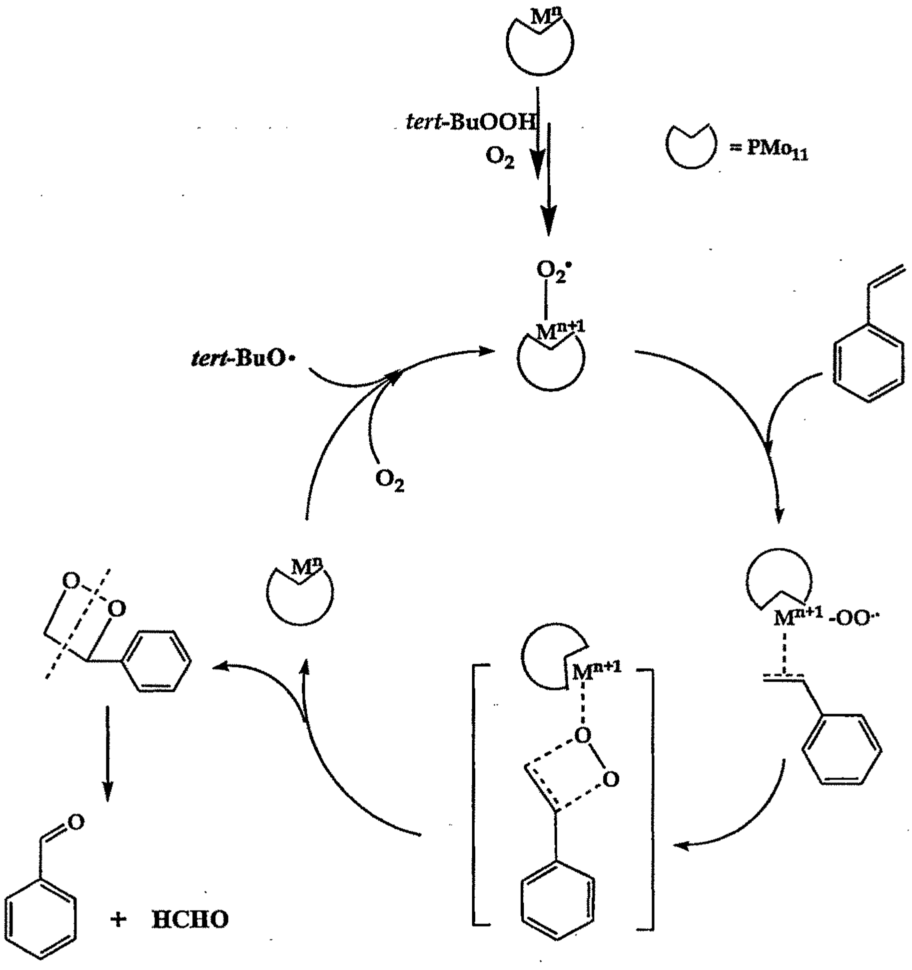


Figure 9. Inhibition experiment with *i*-PrOH as radical terminator (blue), without *i*-PrOH under optimized condition (black), Catalyst= $PMo_{11}Co$

When the free-radical terminator was added to the oxidation of styrene (at 4h), reaction stopped and no significant increase in conversion of styrene was observed. Based on the these observations, a tentative reaction mechanism for aerobic oxidation of styrene with TBHP as an initiator is proposed in Scheme-1.

$$PMo_{11}M^{n} + tert\text{-}BuOOH \longrightarrow PMo_{11}M^{n+1} + tert\text{-}BuO\bullet + OH^{-}$$

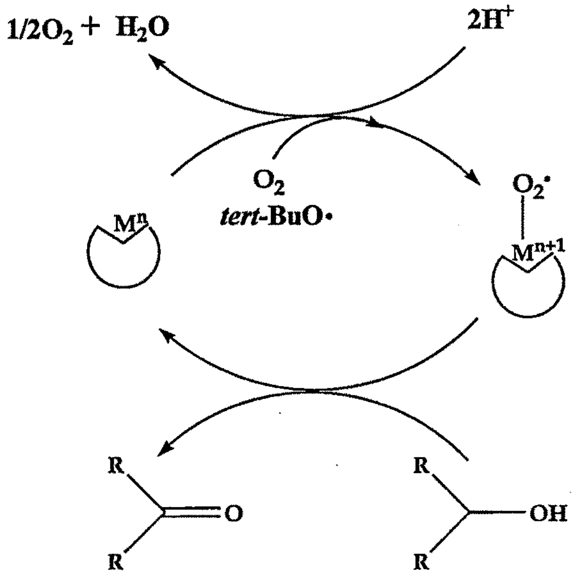


Scheme 1 Proposed reaction mechanism for oxidation of styrene using O_2

It has been reported that, in case of transition metal substituted polyoxotungstates, transition metals behaved as active centre for catalysis [20,41]. It has been also reported that for TMSPOMs catalysts containing metal cations in low valency states and involving O_2 as an oxidant always follow the radical chain mechanism induced by M-O_2 intermediate [42,43].

In the present catalytic system, the mechanism is expected to follow the same path. It is expected that, reaction of M^{2+} with TBHP cause oxidization of M^{2+} to M^{3+} *in situ*,. The activation of this specie takes place with radical (*tert*-BuO·) generated during decomposition of TBHP and attack of O_2 simultaneously, which results in formation of activated specie $\cdot OOM^{3+}PMo_{11}$.

This activated specie ($\cdot OOM^{3+}PMo_{11}$) then attacks the substrate. The metal-superoxo intermediate reversibly binds styrene attacking the reaction site which results in oxidation of substrate to form products. Thus, it is believed that $\cdot OOM^{3+}PMo_{11}$ intermediate may be responsible for the oxidation of styrene. However, activation of catalyst may also possible with different radicals (*tert*-BuOO·, *tert*-BuOOO·, OH·), generated during the decomposition of TBHP. Although, attempt for isolation of activated catalyst have been made. But it was not possible to isolate and characterize the active catalyst, as it highly reactive in nature.



Scheme 2 Proposed reaction mechanism for oxidation of alcohol using O_2

Similarly, mechanism for alcohol oxidation was also proposed in which active specie $\cdot OOM^{3+}PMo_{11}$ is responsible for oxidation of alcohols to corresponding carbonyl compounds (Scheme 2). But at the same time, as describe in the controlled experiment, addenda atoms (Mo species) may also be involved the catalytic cycle.

Oxidation reactions with H_2O_2 as an oxidant

Oxidation of alcohols with H_2O_2

A detail study was carried out on oxidation of benzyl alcohol with H_2O_2 to optimize the conditions. To ensure the catalytic activity, all reactions were carried out without catalyst and no oxidation takes place. The reaction was carried out with 20 mg of catalysts for 24 h at 90 °C. Generally, benzyl alcohol on oxidation gives benzaldehyde and benzoic acid. However, benzaldehyde was characterized as the major oxidation product in the present case.

Effect of temperature

The effect of temperature on the oxidation of benzyl alcohol was investigated at three different temperatures viz. 70, 90 and 110 °C, keeping the other parameters fixed: namely benzyl alcohol (10 mmol), 30% H_2O_2 (30 mmol), amount (20 mg) and reaction time (24 h). The results are shown in Figure 10.

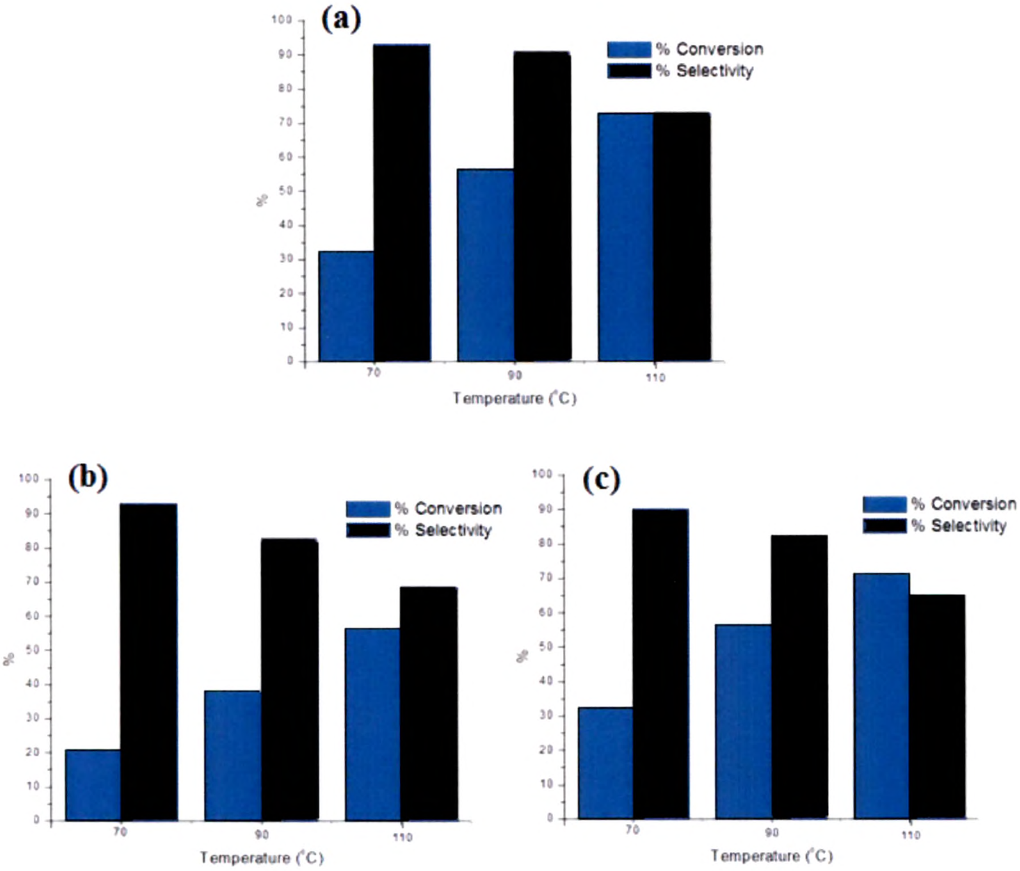


Figure 10. % Conversion is based on benzyl alcohol; benzyl alcohol = 10 mmol, H_2O_2= 30 mmol, Time= 24h, amount of catalyst= 20 mg; (a) $PMo_{11}Co$, (b) $PMo_{11}Mn$ and (c) $PMo_{11}Ni$

From Figure 10 it is clear that on increasing temperature from 70 to 110 ◦C, conversion was also increases. However, at elevated temperature (110 ◦C), decreased in selectivity for benzaldehyde was observed. This is due to over oxidation of benzaldehyde to benzoic acid. Hence, further optimization of the conditions was carried out with 90 ◦C temperature.

Effect of mole ratio

In order to determine the effect of H_2O_2 on the oxidation of benzyl alcohol to benzaldehyde, we studied six different benzyl alcohol: H_2O_2 molar ratios (1:1, 1:2, 1:3, 1:4, 2:1 and 3:1) keeping other parameter fixed: namely catalyst (20 mg), temperature (90 °C) and reaction time (24h). The results are shown in Figure 11.

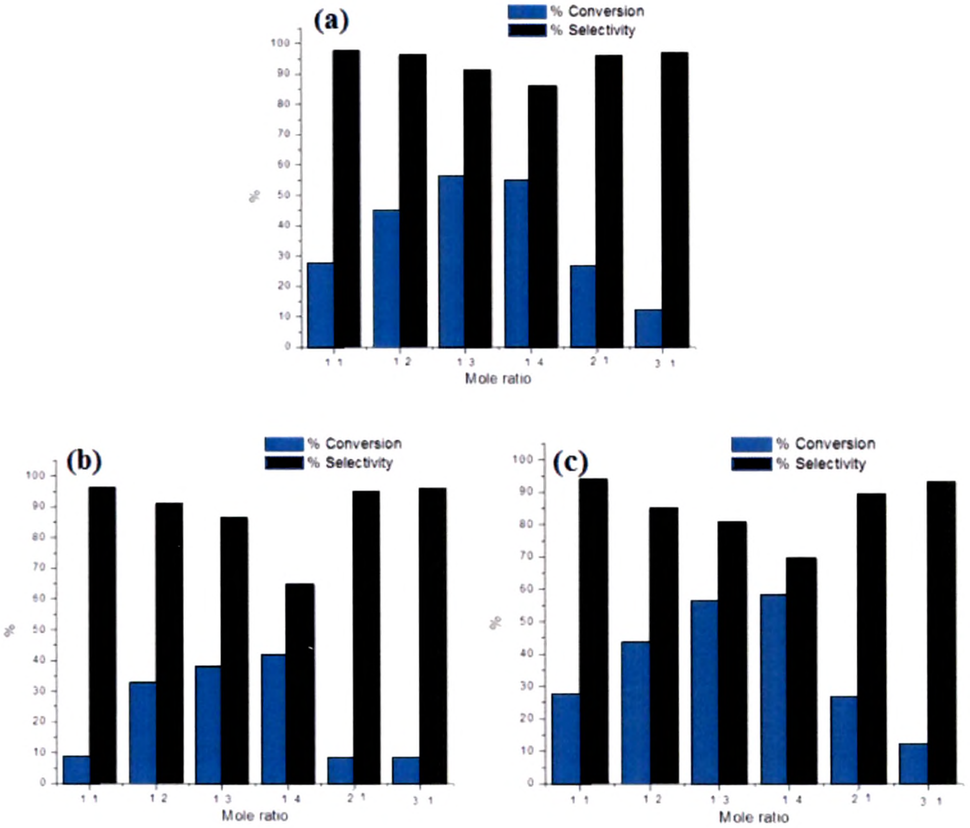


Figure 11. % Conversion is based on benzyl alcohol; Time= 24h, amount of catalyst= 20 mg, Temp= 90 °C; (a) $PMo_{11}Co$, (b) $PMo_{11}Mn$ and (c) $PMo_{11}Ni$

When benzyl alcohol to H_2O_2 molar ratio was increased to 1:1 to 1:3, conversion increased. However, conversion was found to be almost the same when the benzyl alcohol to H_2O_2 molar ratio was further changed to 1:4. At the same time, selectivity for benzaldehyde decreases significantly. This may be due to oxidation of benzaldehyde to benzoic acid in presence of excess of H_2O_2. For other molar ratio, low conversion was found. Therefore, 1:3 molar ratio of benzyl alcohol to H_2O_2 was found to be the optimum in terms of conversion as well as selectivity.

Effect of catalyst amount

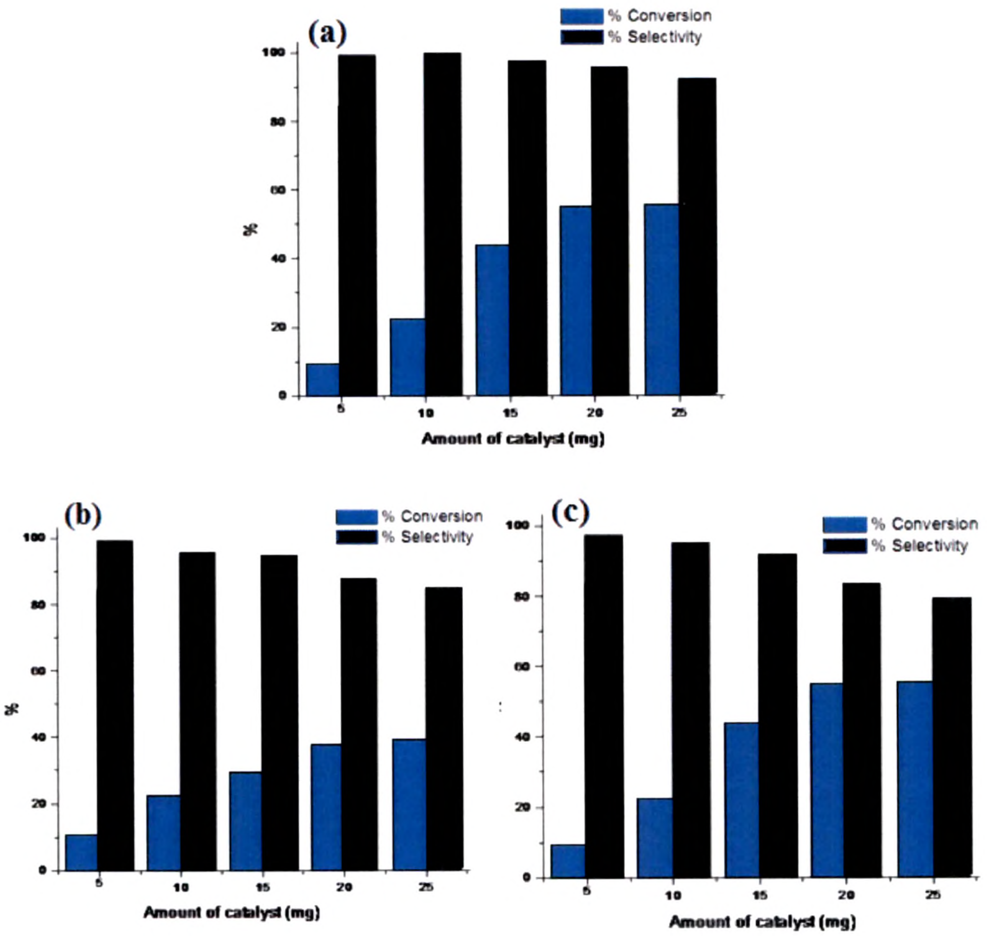


Figure 12. % Conversion is based on benzyl alcohol; benzyl alcohol = 10 mmol, H_2O_2= 30 mmol, Time= 24h, Temp= 90 °C; (a) $PMo_{11}Co$, (b) $PMo_{11}Mn$ and (c) $PMo_{11}Ni$

Five different amounts viz., 5, 10, 15, 20 and 25 mg were used, keeping all other reaction parameters fixed: namely temperature (90 °C), namely benzyl alcohol (10 mmol), 30% H_2O_2 (30 mmol) and reaction time (24 h). The results are shown in Figure 12. With increase in amount of catalysts, % conversion increases. Lower conversion of benzyl alcohol into benzaldehyde with 5 to 15 mg catalyst may be due to fewer catalytic sites. The maximum conversion was observed with 20 mg catalyst but there was no remarkable difference in the progress of reaction when 25 mg of catalyst was employed. Therefore, 20 mg amount of catalyst was taken to be optimal.

Effect of reaction time

The time dependence of catalytic solvent free oxidation of benzyl alcohol was studied by performing the reaction of benzyl alcohol (10 mmol) with 30% H_2O_2 (30 mmol) in the presence of 20 mg of catalysts at 90 °C with constant stirring. The conversion was monitored at different reaction times and results are presented in Figure 13.

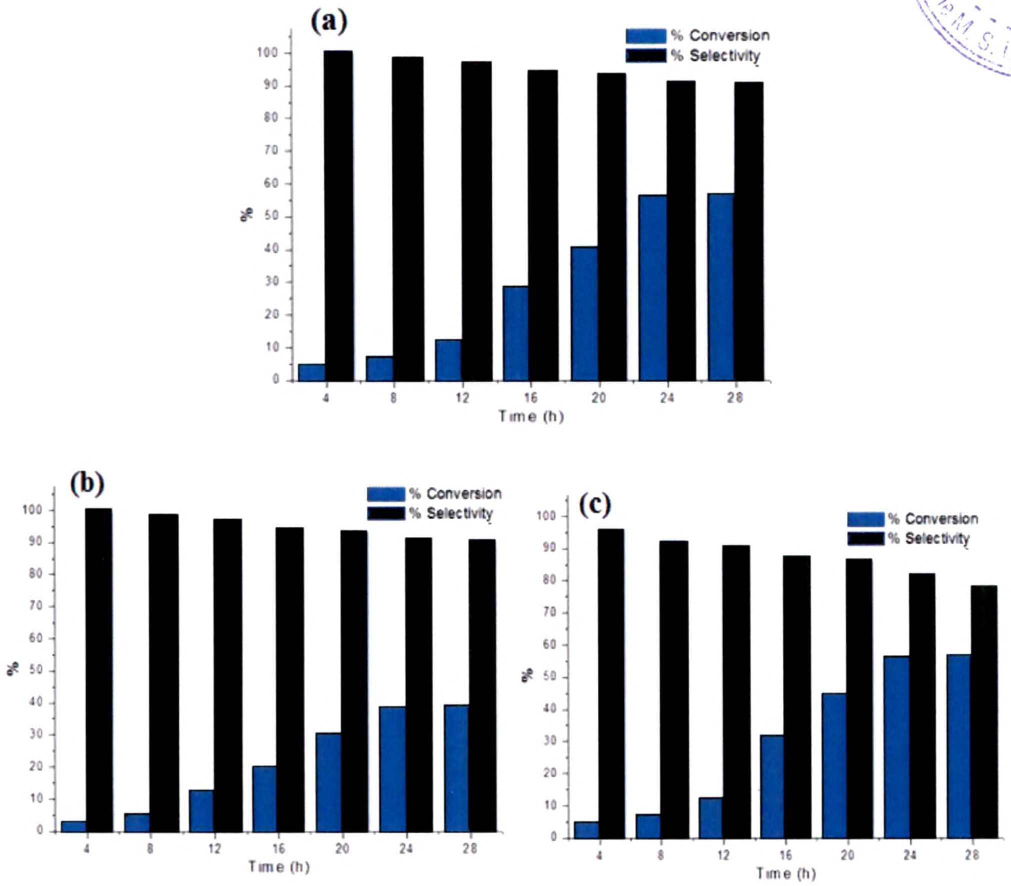


Figure 13. % Conversion is based on benzyl alcohol; benzyl alcohol = 10 mmol, H_2O_2= 30 mmol, amount of catalyst= 20 mg, Temp= 90 ° C; (a) $PMo_{11}Co$, (b) $PMo_{11}Mn$ and (c) $PMo_{11}Ni$

It is seen from Figure 13, that with increase in reaction time, % conversion also increases. This is due to the reason that more time is required for the formation of reactive intermediate which is finally converted into the products. No significant change in % conversion as well as % selectivity was observed from 24 h to 28 h. Hence, reaction time was optimized for 24 h.

The optimum conditions for optimum conversion of benzyl alcohol and selectivity of benzaldehyde over $PMo_{11}M$ (M=Co, Mn, Ni) are; 20 mg of catalyst, 24 h reaction time, reaction temperature 90 °C.

Comparison of $PMo_{11}M$ (M= Co, Mn, Ni) for oxidation of alcohols with H_2O_2

Table 5 Oxidation of alcohols with H_2O_2 using $PMo_{11}M$ (M= Co, Mn, Ni)

Catalyst	Alcohols	% Conv.	Products (%Selectivity)	TON
$PMo_{11}Co$	Benzyl alcohol	56.5	Benzaldehyde(90.9)	742
	Cyclopentanol	55.1	Cyclopentanone(100)	723
	Cyclohexanol	49.1	Cyclohexanone (100)	644
	1-Hexanol	37.2	1-Hexanal (100)	488
	1- Octanol	3.9	-	-
$PMo_{11}Mn$	Benzyl alcohol	37.9	Benzaldehyde(84.9)	486
	Cyclopentanol	34.7	Cyclopentanone(100)	445
	Cyclohexanol	32.9	Cyclohexanone (100)	422
	1-Hexanol	30.0	1-Hexanal (100)	385
	1- Octanol	2.4	-	-
$PMo_{11}Ni$	Benzyl alcohol	56.2	Benzaldehyde(81.3)	718
	Cyclopentanol	50.2	Cyclopentanone(100)	641
	Cyclohexanol	44.5	Cyclohexanone (100)	568
	1-Hexanol	32.7	1-Hexanal (100)	417
	1- Octanol	3.2	-	-

% Conversion is based on alcohol; alcohol = 10 mmol, H_2O_2= 30 mmol, Time= 24h, amount of catalyst= 20 mg, Temp= 90 °C

In order to see the effect of substitution of metal in PMo_{11} as well as to explore scope and limitations of present catalytic system, oxidation of different alcohols with H_2O_2 was also carried out using $PMo_{11}M$ (M=Co, Mn, Ni) under optimized conditions and results are presented in Table 5.

It is seen from Table 5 that, $PMo_{11}Co$ and $PMo_{11}Ni$ show almost same conversion of benzyl alcohol whereas lower conversion of benzyl alcohol was observed for $PMo_{11}Mn$. As mentioned earlier, it is clear that the activity of catalyst is governed by reduction potential of metals used for substitution which are in good agreement with reported one. As seen from Table 5 that, as benzyl alcohol oxidation, similar trend in activity of $PMo_{11}M$ (M = Co, Ni, Mn) was observed for oxidation of other alcohols such as cyclopentanol, 1-hexanol and 1-octanol i.e. $PMo_{11}Co$ shows better activity as compare to $PMo_{11}Mn$ and $PMo_{11}Ni$. The order of activity of catalysts for oxidation is $PMo_{11}Co > PMo_{11}Ni > PMo_{11}Mn$. It was observed from Table 5 that, oxidation of secondary alcohol is easier as compare to primary aliphatic alcohols. The observed trend is in good agreement with reported in art [36]. It is also observed that, in all cases, very good selectivity of desired product with high TON is obtained. It is known that, oxidation of long chain alcohols (C8 and onwards) is still challenging task because of lower reactivity [37] and thus present catalytic system is also not applicable to less reactive long chain primary alcohol such as 1-octanol. For the present catalytic system, the reactivity of the alcohols was found in the order primary < cyclic secondary < aromatic.

Oxidation of alkenes with H_2O_2

A detail study was carried out on oxidation of styrene to optimize the conditions. To ensure the catalytic activity, all reactions were carried out without catalyst and no oxidation takes place. Generally, styrene on oxidation gives styrene oxide, benzaldehyde, and benzoic acid. However, in the present reaction conditions, the major oxidation product obtained was benzaldehyde.

Effect of temperature

The effect of the temperature on the oxidation of styrene was investigated at three different temperatures, viz., 60, 80, and 100 °C, keeping the other parameters fixed (conditions given in caption) and results are shown in Figure 14.

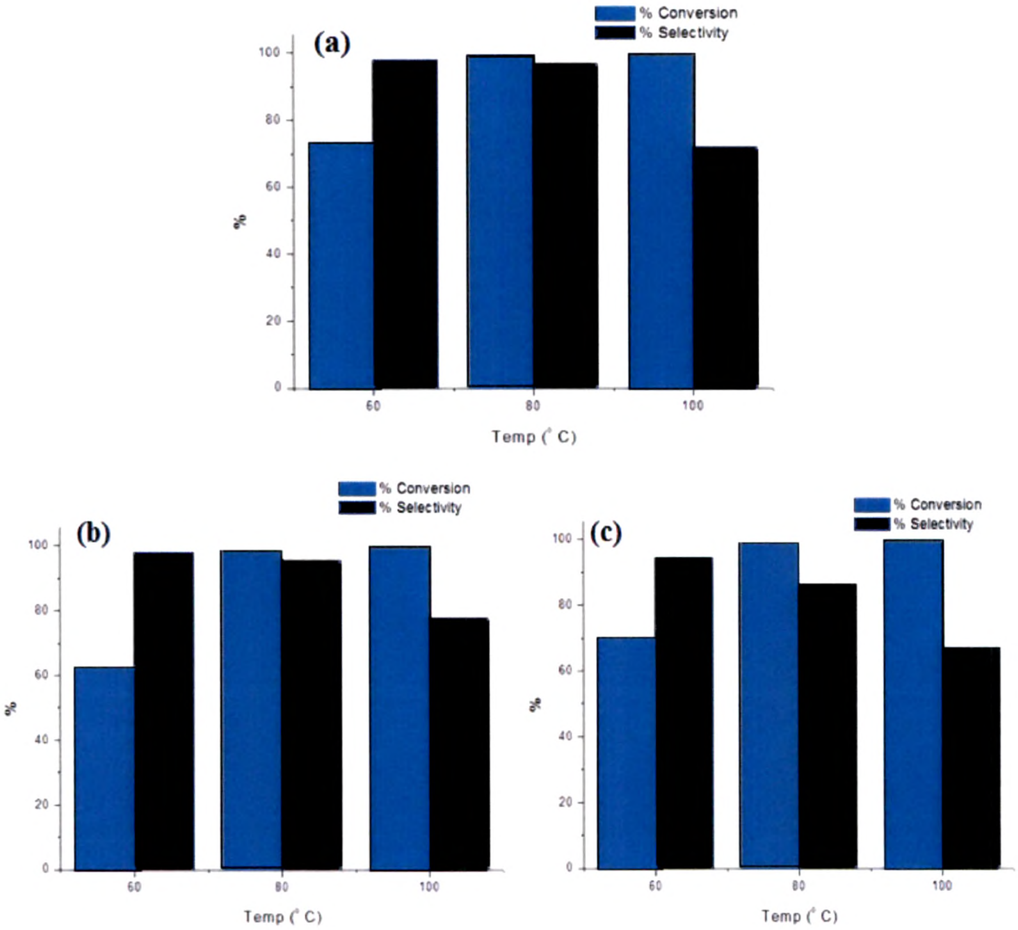


Figure 14. % Conversion is based on styrene; styrene = 10 mmol, H_2O_2= 30 mmol, (a) $PMo_{11}Co$; Time = 10h, amount= 20 mg, (b) $PMo_{11}Mn$; Time = 14h, amount= 25 mg and (c) $PMo_{11}Ni$; Time = 12h, amount= 20 mg

The results show that conversion was increased with increase in temperature. Only a negligible improvement in conversion was observed on increasing temperature from 80 to 100 °C. But, due to over oxidation of benzaldehyde to benzoic acid at elevated temperature, selectivity of benzaldehyde decreased. So the temperature of 80 °C was found optimal for the maximum conversion of styrene.

Effect of mole ratio

The reaction was carried out by varying mole ratio of styrene to H_2O_2 with at 80 ^{o}C. The obtained results are reported in Figure 15.

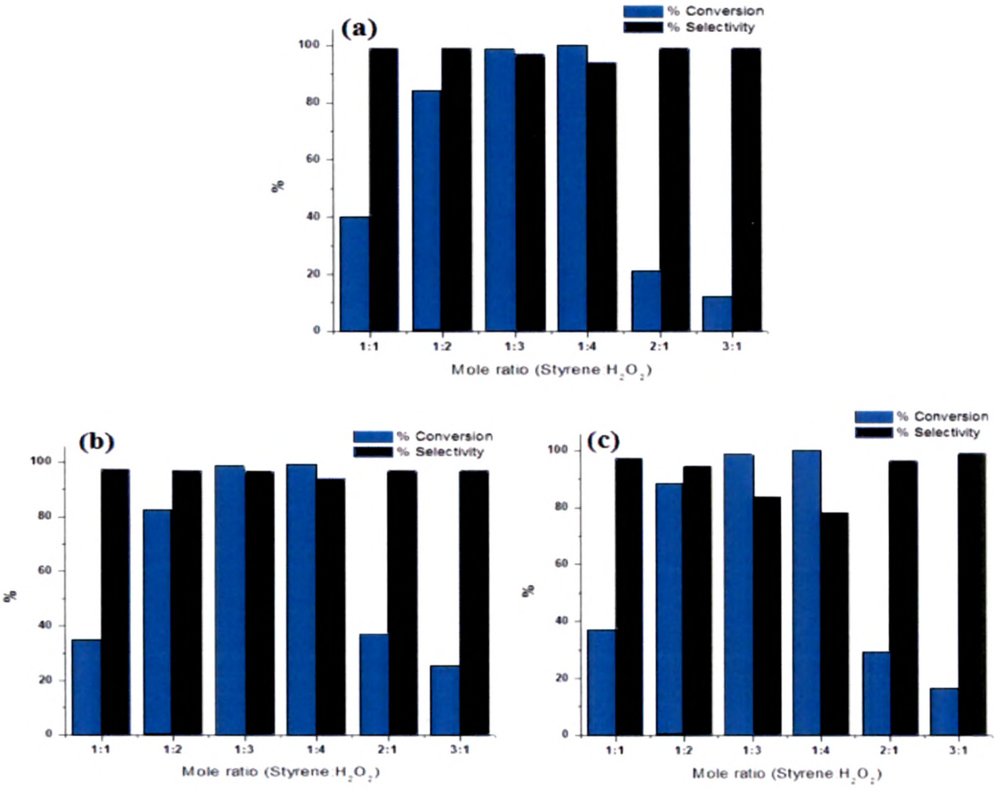


Figure 15. % Conversion is based on styrene; Temp= 80 ^{o} C, (a) $PMo_{11}Co$; Time = 10h, amount= 20 mg, (b) $PMo_{11}Mn$; Time = 14h, amount= 25 mg and (c) $PMo_{11}Ni$; Time = 12h, amount= 20 mg

It is seen from Figure 15 that with increase in molar ratio 1:1 to 1:3, there is a drastic change in the % conversion of styrene. The increase in % conversion is due to increase in concentration of H_2O_2. Almost same conversion of styrene was observed for 1:3 and 1:4. But selectivity of benzaldehyde decreased. So, 1:3 molar ratio was optimized.

Effect of catalyst amount

The reaction was carried out with different amounts of catalysts with 1:3 mole ratio of styrene to H_2O_2 at 80 °C, 10h ($PMo_{11}Co$), 12h ($PMo_{11}Ni$) and 14h ($PMo_{11}Mn$) and result is presented in Figure 16.

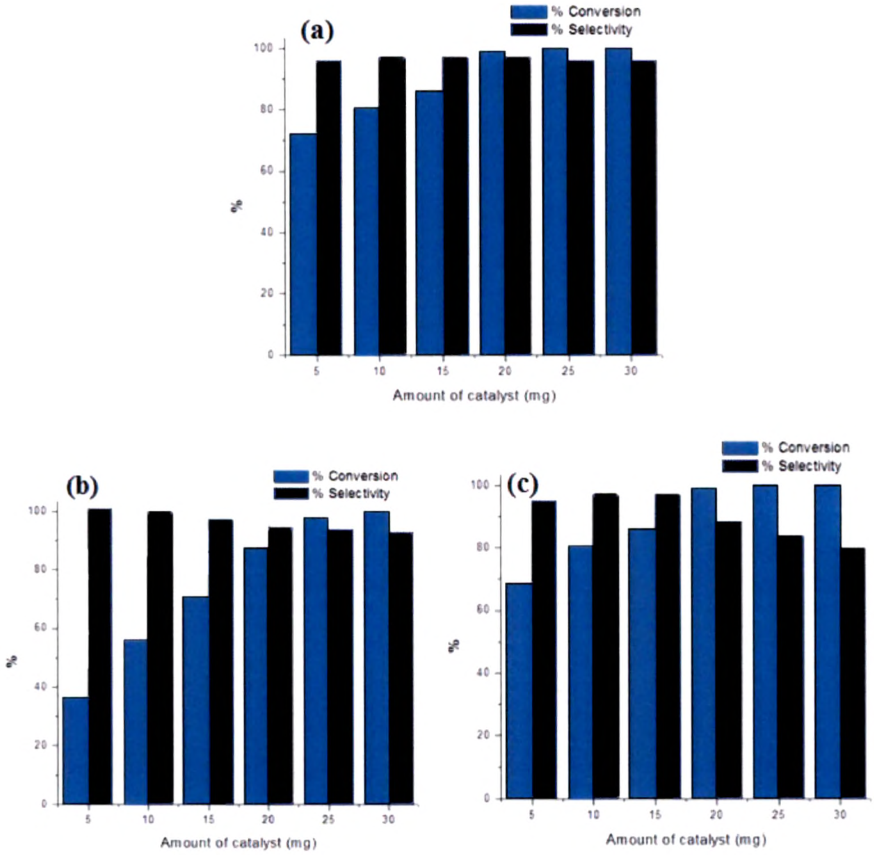


Figure 16. % Conversion is based on styrene; styrene = 10 mmol, H_2O_2= 30 mmol, Temp= 80 ° C, (a) $PMo_{11}Co$; Time = 10h, (b) $PMo_{11}Mn$; Time = 14h, (c) $PMo_{11}Ni$; Time = 12h

It is shown in the Figure 16 that the % conversion increases with an increase in the amount of catalysts. On further increases in the amount of the catalyst, there is a decrease in the % conversion which may be due to blocking of the active sites. It is also seen from the Figure that, >98 % conversion was achieved with 20 mg PMo$_{11}$Co and PMo$_{11}$Ni. However, almost same conversion of styrene was obtained with 25 mg of PMo$_{11}$Mn.

Thus, amount of catalysts was optimized as 20 mg for PMo$_{11}$Co and PMo$_{11}$Ni and 25 mg for PMo$_{11}$Mn.

Effect of reaction time

Oxidation of styrene with H_2O_2 was carried out by varying reaction time at a mole ratio of 1:3 using 20 mg for PMo$_{11}$Co and PMo$_{11}$Ni and 25 mg for PMo$_{11}$Mn. The results are shown in Figure 17.

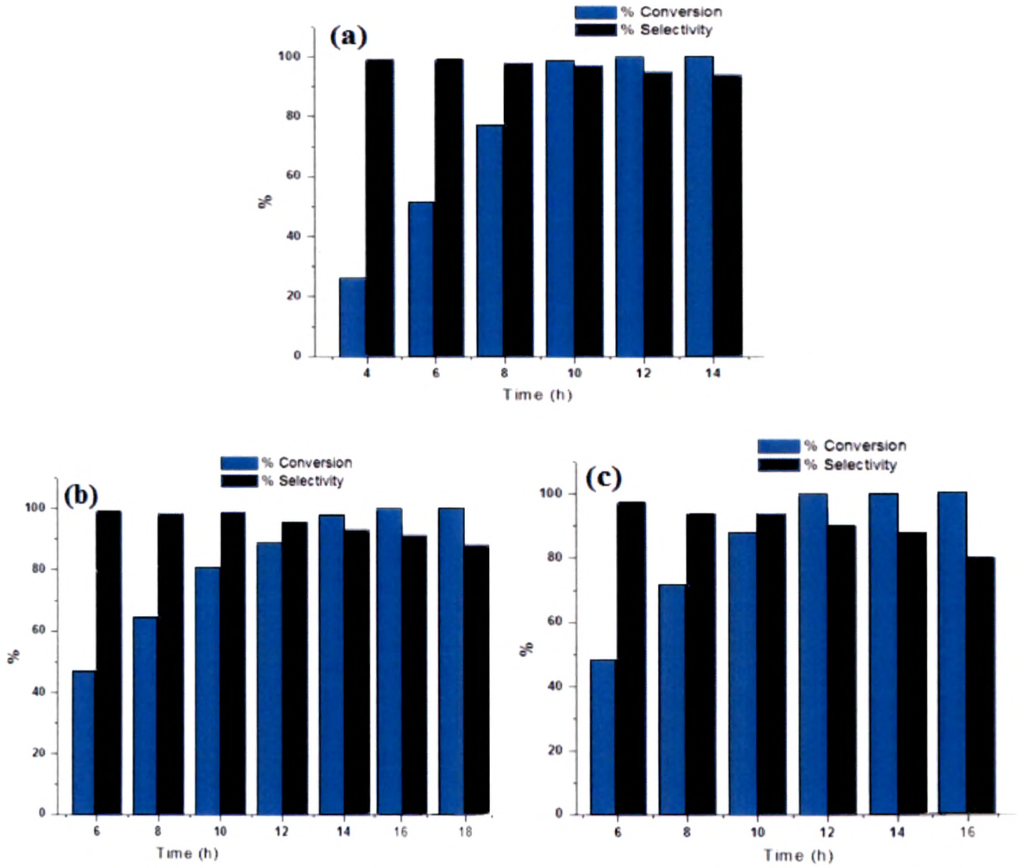


Figure 17. % Conversion is based on styrene; styrene = 10 mmol, H_2O_2= 30 mmol, Temp= 80 °C, (a) PMo$_{11}$Co; amount= 20 mg, (b) PMo$_{11}$Mn; amount= 25 mg and (c) PMo$_{11}$Ni; amount= 20 mg

It is seen from Figure 17 that with increase in reaction time, the % conversion also increases. This is due to the reason that more time is required for the formation of reactive intermediate (substrate + catalyst) which is finally converted into the products.

It is also seen from the Figure 17 that, >98 % conversion was achieved at 10 h for $PMo_{11}Co$, 12 h for $PMo_{11}Ni$. However, almost same conversion of styrene was obtained at 14 h for $PMo_{11}Mn$. Thus, reaction time was optimized as 10 h for $PMo_{11}Co$, 12 h for $PMo_{11}Ni$ and 14 h for $PMo_{11}Mn$.

The optimum conditions for >98 % conversion with >87 % selectivity for benzaldehyde with styrene to H_2O_2 =1:3, temperature = 80 °C, catalyst amount = 20 mg for $PMo_{11}Co$ and $PMo_{11}Ni$ and 25 mg for $PMo_{11}Mn$, time = 10 h for $PMo_{11}Co$, 12 h for $PMo_{11}Ni$ and 14 h for $PMo_{11}Mn$.

Comparison of $PMo_{11}M$ (M= Co, Mn, Ni) for oxidation of alkenes with H_2O_2

In order to see the effect of substitution of metal in PMo_{11}, oxidation of styrene with H_2O_2 under optimized condition of $PMo_{11}Co$ was carried out (Table 6). In addition, to explore scope and limitations of present catalytic system, oxidation of alkenes with H_2O_2 was also carried out using $PMo_{11}M$ (M=Co, Mn, Ni) under optimized conditions and results are presented in Table 7.

Table 6. Comparative data for oxidation of styrene

Catalyst	%	% Selectivity	TON
	Conversion	Benzaldehyde	
PMo$_{11}$Co	98.9	97.1	1264
PMo$_{11}$Mn	78.1	98.0	998
PMo$_{11}$Ni	92.7	87.1	1174

% Conversion is based on styrene, styrene:H_2O_2, 1:3; amount of catalyst, 20 mg; temperature, 80 °C; time, 10 h

Table 7. Oxidation of alkenes with H_2O_2 using PMo$_{11}$M (M= Co, Mn, Ni)

Catalyst	Alkenes	%Conv	Products (%Selectivity)	TON
^{1}PMo$_{11}$Co	Styrene	98.9	Benzaldehyde (97.1)	1264
	α- Methyl styrene	91.4	Acetophenone (95.3)	1168
	^{a}cyclohexene	Nc	-	-
^{2}PMo$_{11}$Mn	Styrene	98.2	Benzaldehyde (94.4)	1002
	α- Methyl styrene	90.3	Acetophenone (93.3)	921
	^{a}cyclohexene	Nc	-	-
^{3}PMo$_{11}$Ni	Styrene	98.8	Benzaldehyde (87.1)	1256
	α- Methyl styrene	93.4	Acetophenone (89.0)	1188
	^{a}cyclohexene	Nc	-	-

% Conversion is based on styrene; styrene = 10 mmol, H_2O_2= 30 mmol, Temp= 80 ° C, (a) PMo$_{11}$Co; Time = 10h, amount= 20 mg, (b) PMo$_{11}$Mn; Time = 14h, amount= 25 mg and (c) PMo$_{11}$Ni; Time = 12h, amount= 20 mg

It is also observed from the results of Table 6 and Table 7 that an order of activity of catalysts for oxidation of styrene is $PMo_{11}Co$ > $PMo_{11}Ni$ > $PMo_{11}Mn$. As described earlier, the difference in the reactivity of these catalysts can be explained on the basis of reduction potential of the transition metal ion substituted into the lacuna of phosphomolybdate moiety. From the reduction potential value it is clear that, catalyst consisting Mn is expected to be least active as compare to Co and Ni. So, results are expected. However, significant difference in selectivity of benzaldehyde was observed. Excellent conversion and selectivity was observed for $PMo_{11}Co$ as compare to other catalysts.

Controlled experiment

A Controlled experiment for oxidation of benzyl alcohol (Table 8) and styrene (Table 9) with Na_2MoO_4, $CsPMo_{12}$, $M(CH_3COO)_2$ and $PMo_{11}M$ (M=Co, Mn, Ni) was carried out under optimized conditions.

Table 8 Controlled experiments Controlled experiment for oxidation of benzyl alcohol under optimized conditions.

Entry	Catalyst	% Conversion	% Selectivity	
			Benzaldehyde	Benzoic acid
1	Without catalyst	1.1	100	-
2	Na_2MoO_4	48.8	51.8	48.2
3	$M(CH_3COO)_2$	45.2[a]	58.6	41.4
		27.7[b]	64.5	35.5
		43.2[c]	51.8	48.2
4	$CsPMo_{12}$	37.9	97.3	2.7
5	$PMo_{11}M$	56.5[a]	90.9	9.1
		37.9[b]	84.9	15.1
		56.2[c]	81.3	18.7

% Conversion is based on benzyl alcohol; amount of catalyst 20 mg ($PMo_{11}M$), 14.5mg ($CsPMo_{12}$), 2mg ($M(CH_3COO)_2$), 20.8 mg (Na_2MoO_4); mole ratio of alcohol to H_2O_2: 1:3, Time 24 h, Temperature 90 °C, M= [a] Co, [b] Mn, [c] Ni

It is seen from Table 8 and Table 9 that in metal salts- catalyzed oxidation reactions, good conversion of substrates with poor selectivity of benzaldehyde was obtained and they are not recyclable. Whereas, $PMo_{11}M$, show good conversion as well as excellent selectivity for benzaldehyde as compared to their metal salts. Also, they can be recyclable. $PMo_{11}M$ combines properties of both PMo_{12} as well as their individual metal salts. At the same time, it is seen from Table 8 that, similar trend in activity of oxidation of benzyl alcohol was also observed for both metal salts as well as $PMo_{11}M$. i.e. Co>Ni>Mn, which shows $PMo_{11}M$ retained the character of their metal salts with improved selectivity for desired product. Also, synthesized catalysts are more efficient than Cs salt of parent PMo_{12}.

Table 9 Controlled experiments Controlled experiment for oxidation of styrene under optimized conditions.

Entry	Catalyst	% Conversion	% Selectivity	
			Benzaldehyde	Other
1	Without catalyst	-	-	-
2	Na_2MoO_4	62.1	83.9	16.1
3	$M(CH_3COO)_2$	59.8[a]	77.4	22.6
		45.5[b]	82.2	17.8
		53.7[c]	65.6	34.4
4	$CsPMo_{12}$	68.4	96.5	3.5
5	$PMo_{11}M$	98.9[a]	97.1	2.9
		78.1[b]	98.0	2.0
		92.7[c]	87.1	12.9

% Conversion is based on styrene; amount of catalyst 20 mg ($PMo_{11}M$), 14.5mg ($CsPMo_{12}$), 2mg ($M(CH_3COO)_2$), 20.8 mg (Na_2MoO_4); mole ratio of styrene to H_2O_2: 1:3, Time 10 h, Temperature 80 °C, M= [a] Co, [b] Mn, [c] Ni

Regeneration and Recycling of Catalysts

Catalytic activity of regenerated catalysts

All the catalysts are insoluble in aqueous as well as organic solvents. On addition of H_2O_2, the insoluble catalysts dissolved in the reaction mixture due to formation of peroxo specie. This peroxo specie gives oxygen to substrates and changed back to the insoluble state, which can be easily separated by simple filtration. The decomposition or leaching of metal contain from $PMo_{11}M$ was confirmed by carrying out an analysis of the used catalyst (EDS) as well as the product mixtures (AAS). For all catalysts, the analysis of the used catalyst (upto two cycles) did not show appreciable loss in the metal content as compared to the fresh catalyst. Analysis of the product mixtures shows that if any metal was present it was below the detection limit, which corresponded to less than 1 ppm.

The separated catalysts were washed with dichloromethane and dried at 100 °C. Oxidation of benzyl alcohol and styrene was carried out with the regenerated catalysts, $PMo_{11}M$, under the optimized conditions and results are shown in Table 10 and Table 11.

Table 10 Oxidation of benzyl alcohol with fresh and recycled catalysts

Catalyst	Cycle	% Conv	% Selectivity	
			Benzaldehyde	Benzoic acid
$PMo_{11}Co$	Fresh	56.5	90.9	9.1
	1	56.4	90.5	9.5
	2	56.1	90.1	9.9
	3	50.2	69.9	30.1
$PMo_{11}Mn$	Fresh	37.9	84.9	15.1
	1	37.9	84.7	15.3
	2	37.8	84.8	15.2
	3	40.2	70.2	29.8
$PMo_{11}Ni$	Fresh	56.2	81.3	18.7
	1	55.8	80.3	19.7
	2	55.8	80.5	19.5
	3	52.7	67.8	32.2

% Conversion is based on benzyl alcohol; benzyl alcohol = 10 mmol, H_2O_2= 30 mmol, Temp= 90 °C, amount= 20 mg, time= 24 h.

Table 11 Oxidation of styrene with fresh and recycled catalysts

Catalyst	Cycle	% Conversion	% Selectivity	
			Benzaldehyde	Other
$PMo_{11}Co$	Fresh	98. 9	97.1	2.9
	1	95.1	97.2	2.8
	2	94.2	97.0	3.0
	3	63.1	69.9	31.1
$PMo_{11}Mn$	Fresh	98.2	94.4	5.6
	1	98.1	94.2	5.8
	2	97.8	94.1	5.9
	3	50.6	72.3	37.7
$PMo_{11}Ni$	Fresh	98.8	87.1	12.9
	1	98.0	87.0	3.0
	2	97.9	86.3	3.7
	3	58.2	64.5	35.5

% Conversion is based on styrene; styrene = 10 mmol, H_2O_2= 30 mmol, Temp= 80 °C, (a) $PMo_{11}Co$; Time = 10h, amount= 20 mg, (b) $PMo_{11}Mn$; Time = 14h, amount= 25 mg and (c) $PMo_{11}Ni$; Time = 12h, amount= 20 mg

The regenerated catalysts show no significant change in conversion as well as selectivity upto two catalytic cycles. For third cycle, remarkable change in conversion as well selectivity is observed. On observing these data carefully, it was found that the obtained data, especially % conversion is quite similar to controlled experiment data of Mo-salt. While obtained difference in % selectivity may be due to the presence of metal ion. In other words, observed change in selectivity and conversion for third cycle may be due to the decomposition of Keggin framework into their corresponding metal oxides. So, the present catalysts can be reused upto two cycles only.

Effect of oxidants on oxidation of benzyl alcohol and styrene

Under the optimized conditions, oxidation of styrene and benzyl alcohol with $PMo_{11}M$ was carried out using both the oxidants. The results for the same are presented in Table 12.

Table 12 Oxidation of benzyl alcohol and styrene using different oxidants

Catalyst	Oxidant	Substrate	(%) Conversion	(%) Selectivity (Benzaldehyde)	TON
$PMo_{11}Co$	$^xH_2O_2$	Benzyl alcohol	56.5	90.9	742
		styrene	98.9	97.1	1264
	$^yO_2$	Benzyl alcohol	32.6	92.3	4281
		styrene	41.1	92.2	5253
$PMo_{11}Mn$	$^xH_2O_2$	Benzyl alcohol	37.9	84.9	498
		styrene	78.1	98.0	998
	$^yO_2$	Benzyl alcohol	28.3	93.6	3628
		styrene	35.9	90.7	4602
$PMo_{11}Ni$	$^xH_2O_2$	Benzyl alcohol	56.2	81.3	723
		styrene	92.7	87.1	1174
	$^yO_2$	Benzyl alcohol	31.9	92.3	4075
		styrene	39.9	87.2	5047

% Conversion is based on substrate (^{a}benzyl alcohol/^{b}styrene); amount of catalyst = 20 mg; temperature ^{a}90 °C, ^{b}80 °C

^{x}Reaction conditions; molar ratio of substrate to H_2O_2= 10: 30 mmol, Time, ^{a}24 h, ^{b}10 h; ^{y}Reaction conditions; substrate = 10 mmol, O_2, TBHP= 0.2 %, Time, ^{a}24 h, ^{b}8 h;

Result it is seen from results that, with O_2 as an oxidant, higher turn over number (TON) was obtained as compared to that of H_2O_2. It is known that O_2 has the highest content of active oxygen (i.e. singlet oxygen) and is the most reactive oxygen. The activation of metal centre by O_2 occurs in a single step via formation of M-O_2 species. Where as in case of oxidation involving H_2O_2 the activation of the metal centre occurs in two steps (i) via formation of hydroperoxo or peroxo species and (ii) these formed hydroperoxo or peroxo species rearranges to form oxo intermediate which attacks the substrate resulting in oxidation of substrate. In case of H_2O_2, the activation of the catalyst takes place in two steps, as a result it requires more time as compared to O_2, to achieve maximum conversion. Thus results are as expected.

Kinetics of oxidation of styrene with H_2O_2

A study on the kinetic behavior was carried out for all three catalysts. In all the experiments, reaction mixtures were analyzed at fixed interval of time using gas chromatography.

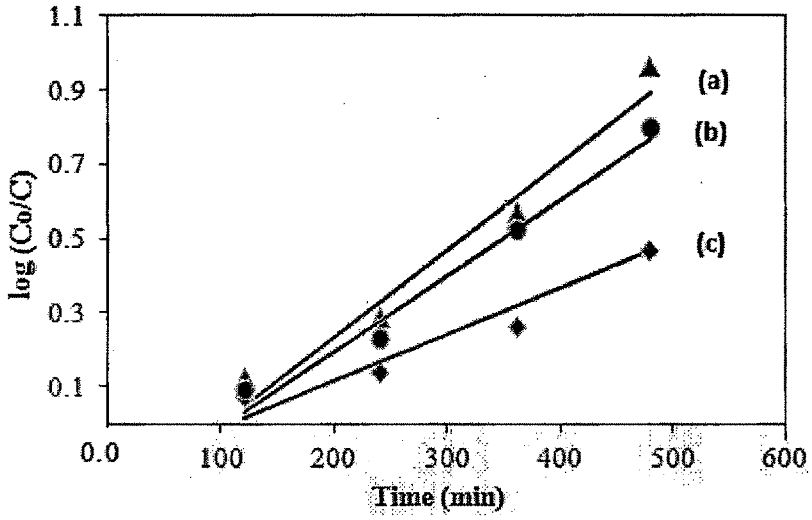


Figure 18. Styrene consumption as a function of reaction time; catalyst amount= 20 mg; T = 353 K (a) $PMo_{11}Co$ (b) $PMo_{11}Ni$ and (c)$PMo_{11}Mn$

The plot of ln Co/C versus time (Figure 18) shows a linear relationship of styrene consumption with respect to time. With an increase in reaction time, there is a gradual decrease in the styrene concentration over both the catalysts. A slight deviation from linearity was observed for all the catalysts. These observations indicate that the oxidation of styrene is expected to follow pseudo first-order. This was further supported by the study of the effect of catalyst concentration on the rate of the oxidation of styrene.

The catalyst amount was varied from 5 to 25 mg at a fixed substrate concentration of 10 mmol and at a temperature of 80 °C. The plot of reaction rate versus catalyst amount (Figure 19) also shows a linear relationship for $PMo_{11}Mn$, while a pseudo linear relationship for $PMo_{11}Co$ and $PMo_{11}Ni$.

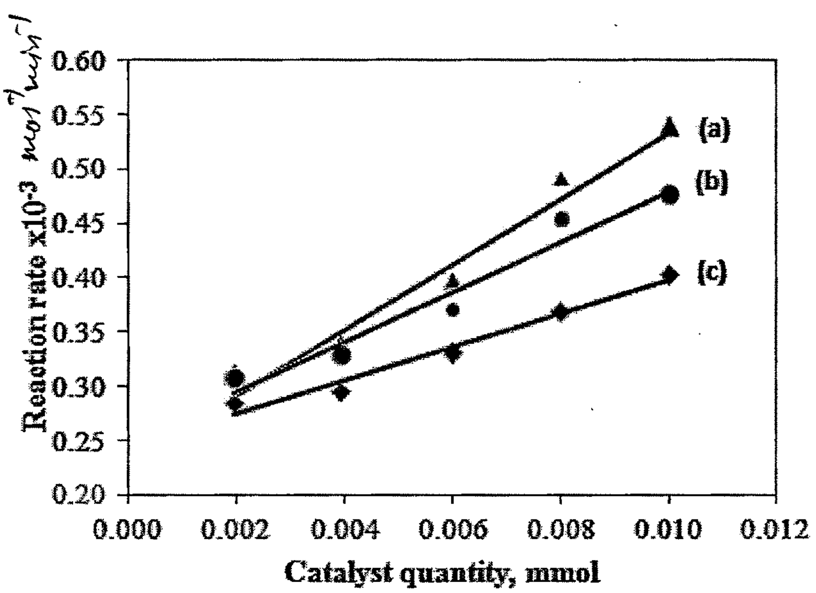


Figure 19. Effect of catalyst amount on rate of reaction; (a) $PMo_{11}Co$ (b) $PMo_{11}Ni$ and (c) $PMo_{11}Mn$

As the concentration of the active species, increased from 5 to 20 mg, the rate of reaction also increased for both the catalysts. The above study confirms that the initial rates of oxidation of styrene follow pseudo first-order kinetics with respect to the substrate as well as the catalyst for all the catalysts. Based on the above results, the rate law was also deduced for both catalysts and was found to obey Eq. 1. Furthermore, the rate constants were determined using Eq. 1 and the values for the same are reported in Table 13.

$$\frac{-d[BA]}{dt} = k[sty][cat] \qquad \text{(Eq. 1)}$$

As most of the oxidation reactions are temperature sensitive, the effect of temperature on the oxidation of styrene was also studied by varying the temperature between 333 and 373 K, keeping the styrene: H_2O_2 ratio of 1:3 and catalyst amount of 20 mg. As the temperature increases from 333 to 373 K, the conversion of styrene also increases drastically for all catalysts. This may be due to the activation of the catalytic species with temperature. The graph of ln k versus 1/T was plotted (Figure 20) and the value of activation energy (Ea) was determined from the plot.

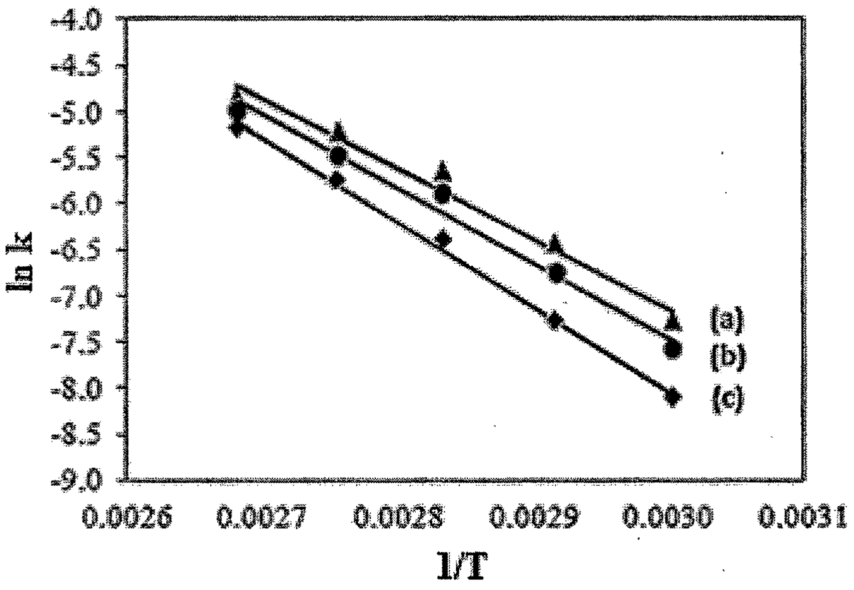


Figure 20. Arrhenius plot; (a) $PMo_{11}Co$ (b) $PMo_{11}Ni$ and (c) $PMo_{11}Mn$

The rate constants were determined using Eq. 1 and the values for the rate constant and activation energy are reported in Table 13.

Table 13 Kinetic parameters for oxidation of styrene over $PMo_{11}Co$, $PMo_{11}Mn$ and $PMo_{11}Ni$

Catalyst	Rate constant k X 10^{-3} (m^{-1})	Activation Energy (Ea) (kJ/mol)	Pre- exponential factor A
$PMo_{11}Co$	3.87	62.9	5.9 x 10^6
$PMo_{11}Mn$	2.03	76.1	2.6 x 10^8
$PMo_{11}Ni$	3.03	67.3	2.3 x 10^7

The catalytic as well as kinetic data indicates that all the catalysts are highly reactive towards solvent free liquid phase oxidation of styrene under mild reaction conditions and an order of activity of catalysts is $PMo_{11}Co$> $PMo_{11}Ni$> $PMo_{11}Mn$ for the present reactions.

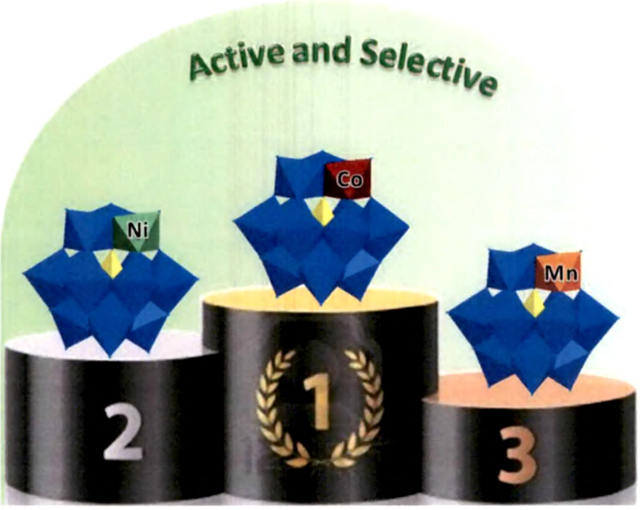
$PMo_{11}Co$ was found the best catalysts with both oxidants (O_2 and H_2O_2) in terms of conversion of substrates and selectivity of desire product as well as TON.

CONCLUSIONS

1. The use of $PMo_{11}M$ (M= Co, Mn, Ni) was established as sustainable catalysts for oxidation of alcohols and alkenes catalyzed by with environmentally benign oxidants viz. O_2 and H_2O_2 under mild reaction conditions.
2. 28-33 % conversion of benzyl alcohol with 92-93 % selectivity for benzaldehyde was obtained in 24h with O_2. 35-41 % conversion of styrene with 87-92 % selectivity for benzaldehyde was obtained in 8 h with O_2.
3. 38-56 % conversion of benzyl alcohol with 81-91 % selectivity for benzaldehyde was obtained in 24h with H_2O_2. 78-99 % conversion of styrene with 87-97 % selectivity for benzaldehyde was obtained in 10 h with H_2O_2.
4. $PMo_{11}M$ act as homogeneous catalysts with H_2O_2 while as heterogeneous catalysts with O_2.
5. In all cases, good conversion of substrates and excellent selectivity of desire products and with very high TON was obtained. O_2 is a better oxidant as compared to H_2O_2.
6. $PMo_{11}M$ can be successfully regenerated and reused upto 4 cycles in case of O_2 and 2 cycles in case of H_2O_2 without any significant loss in the catalytic activity. FT-IR study of reused catalysts shows no structural changes indicating catalytic systems are stable.
7. For the first time, a reaction mechanism for oxidation of alkenes and alcohols involving TBHP as an initiator was proposed.
8. For the present catalytic systems, the reactivity of the alcohols was found in the order primary < cyclic secondary < aromatic. At the same

time, present catalytic systems are not applicable for oxidation of cyclic olefins and long chain (C8 onwards) alcohols with both oxidants.

9. The value of activation energy of $PMo_{11}Co$, $PMo_{11}Ni$ and $PMo_{11}Mn$ is 62.9 kJ/mol, 67.3 kJ/mol, 76.1 kJ/mol respectively. Catalytic and kinetic studies revealed that $PMo_{11}Co$ is the best catalyst among all and an order of activity of catalysts for oxidation of styrene is $PMo_{11}Co$ > $PMo_{11}Ni$ > $PMo_{11}Mn$.



10. The advantages of reusable and sustainable catalysts with O_2 and H_2O_2 for oxidation under solvent free conditions make this methodology interesting from an economic and an ecological point of view.

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