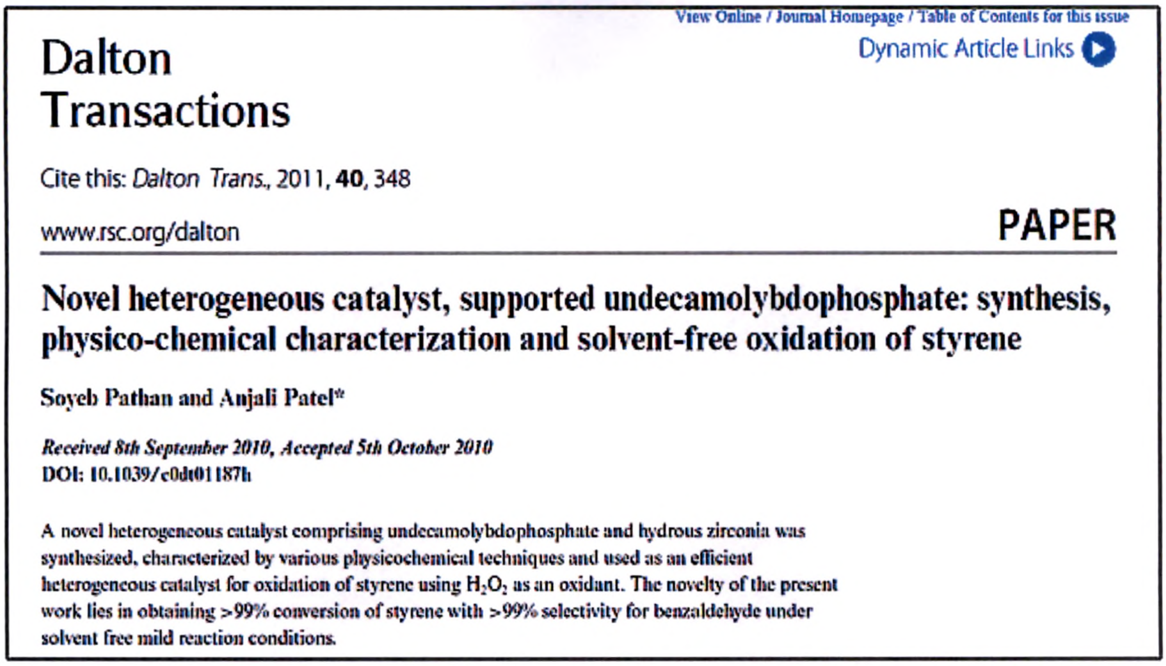
Chapter

3

Supported Undecamolybdophosphates as Sustainable Catalysts



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PAPER

Novel heterogeneous catalyst, supported undecamolybdophosphate: synthesis, physico-chemical characterization and solvent-free oxidation of styrene

Soyeb Pathan and Anjali Patel*

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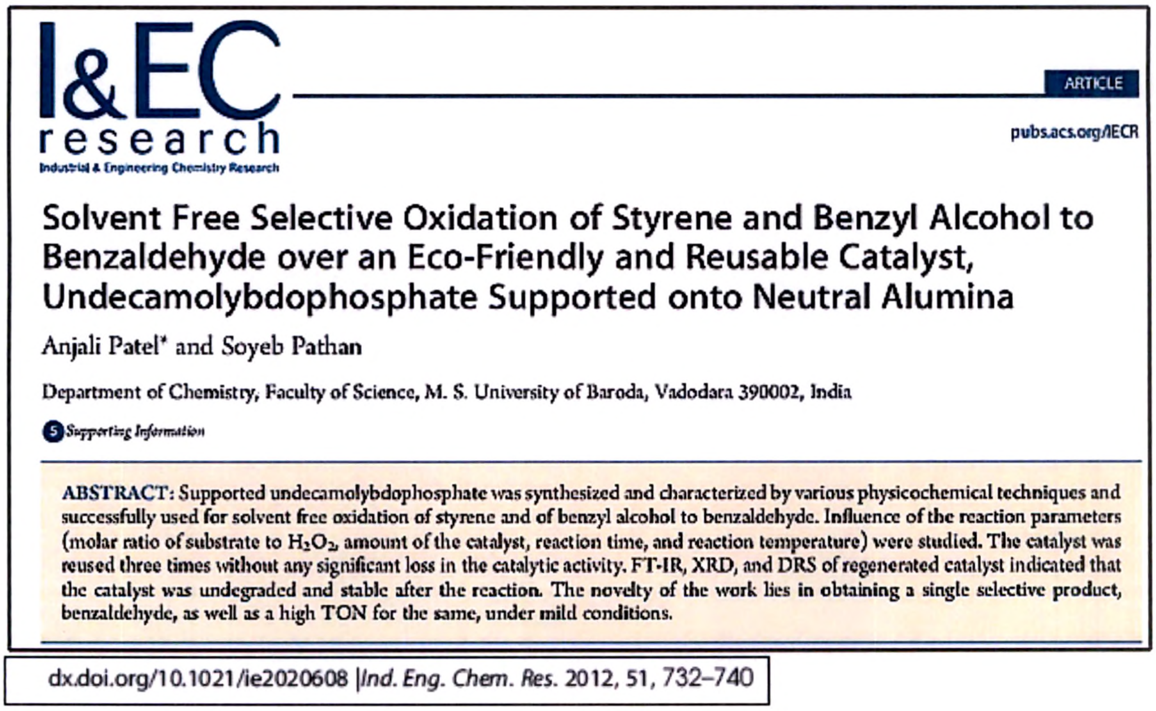
A novel heterogeneous catalyst comprising undecamolybdophosphate and hydrous zirconia was synthesized, characterized by various physicochemical techniques and used as an efficient heterogeneous catalyst for oxidation of styrene using H_2O_2 as an oxidant. The novelty of the present work lies in obtaining >99% conversion of styrene with >99% selectivity for benzaldehyde under solvent free mild reaction conditions.



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Solvent Free Selective Oxidation of Styrene and Benzyl Alcohol to Benzaldehyde over an Eco-Friendly and Reusable Catalyst, Undecamolybdophosphate Supported onto Neutral Alumina

Anjali Patel* and Soyeb Pathan

Department of Chemistry, Faculty of Science, M. S. University of Baroda, Vadodara 390002, India

Supporting Information

ABSTRACT: Supported undecamolybdophosphate was synthesized and characterized by various physicochemical techniques and successfully used for solvent free oxidation of styrene and of benzyl alcohol to benzaldehyde. Influence of the reaction parameters (molar ratio of substrate to H_2O_2, amount of the catalyst, reaction time, and reaction temperature) were studied. The catalyst was reused three times without any significant loss in the catalytic activity. FT-IR, XRD, and DRS of regenerated catalyst indicated that the catalyst was undegraded and stable after the reaction. The novelty of the work lies in obtaining a single selective product, benzaldehyde, as well as a high TON for the same, under mild conditions.

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Anjali Patel

Environmentally Benign Catalysts

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Chapter 10
Solvent-Free Selective Oxidation of Benzyl Alcohol to Benzaldehyde over Monolacunary Phosphomolybdate Supported onto Hydrous Zirconia

Soyeb Pathan and Anjali Patel

Abstract The present chapter describes synthesis and characterization of supported lacunary phosphomolybdate as well as its use as heterogeneous catalyst for solvent-free oxidation of benzyl alcohol. Influence of the reaction parameters (molar ratio of substrate to H_2O_2, amount of the catalyst, reaction time, and reaction temperature) was studied. The catalyst was reused three times without any significant loss in the catalytic activity. Present catalyst gives single selective product, benzaldehyde, as well as high TON for the same, under mild reaction conditions.

S. Pathan • A. Patel (✉)
Department of Chemistry, Faculty of Science, M. S. University of Baroda,
Vadodara 390002, India
e-mail: aupatel_chem@yahoo.com

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Majority of chemical processes though beneficial, leads to production of unwanted wastes. The in-efficient recovery of organic solvents, wastes and their disposal are problems which damage environment. Catalysis is a key technology to provide realistic solutions to many environmental issues [1]. The central tasks of catalysts are to lower the raw material and energy requirement of chemical reactions, the diminution of side products/waste products, as well as the control of hazardous effects of chemical substances for the sound establishment of chemical science and technology. To cope up with the problems, the development of ecofriendly catalysts as well as processes is gaining world wide attention.

The modern research on sustainable catalysts focuses on five main areas [2]:

1. Predicting and controlling catalyst structure
2. Improving the integration of catalytic processes
3. Energy consumption and raw material cost
4. Reducing waste
5. Reducing the cost of the process

In one of the largest generic areas of chemistry, i.e. oxidations, there are countless processes operated by almost every type of chemical manufacturing company, producing products of incalculable value, still producing almost immeasurable volumes of waste. One of the important development areas in this context will be the more widespread use of heterogeneous catalysts in liquid phase organic reactions. The enormous range of reactions and the rapidly growing number of new catalysts will require the use of rapid screening methods and the use of innovative engineering to fully exploit the new chemistry.

Liquid phase oxidation of organic compound to their oxygenated products especially carbonyl compounds has become important synthetic reaction with numerous applications. Carbonyl compounds are very valuable chemical that has widespread applications in perfumery, dyestuff, and agro chemical industries [3]. Among carbonyl compounds, benzaldehyde is the second most important aromatic molecule (after vanillin) used in the cosmetics and flavor industries. Generally it is obtained by oxidation of styrene, benzyl alcohol, and toluene as well as hydrolysis of benzyl chloride [4-6]. However, along with carbonyl compounds, oxidation of styrenes gives a variety of products such as, epoxides, diols, and acids. Production of benzaldehyde is the first step in oxidation of benzyl alcohol and further oxidation leads to the production of benzoic acid with side reactions leading to the other products like toluene, dibenzyl acetal, and benzyl benzoate [7]. Oxidation of toluene is usually carried out in organic solvents which are environmentally undesirable and benzaldehyde produced from hydrolysis of benzyl chloride often contains traces of chlorine impurities and copious waste is generated in this process [8]. Most of these procedures suffer from a lack of selectivity, high temperature, use of organic solvents, toxicity of the reagents, and waste production.

Environmental concerns have forced the chemical industries to re-evaluate many of its processes to reduce or eliminate the formation of by-products. Therefore, selective liquid catalytic oxidation of organic compounds with environmentally benign, cheap and readily available oxidants is the most economic and ecological route to a wide variety of products [9-14].

Generally, Catalytic oxidations in the liquid phase generally employ soluble metal salts or complexes in combination with clean, inexpensive oxidants such as O_2, H_2O_2, or RO_2H. However, heterogeneous catalysts have the advantage, compared to their homogeneous counterparts, of facile recovering and recycling.

Thus, design of active, selective, and recyclable sustainable heterogeneous catalysts have come into prominence.

POMs have received increasing attention as oxidation catalysts due to their unique redox properties [15-20]. As mentioned in chapter 1, a sub class of POMs, LPOMs forms an important class of compounds. However, most of the reported articles describe the use of LPOMs form the bulk of homogeneous catalysts [21-31]. To the best of our knowledge, first reports on catalytic evaluation of supported LPOMs, i.e. supported $[PW_{11}O_{39}]^{7-}$ for liquid phase oxidation reaction was reported by our group only [32]. Our group reported use of PW_{11}/ZrO_2 and PW_{11}/Al_2O_3 as bifunctional catalysts for esterification of alcohols and selective oxidation of styrene [32,33]. Recently, Granadeiro et al. reported liquid phase oxidation of cis-cyclooctene, geraniol and R-(+)-limonene over PW_{11}@MIL-101 and SiW_{11}@MIL-101 using the H_2O_2 as oxidant [34].

A literature survey shows that all the reports described oxidation reactions over supported $[XW_{11}O_{39}]^{n-}$ (X= P, Si). At the same time, no report is available on catalytic aspects of supported undecamolybdophosphate, $[PMo_{11}O_{39}]^{7-}$. Keeping in mind oxidation ability of phosphomolybdates as well as economical and ecological aspects, attempts were made to establish the use of supported undecamolybdophosphate, as sustainable heterogeneous catalysts for oxidation reactions.

The oxidation of alcohols and alkenes to the corresponding epoxides as well as oxygen containing carbonyl compounds is a well-documented reaction that has been investigated for decades. Epoxides are important commodity products and, at the same time, pivotal/basic building blocks for organic synthesis, both from industrial and academic standpoints. At the same time, carbonyl compounds are also widely used as solvents, perfumes, and flavouring agents or as intermediates in the manufacture of plastics, dyes, and pharmaceuticals.

Most of the oxidation reactions have been carried out in presence of solvents such as such as acetone, acetonitrile, hexane as well as phase transfer catalyst (PTC) [35-70]. It would be more beneficial if reactions could be carried out without solvent. In the recent years, hydrogen peroxide has emerged as the oxidant of choice for many transformations because it is environmentally benign, having high atom efficiency [2], it can be handled and stored safely, and it produces water, only by-product [71,72].

In addition to hydrogen peroxide, molecular oxygen has also emerged to be one of the strong contenders for the same. The utilization of molecular oxygen for catalytic oxygenation is a rewarding goal because among oxidants, molecular oxygen has the highest content of active oxygen and forms no byproducts [73-79].

Keeping these aspects in mind, following reaction over PMo_{11}/ZrO_2 and PMo_{11}/Al_2O_3 was planned.

- **with O_2**
  - Oxidation of alcohols
  - Oxidation of alkenes
- **with H_2O_2**
  - Oxidation of alcohols
  - Oxidation of alkenes

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 % loading of PMo_{11}, mole ratio of substrate to H_2O_2, reaction temperature, catalyst amount and reaction time. Further, the heterogeneity test was also performed for the catalysts, to confirm the absence of leaching of the active species from the support surface. The catalysts were also regenerated and reused. Under the optimized conditions oxidation of other alkenes and alcohols was also evaluated over both the catalysts. Effect of nature of supports and effect of different oxidants on oxidation was studied. A kinetic study for oxidation of styrene with H_2O_2 over supported catalysts was also studied.

EXPERIMENTAL

Materials

All the chemicals used were of A. R. grade. Sodium molybdate, Disodium hydrogen phosphate, zirconium oxychloride, Liquor ammonia, neutral active Al_2O_3 (Activity I-II, according to Brockmann), Nitric acid, acetone, 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 Reactions

Oxidation with molecular oxygen

The catalytic activity was evaluated for oxidation of alcohols using molecular oxygen as an oxidant and *tert*-Butyl hydrogen peroxide **(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 % loading of PMo_{11}, 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 % loading, 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 identification was done by comparison with authentic samples and finally by a combined Gas Chromatography Mass Spectrometer (Hewlett-Packard column) using HP-1 capillary column (30m, 0.5mm id) with EI and 70eV ion source.

The conversion as well as selectivity was calculated on the basis of mole percent of substrates.

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

$$\text{Selectivity (\%)} = \frac{\text{moles of product formed}}{\text{moles of substrate consumed}} \times 100$$

The turn over number **(TON)** was calculated using the following equation

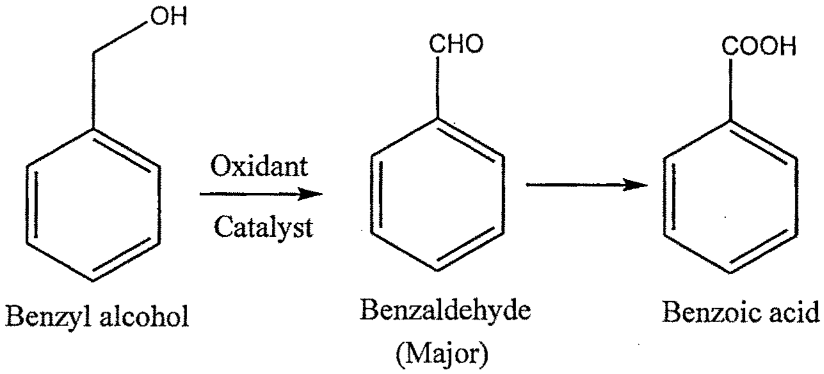
$$\text{TON} = \frac{\text{moles of product}}{\text{moles of catalyst}}$$

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 25 mg of PMo_{11}/ZrO_2 and PMo_{11}/Al_2O_3 for 24 h at 90°C. Generally, benzyl alcohol on oxidation gives benzaldehyde and benzoic acid. However, benzaldehyde was found as the major oxidation product in the present case (Scheme 1).



Scheme 1. Oxidation of benzyl alcohol

Effect of % loading of PMo_{11}

The oxidation of benzyl alcohol was carried out using 25 mg of catalysts for 24 h at 90 °C are presented in Figure 1.

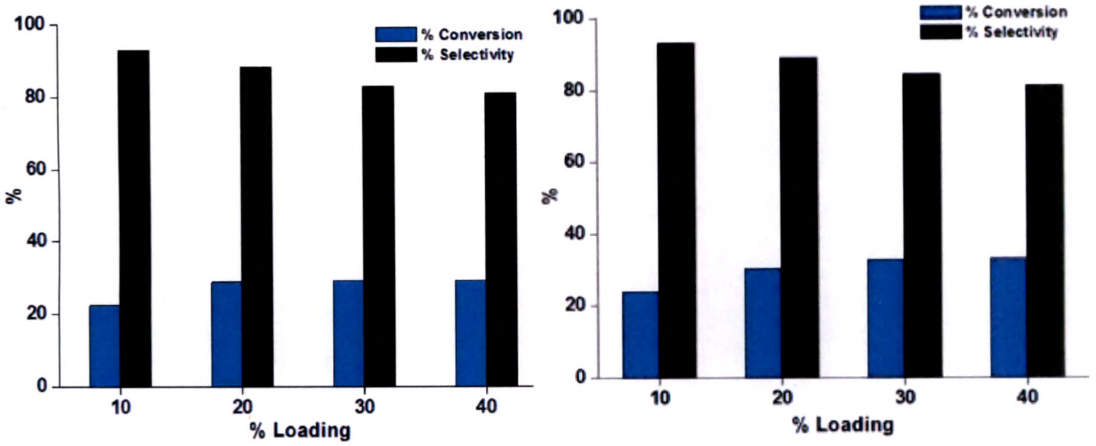


Figure 1. % Conversion is based on benzyl alcohol; benzyl alcohol = 100mmol, TBHP= 0.2%, Temp= 90°C, Time= 24h, amount of catalyst= 25 mg, PMo_{11}/ZrO_2 (Left) and PMo_{11}/Al_2O_3 (Right)

From Figure 1 it is clear that, increase in the conversion was observed with increase in the % loading of PMo_{11} from 10% to 20%. On increase in % loading from 20% to 40%, no significant increase in conversion was observed. This may be due to at higher % loading, the particles may agglomerate on the surface, results in reduce accessibility to the active sites. Thus, loading of PMo_{11} on the supports was fixed at 20% and detail studies were carried out over 20% PMo_{11}/ ZrO_2 and 20% PMo_{11}/ Al_2O_3.

Effect of temperature

In order to determine the optimum temperature the reaction was investigated at four different temperatures 80, 90 and 100 °C, using both the catalysts keeping other parameters fixed (amount 25mg, time 24h). The results for the same are presented in Figure 2.

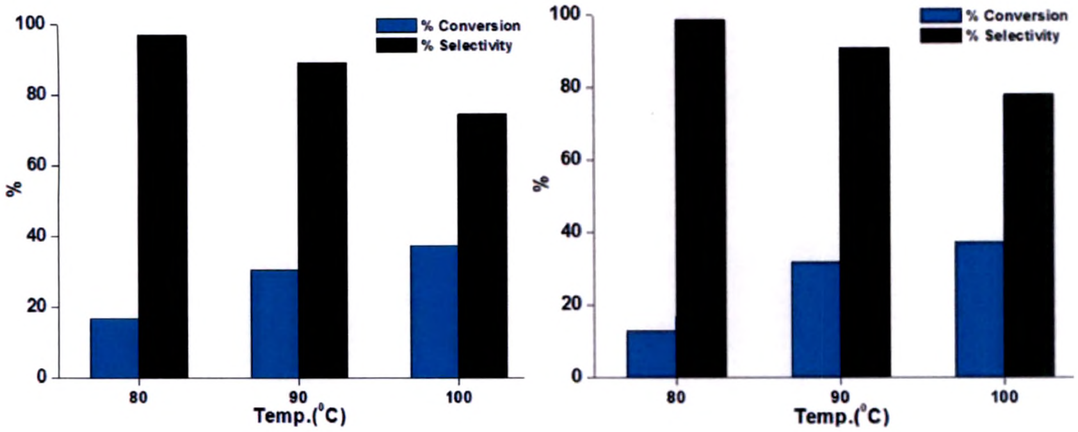


Figure 2. % Conversion is based on benzyl alcohol; benzyl alcohol = 100mmol, TBHP= 0.2%, Time= 24h, amount of catalyst= 25 mg, PMo_{11}/ZrO_2 (Left) and PMo_{11}/Al_2O_3 (Right)

The results show that conversion increased with increasing temperature. At the same time, on increasing temperature from 90 to 100 °C, selectivity of benzaldehyde was decrease for both catalysts, this is due to over oxidation of benzaldehyde to benzoic acid at elevated temperature. So temperature of 90°C was fixed for the optimum conversion of benzyl alcohol as well selectivity of desire product.

Effect of catalyst amount

The effect of the catalyst amount on the conversion of benzyl alcohol over both the catalysts is represented in Figure 3.

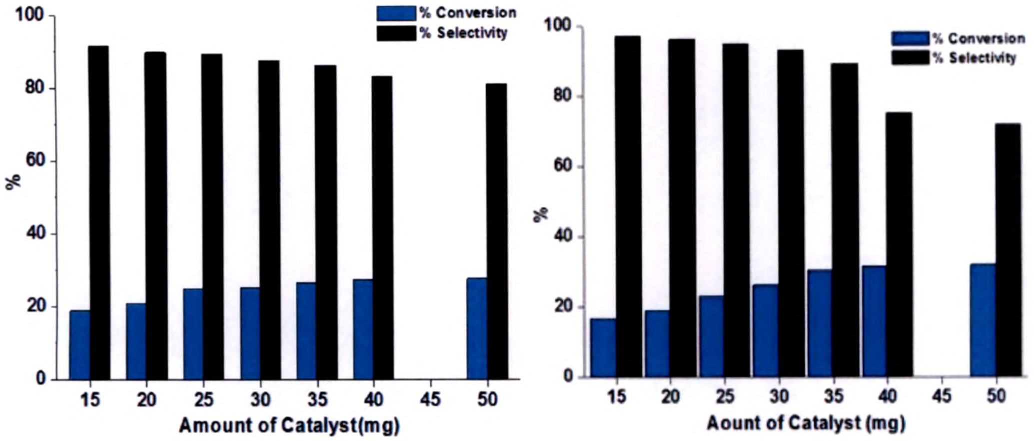


Figure 3. % Conversion is based on benzyl alcohol; benzyl alcohol = 100mmol, TBHP= 0.2%, Temp= 90°C, Time= 24h, PMo_{11}/ZrO_2 (Left) and PMo_{11}/Al_2O_3 (Right)

The catalyst amount was varied from 15 mg to 50 mg. It is seen from this figure that the activity increases initially up to 25mg and then becomes constant with further increase in the amount of catalyst. However, decrease in selectivity was observed. In the present case, water is formed as a by-product which is polar in nature. In presence of polar molecules, heteropolyacids exhibit pseudoliquid behaviour [80] in which catalytic activity is directly proportional to the active amount of the catalyst. So the same observation is expected in case of LPOMs. Further, increase in the amount blocks/stabilizes the active sites. Hence, no change in conversion is expected. The obtained results are in good agreement with the proposed explanation.

Effect of reaction time

The effect of reaction time is shown in Figure 4. It is seen from figure that initially with increase in reaction time, the conversion also increases. After some time, the conversion attains stability. This may be due to the fact that the activation of the catalyst as well as the attainment of equilibrium requires time.

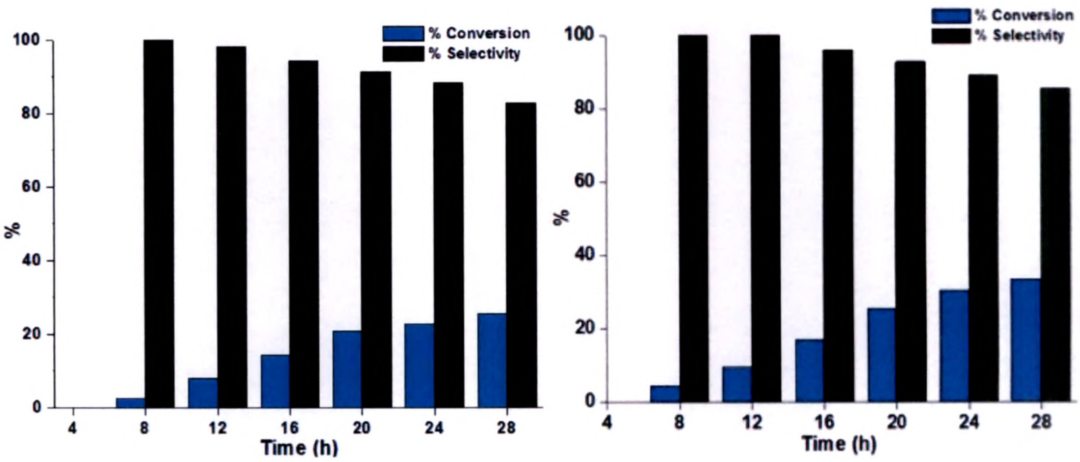


Figure 4. % Conversion is based on benzyl alcohol; benzyl alcohol = 100mmol, TBHP= 0.2%, Temp= 90°C, amount of catalyst= 25 mg, PMo_{11}/ZrO_2 (Left) and PMo_{11}/Al_2O_3 (Right)

Once the equilibrium is attained, the conversion becomes almost constant. But at the same time, selectivity of benzaldehyde decreases. This may be due to over oxidation of benzaldehyde to benzoic acid. Thus, reaction time at 24 h was optimized for optimum conversion of benzyl alcohol as well selectivity of benzaldehyde.

The optimum conditions for 23.7 % conversion with 92.3 % selectivity for benzaldehyde with 20%-PMo_{11}/ZrO_2 and 22.5 % conversion with 94.8 % selectivity for benzaldehyde with 20%-PMo_{11}/Al_2O_3 are, catalyst amount = 25mg, temperature = 90°C, time = 24 h .

In order to see scope and limitations of present catalytic systems, oxidation of various alcohols was carried out with supported catalysts under optimized conditions and results are shown in Table 1. It was observed from Table 1 that, oxidation of secondary alcohol is easier as compare to primary alcohols.

Table 1 Oxidation of various alcohols with O_2, under optimized conditions

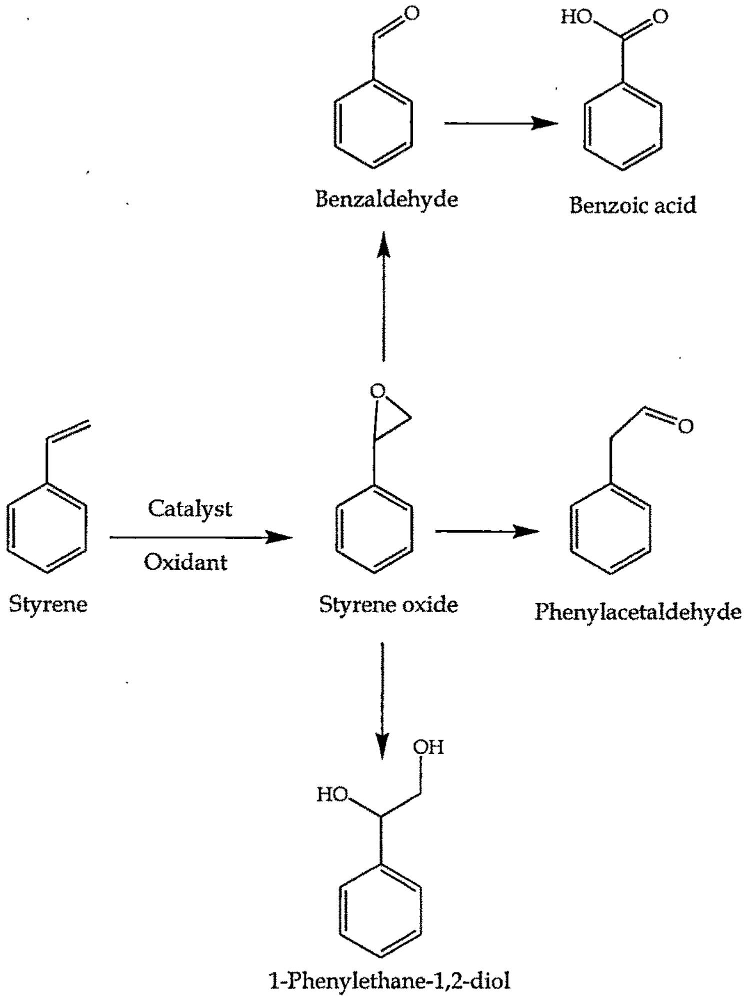
Alcohols	Conversion (%)	Products	Selectivity (%)	TON
[a]Benzyl alcohol	23.7	Benzaldehyde	92.3	11814
		Benzoic acid	7.7	
[a]Cyclopentanol	22.7	Cyclopentanone	>99	11609
[a]Cyclohexanol	22.4	Cyclohexanone	>99	11456
[a]1-Hexanol	9.1	1-Hexanal	>99	4654
1-Octanol	-	-	-	-
[b]Benzyl alcohol	22.5	Benzaldehyde	94.8	11216
		Benzoic acid	5.2	
[b]Cyclopentanol	22.2	Cyclopentanone	>99	11353
[b]Cyclohexanol	21.6	Cyclohexanone	>99	11046
[b]1-Hexanol	8.2	1-Hexanal	>99	4194
[b]1-Octanol	-	-	-	-

% Conversion is based on alcohol; alcohol = 100mmol, TBHP= 0.2%, Temp= 90°C, Time= 24h, amount of catalyst= 25 mg; [a]$(PMo_{11})_2/ZrO_2$, [b]$(PMo_{11})_2/Al_2O_3$

The observed trend is in good agreement with reported in art [81]. In all cases, very high TON is observed. It is known that, oxidation of long chain alcohols (C_8 and onwards) is still challenging task because of lower reactivity [82] 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 O_2 as an oxidant

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 25 mg of PMo_{11}/ZrO_2 and PMo_{11}/Al_2O_3 for 8 h at 80 °C. Generally, styrene on oxidation gives styrene oxide, benzaldehyde, and benzoic acid (Scheme 2). However, in the present reaction conditions, the major oxidation product obtained was benzaldehyde.



Scheme 2. Products for oxidation of styrene

Effect of % loading of PMo_{11}

The oxidation of styrene with molecular oxygen was carried out with 25 mg of catalysts for 8 h at 80 °C. The results are presented in Figure 5, which shows, as an increase in the conversion with increase in the % loading of PMo_{11} from 10% to 20%.

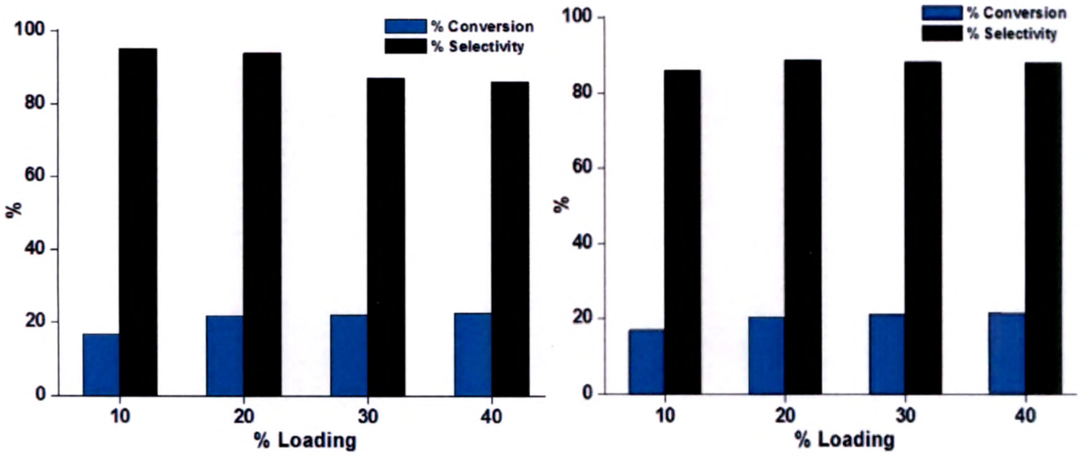


Figure 5. % Conversion is based on styrene; styrene = 100mmol, TBHP= 0.2%, Temp= 80°C, Time= 8h, amount of catalyst= 25 mg, PMo_{11}/ZrO_2 (Left) and PMo_{11}/Al_2O_3 (Right)

Further, with increase in % loading from 20 to 40, almost similar conversion is found. However, selectivity for benzaldehyde was decreased for 30% and 40% PMo_{11}/ZrO_2. At the same time no significant change in conversion as well as selectivity was observed for 30% and 40% PMo_{11}/Al_2O_3. Thus, loading of PMo_{11} was optimizing as 20% for further studies.

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 6.

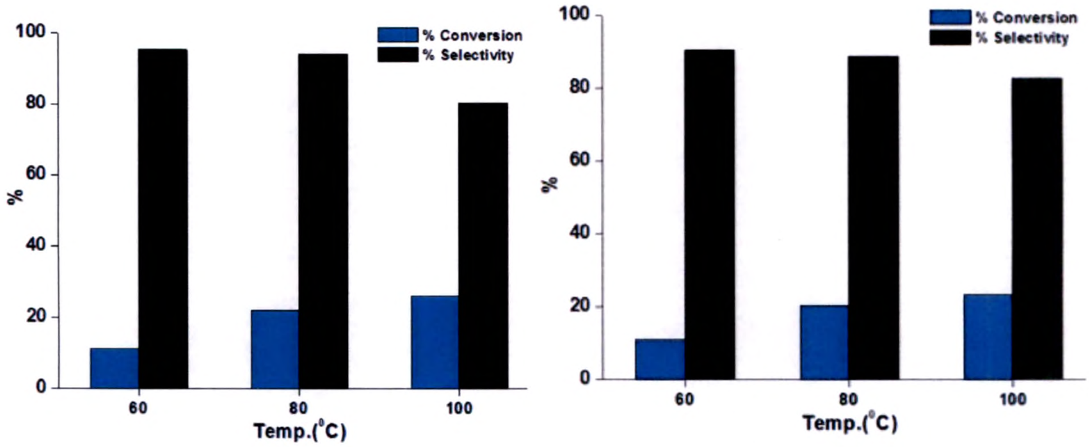


Figure 6. % Conversion is based on styrene; styrene = 100mmol, TBHP= 0.2%, Time= 8h, amount of catalyst= 25 mg, PMo_{11}/ZrO_2 (Left) and PMo_{11}/Al_2O_3 (Right)

The results show that conversion increased with increasing temperature. Only a negligible improvement in conversion was observed on increasing temperature from 80 to 100 °C. But at the same time, selectivity of benzaldehyde decrease. So the temperature of 80 °C was found optimal for the maximum conversion of styrene as well selectivity of benzaldehyde.

Effect of catalyst amount

The effect of amount of catalysts on the conversion was studied and the obtained results are shown in Figure 7.

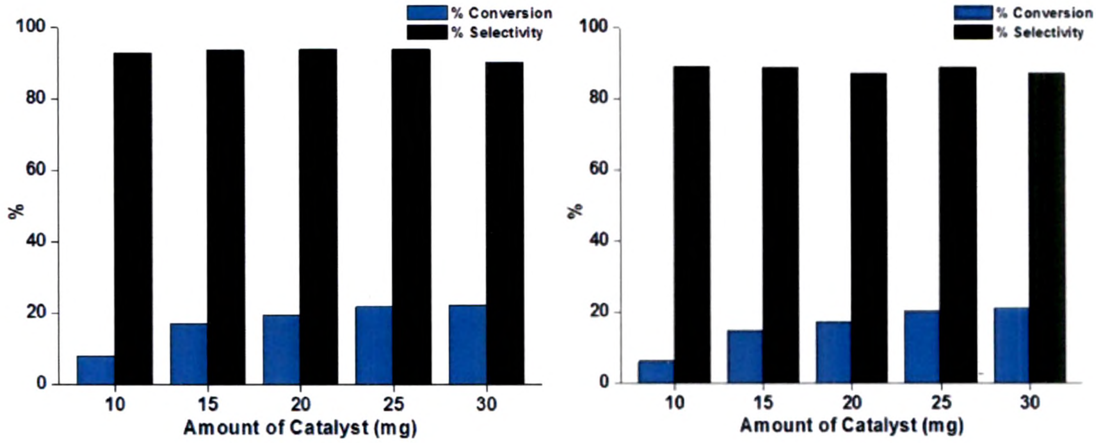


Figure 7. % Conversion is based on styrene; styrene = 100mmol, TBHP= 0.2%, Temp= 80°C, Time= 8h, PMo_{11}/ZrO_2 (Left) and PMo_{11}/Al_2O_3 (Right)

With increase in the amount of catalysts % conversion also increases. This suggests that PMo_{11} functions as active sites for oxidation. It was also observed that with increase in the amount catalyst, no significant change in the selectivity of the benzaldehyde. Thus, amount of catalysts was optimized to 25 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 8. It is seen from Figure 8, that with increase in reaction time, the % conversion also increases.

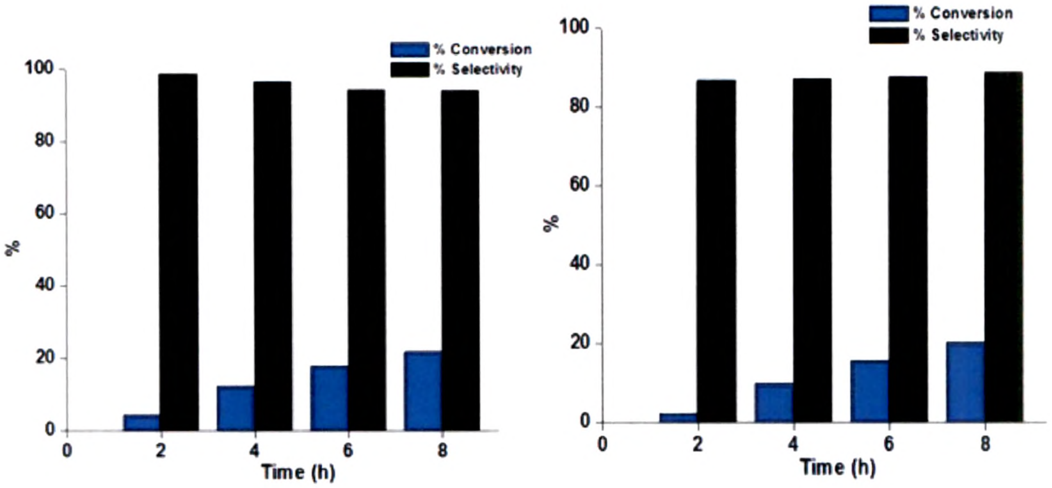


Figure 8. % Conversion is based on styrene; styrene = 100mmol, TBHP= 0.2%, Temp= 80°C, amount of catalyst= 25 mg, PMo_{11}/ZrO_2 (Left) and PMo_{11}/Al_2O_3 (Right)

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 21.7% conversion with 93.9 % selectivity for benzaldehyde with 20%-PMo_{11}/ZrO_2 and 20.2 % conversion with 88.7 % selectivity for benzaldehyde with 20% PMo_{11}/Al_2O_3 are, catalyst amount = 25mg, temperature = 80^{o}C, time = 8 h .

In order to see the scope of the present catalytic system, oxidation of alkenes was also carried out over both supported catalysts under optimized condition and results are presented in Table 2.

Table 2 Oxidation of alkenes under optimized conditions

Alkenes	Conversion (%)	Products	Selectivity (%)	TON
[a]Styrene	21.7	Benzaldehyde	93.9	11329
		Styrene oxide	1.1	
		Other	5.0	
[a]α-methyl styrene	17.5	Acetophenone	91.3	9136
		Epoxide	1.2	
		Other	7.6	
[a]Cyclic Olefins	Nc	-	-	-
[b]Styrene	20.2	Benzaldehyde	88.7	10546
		Styrene oxide	8.9	
		Other	2.4	
[b]α-methyl styrene	17.0	Acetophenone	89.1	8912
		Epoxide	4.5	
		Other	6.4	
[b]Cyclic Olefins	Nc	-	-	-

% Conversion is based on alkene; alkene = 100mmol, TBHP= 0.2%, Temp= 80 °C, Time= 8h, amount of catalyst= 25 mg; [a]PMo_{11}/ZrO_2, [b]PMo_{11}/Al_2O_3

It is seen from Table 2 that, for PMo_{11}/ZrO_2 and PMo_{11}/Al_2O_3, almost similar conversion of styrene as well as substituted styrene is obtained, but at the same time product selectivity was found to be different. 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

The control experiments with ZrO_2, Al_2O_3 and PMo_{11} were also carried out under optimized conditions with benzyl alcohol as well as styrene (Table 3).

Table 3 Controlled experiments

Materials	Conversion (%)	Selectivity (%) Benzaldehyde
ZrO_2	0.1^a/ NC^b	$>99^a$ / $-^b$
Al_2O_3	0.1^a/ NC^b	$>99^a$ / $-^b$
PMo_{11}	$25.2^a/18.2^b$	90.7^a / 90.1^b

% Conversion is based on substrate; benzyl alcohol^a, styrene^b, substrate = 100mmol, TBHP= 0.2%, Temp= ^{a}90, ^{b}80°C, Time= ^{a}24h, ^{b}8h, amount of catalyst= 4.2 mg (PMo_{11}), 21.8 mg (Al_2O_3, ZrO_2).

It can be seen from Table 3 that ZrO_2 and Al_2O_3 are inactive toward the oxidation of styrene and oxidation of benzyl alcohol indicating the catalytic activity is due to only PMo_{11}. The same reaction was carried out by taking the active amount of PMo_{11} (4.2 mg). It was found that the active catalyst gives 18.2% conversion of styrene with 90.1 % selectivity of benzaldehyde and 25.2% conversion of benzyl alcohol with 90.7 % selectivity of benzaldehyde. Similar obtained activity for supported catalyst indicates that PMo_{11} is the real active species. Thus, we are successful in supporting PMo_{11} onto supports without any significant loss in activity and hence in overcoming the traditional problems of homogeneous catalysis.

Heterogeneity Test

Heterogeneity test was carried out for the oxidation of benzyl alcohol (Figure 9a) and styrene (**Figure** 9b) over PMo_{11}/ZrO_2 as examples.

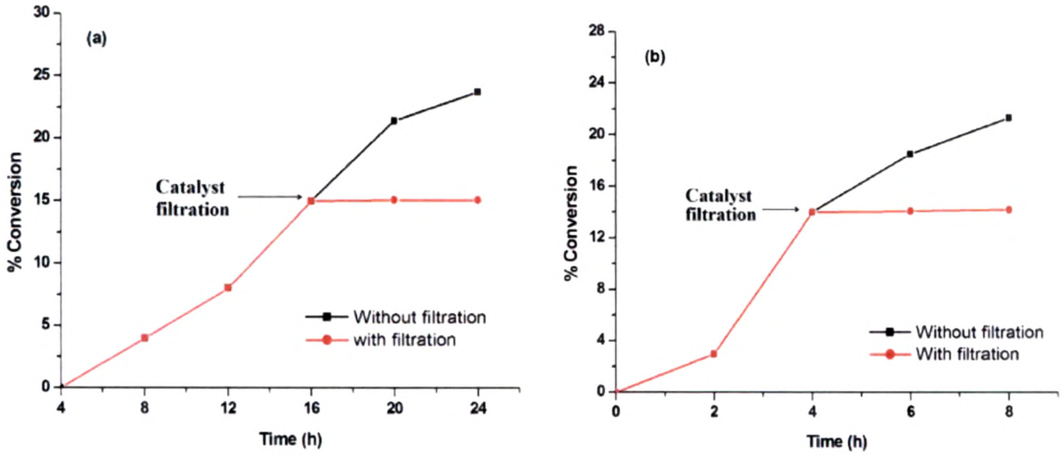


Figure 9. % Conversion is based on substrate (^{a}benzyl alcohol / ^{b}styrene); amount of 20% PMo_{11}/ZrO_2 =25 mg; molar ratio of substrate (100 mmol), O_2, TBHP= 0.2%, temperature ^{a}90 ^{o}C, ^{b}80 ^{o}C

For the rigorous proof of heterogeneity, a test [83] was carried out by filtering catalyst from the reaction mixture at 90 °C after 16 h (for styrene; 80 °C after 4 h) and the filtrate was allowed to react up to 24 h (for styrene; 8 h). The reaction mixture of 16 h and the filtrate were analyzed by gas chromatography. Similar test was carried for PMo_{11}/Al_2O_3. No change in the % conversion as well as % selectivity was found indicating the present catalysts fall into category C [83] 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 leaching of Mo from catalyst support was confirmed by carrying out an analysis of the used catalyst (EDS) as well as the product mixtures (AAS). The analysis of the used catalyst did not show an appreciable loss in the Mo content as compared to the fresh catalyst. The analysis of the product mixtures showed that if any Mo was present it was there in an amount below the detection limit, which corresponded to less than 1ppm. 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

Catalyst	Cycle	Conversion (%)	Selectivity (%)
			Benzaldehyde
PMo_{11}/ZrO_2	Fresh	$23.1^a/21.7^b$	$92.3^a/93.9^b$
	1	$22.9^a/21.7^b$	$92.2^a/93.9^b$
	2	$22.9^a/21.4^b$	$92.2^a/93.4^b$
	3	$22.9^a/21.3^b$	$92.0^a/93.2^b$
	4	$22.7^a/21.3^b$	$92.0^a/93.0^b$
PMo_{11}/Al_2O_3	Fresh	$23.0^a/20.2^b$	$94.8^a/88.7^b$
	1	$22.9^a/20.2^b$	$95.0^a/88.7^b$
	2	$22.9^a/20.0^b$	$94.9^a/88.7^b$
	3	$22.5^a/20.2^b$	$94.9^a/88.5^b$
	4	$22.6^a/20.1^b$	$94.2^a/88.3^b$

% Conversion is based on substrate; benzyl alcohol^a, styrene^b, substrate = 100mmol, TBHP= 0.2%, Temp= ^{a}90, ^{b}80°C, Time= ^{a}24h, ^{b}8h amount of catalyst= 25 mg.

It is seen from the table that there was no change in selectivity, however, a little decrease in conversion was observed. This shows that the catalysts are stable, regenerated and reused successfully up to 4 cycles.

Characterization of Regenerated Catalysts

20% PMo_{11}/ZrO_2 and 20% PMo_{11}/Al_2O_3 were regenerated in order to test its stability. The regenerated catalysts were characterized for FT-IR and XRD in order to confirm the retention of the catalyst structure, after the completion of the reaction.

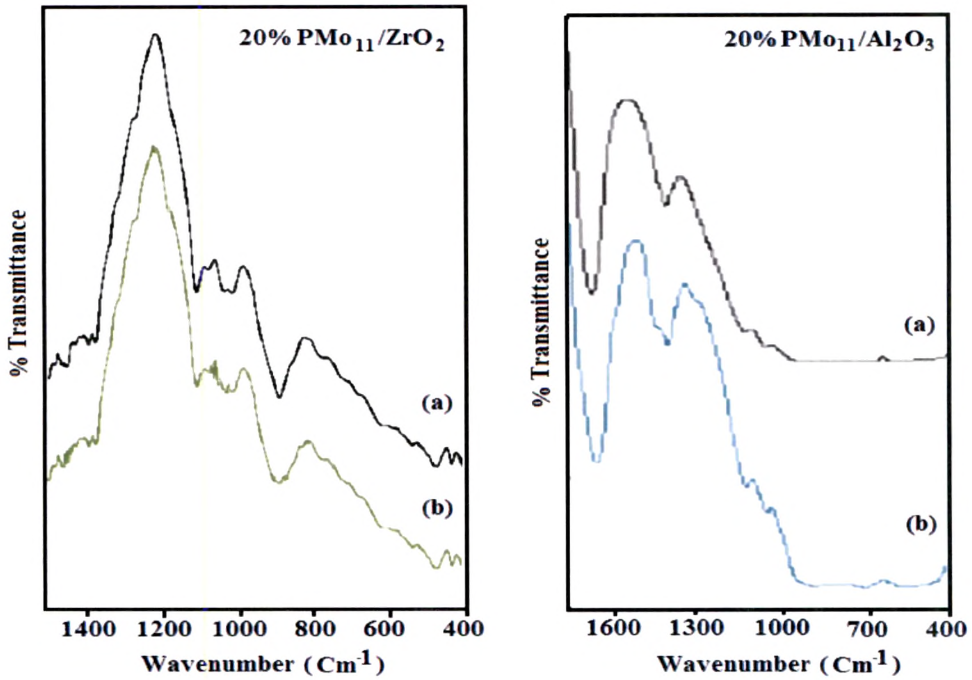


Figure 10. FT-IR spectra of (a) fresh and (b) recycled (fourth cycle) catalysts

The FT-IR data for the fresh as well as the regenerated catalysts are represented in Figure 10. No appreciable shift in the FT-IR band position of the regenerated catalyst indicates the retention of Keggin type PMo_{11} onto supports.

Further to see any structural change of the supported PMo_{11}, XRD pattern of regenerated catalysts was also recorded. The XRD pattern for the fresh as well as the regenerated catalysts is shown in Figure 11.

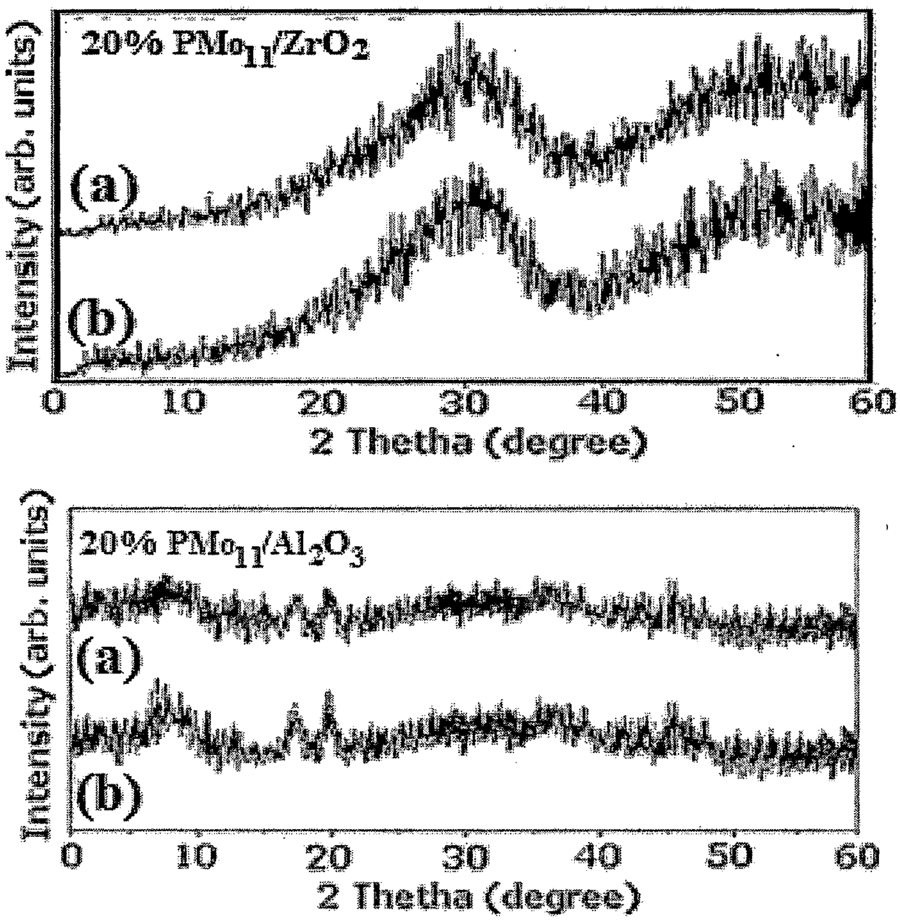


Figure 11. XRD of (a) fresh and (b) recycled (fourth cycle) catalysts

There is no appreciable change in XRD pattern of fresh as well as regenerated catalyst indicating the stability of PMo_{11} after regeneration. The powder XRD of recycled catalysts does not show any additional peak indicating the PMo_{11} species do not decompose after regeneration and the Keggin unit remains intact on the surface of supports.

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 25 mg of PMo_{11}/ZrO_2 and PMo_{11}/Al_2O_3 for **24 h at 90** °C. Generally, benzyl alcohol on oxidation gives benzaldehyde and benzoic acid. However, benzaldehyde was found as the major oxidation product in the present case.

Effect of % loading of PMo_{11}

The oxidation of benzyl alcohol was carried out with H_2O_2 in 1:3 molar ratio by using 25 mg of fresh catalysts for 24 h at 90 °C are presented in Figure 12.

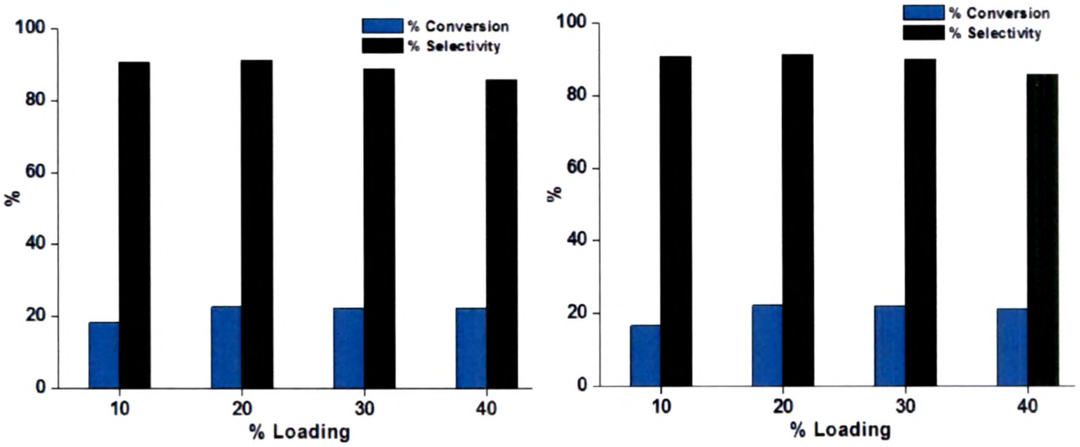


Figure 12. % Conversion is based on benzyl alcohol; benzyl alcohol = 10 mmol, H_2O_2= 30 mmol, Temp= 90°C, Time= 24h, amount of catalyst= 25 mg, PMo_{11}/ZrO_2 (Left) and PMo_{11}/Al_2O_3 (Right)

Figure 12 shows, as increase in the conversion with increase in the % loading of PMo_{11} from 10% to 20%. Further, with increase in % loading from 20% to 40%, decrease in conversion is found. This may be due to the blocking of the active sites.

Thus the loading of PMo_{11} on the support was fixed at 20%. A detail study was carried out over 20% PMo_{11}/ ZrO_2 and 20% PMo_{11}/ Al_2O_3.

Effect of temperature

The effect of temperature (Figure 13) on the oxidation of benzyl alcohol was investigated at three different temperatures viz. 80, 90 and 100 °C, keeping the other parameters fixed: namely benzyl alcohol (10 mmol), 30% H_2O_2 (30 mmol), catalyst (25 mg) and reaction time (24h).

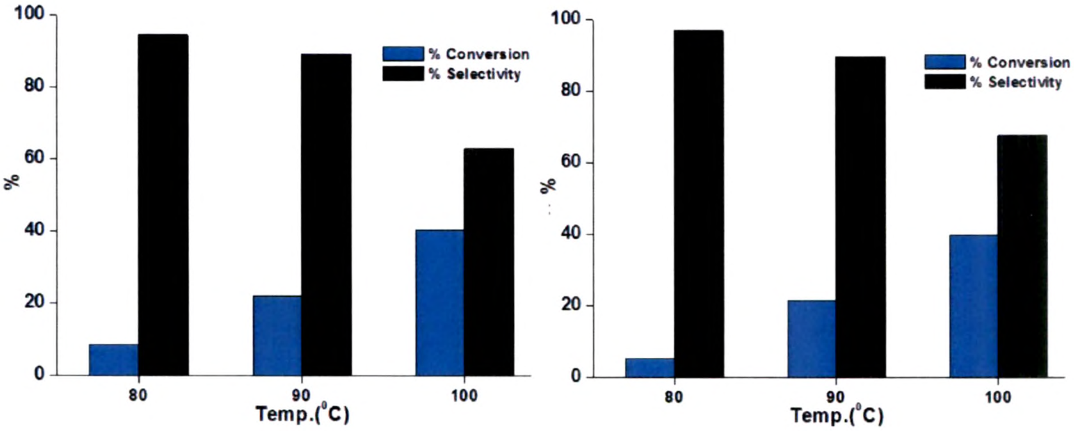


Figure 13. % Conversion is based on benzyl alcohol; benzyl alcohol = 10 mmol, H_2O_2= 30 mmol, Time= 24h, amount of catalyst= 25 mg, PMo_{11}/ZrO_2 (Left) and PMo_{11}/Al_2O_3 (Right)

On increasing the temperature from 90 to 100 °C, improvement in conversion was observed, but selectivity for benzaldehyde decreases drastically. This may be due to oxidation of benzaldehyde to benzoic acid at elevated temperature.

Hence, further optimization of the conditions was carried out with a 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 (25 mg), temperature (90 °C) and reaction time (24h). The results are shown in Figure 14.

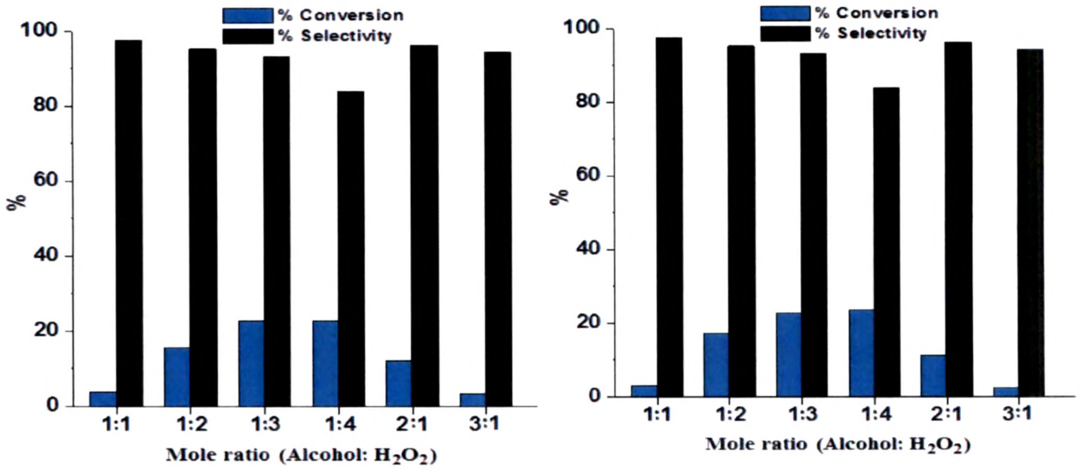


Figure 14. % Conversion is based on benzyl alcohol; Temp= 90 °C, Time= 24h, amount of catalyst= 25 mg, PMo_{11}/ZrO_2 (Left) and PMo_{11}/Al_2O_3 (Right)

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

The amount of catalyst has a significant effect on the oxidation of benzyl alcohol. Five different amounts of catalysts viz., 15, 20, 25, 30, 35 and 40 mg were used, keeping with all other reaction parameters fixed: namely temperature (90 °C), namely benzyl alcohol (10 mmol), 30% H_2O_2 (30 mmol) and reaction time (24h). The results are shown in Figure 15.

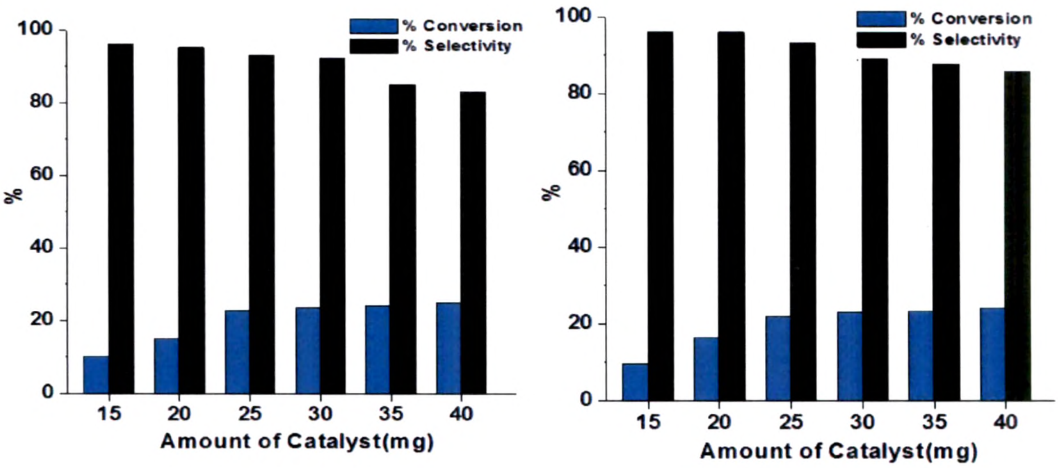


Figure 15. % Conversion is based on benzyl alcohol; benzyl alcohol = 10 mmol, H_2O_2= 30 mmol, Temp= 90°C, Time= 24h, PMo_{11}/ZrO_2 (Left) and PMo_{11}/Al_2O_3 (Right)

Lower conversion of benzyl alcohol into benzaldehyde with 10 to 20mg catalyst may be due to fewer catalytic sites. The maximum percentage conversion was observed with 25mg catalyst but there was no remarkable difference in the progress of reaction when 30 or 40 mg of catalyst was employed. Therefore, 25mg 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 25mg of catalyst at 90 °C with constant stirring. The percentage of conversion was monitored at different reaction times. It is seen from Figure 16, 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. It was seen that almost similar conversion was observed for 24 and 28 h. but at the same time, because of over oxidation, selectivity of benzaldehyde decreases.

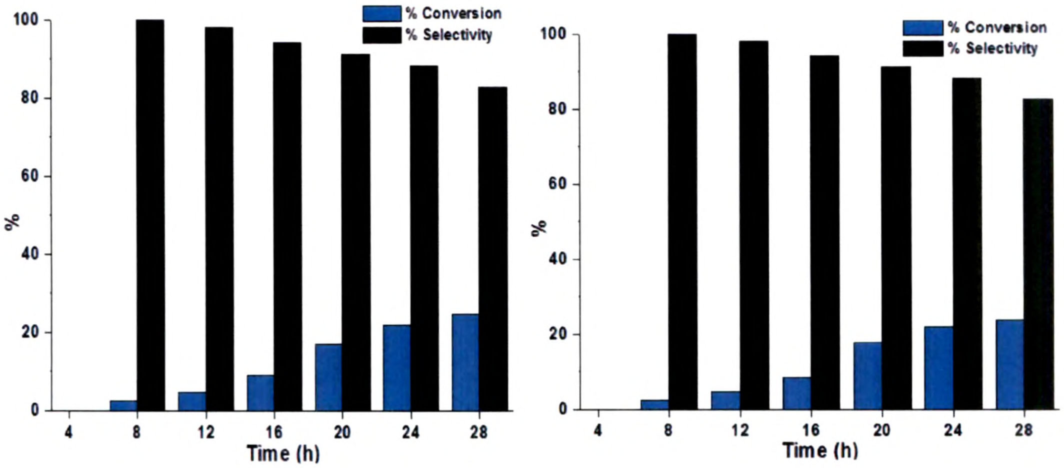


Figure 16. % Conversion is based on benzyl alcohol; benzyl alcohol = 10 mmol, H_2O_2= 30 mmol, Temp= 90°C, amount of catalyst= 25 mg, PMo_{11}/ZrO_2 (Left) and PMo_{11}/Al_2O_3 (Right)

The optimum conditions for 24.5 % conversion with 93 % selectivity for benzaldehyde with 20% PMo_{11}/ZrO_2 and 22.0 % conversion with 91 % selectivity for benzaldehyde with 20% PMo_{11}/Al_2O_3 are, benzyl alcohol to H_2O_2 =1:3, catalyst amount = 25mg, temperature = 90°C, time = 24 h .

In order to see scope and limitations of present catalytic systems, oxidation of various alcohols was carried out with supported catalysts under optimized conditions and results are shown in Table 5.

Table 5 Oxidation of various alcohols with H_2O_2 over supported catalysts, under optimized conditions

Alcohols	Conversion (%)	Products	Selectivity (%)	TON
[a]Benzyl alcohol	24.5	Benzaldehyde	93.0	1253
[a]Cyclopentanol	23.1	Cyclopentanone	>99	1181
[a]Cyclohexanol	22.1	Cyclohexanone	>99	1130
[a]1-Hexanol	7.3	1-Hexanal	>99	373
1-Octanol	-	-	-	-
[b]Benzyl alcohol	22.0	Benzaldehyde	91.0	1125
[b]Cyclopentanol	20.5	Cyclopentanone	>99	1048
[b]Cyclohexanol	20.3	Cyclohexanone	>99	1038
[b]1-Hexanol	7.1	1-Hexanal	>99	363
[b]1-Octanol	-	-	-	-

% Conversion is based on alcohol; alcohol = 10mmol, H_2O_2= 30 mmol, Temp= 90°C, Time= 24h, amount of catalyst= 25 mg; [a]$(PMo_{11})_2/ZrO_2$, [b]$(PMo_{11})_2/Al_2O_3$

It was observed from Table 5 that, similar to aerobic oxidation, oxidation of secondary alcohol with H_2O_2 over supported catalysts is easier as compare to primary alcohols. For all alcohols, very good selectivity of desire product with very high TON was observed. At the same time, present catalytic system is also not applicable to less reactive long chain primary alcohol such as 1-octanol.

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. The reaction was carried out with 25 mg of PMo_{11}/ZrO_2 and PMo_{11}/Al_2O_3 for 20 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 % loading of PMo_{11}

The oxidation of styrene was carried out with H_2O_2 in 1 : 3 molar ratio by using 25 mg of catalysts for 20 h at 80 °C are presented in Figure 17.

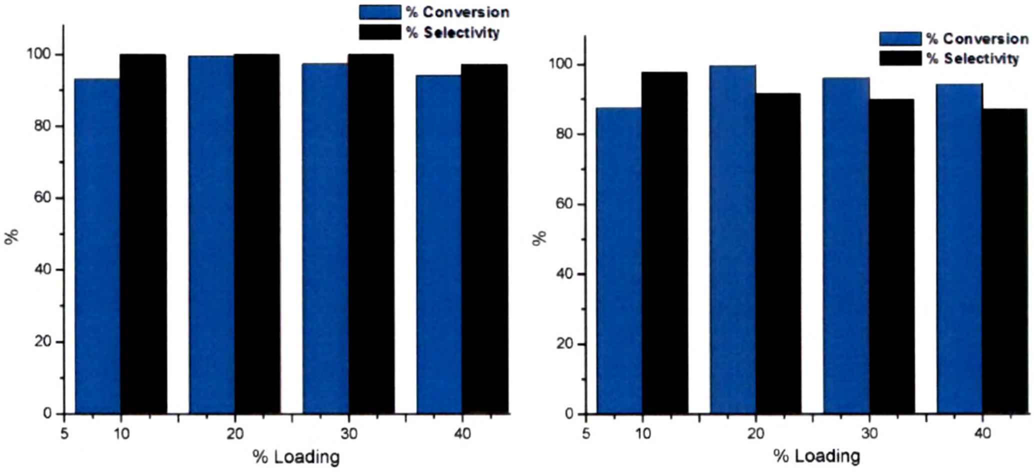


Figure 17. % Conversion is based on styrene; styrene = 10 mmol, H_2O_2= 30 mmol, Temp= 80°C, Time= 20h, amount of catalyst= 25 mg, PMo_{11}/ZrO_2 (Left) and PMo_{11}/Al_2O_3 (Right)

Figure 17 shows an increase in the conversion with increase in the % loading of PMo_{11} from 10% to 20%. Further, with increase in % loading from 20% to 40%, a decrease in conversion was found. This may be due to the blocking of the active sites. Thus, the loading of PMo_{11} on the supports was fixed at 20%. A detail study was carried over 20% PMo_{11}/ZrO_2 and 20% PMo_{11}/ZrO_2.

Effect of temperature

In order to determine the optimum temperature the reaction was investigated at four different temperatures 60, 80 and 100 ^{o}C, using both the catalysts keeping other parameters fixed (mole ratio 1:3, amt 25mg, time 20h). The results for the same are presented in Figure 18.

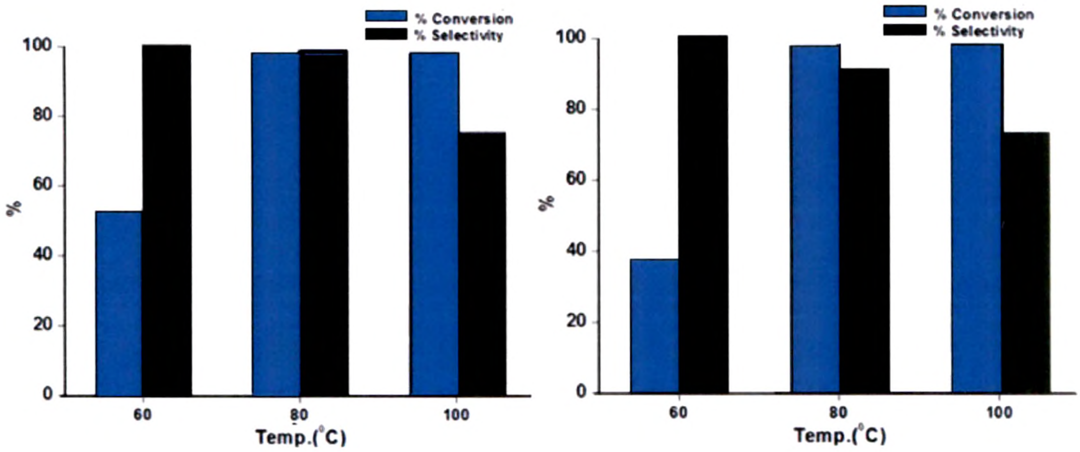


Figure 18. % Conversion is based on styrene; styrene = 10 mmol, H_2O_2= 30 mmol, Time= 20h, amount of catalyst = 25 mg, PMo_{11}/ZrO_2 (Left) and PMo_{11}/Al_2O_3 (Right)

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

Effect of mole ratio

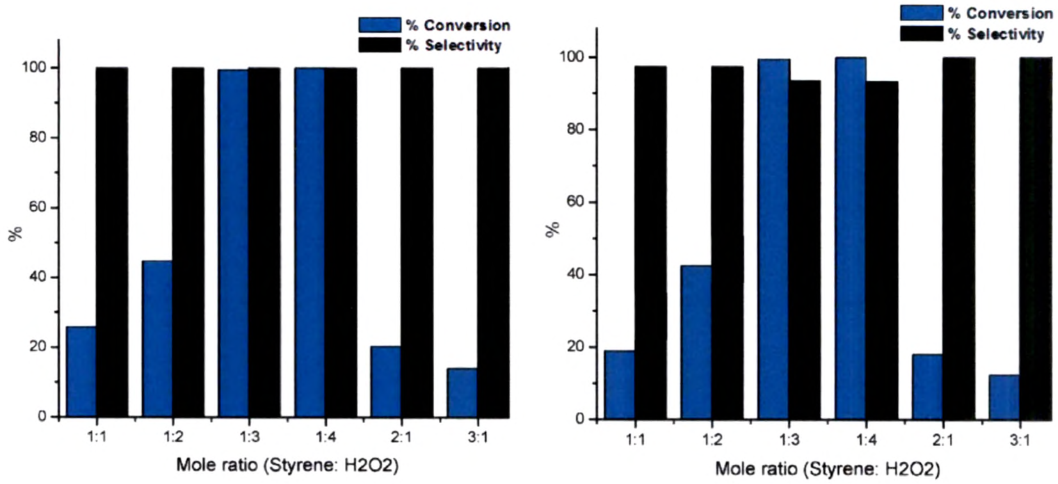


Figure 19. % Conversion is based on styrene; Temp= 80 °C, Time= 20h, amount of catalyst= 25 mg, PMo_{11}/ZrO_2 (Left) and PMo_{11}/Al_2O_3 (Right)

The reaction was carried out by varying mole ratio of styrene to H_2O_2 with 25 mg of the catalyst for 20 h at 80 °C. The obtained results are reported in Figure 19. It is seen from Figure 19 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 benzoic acid 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 for 20 h at 80 °C. The conversion and selectivity are reported in Figure 20.

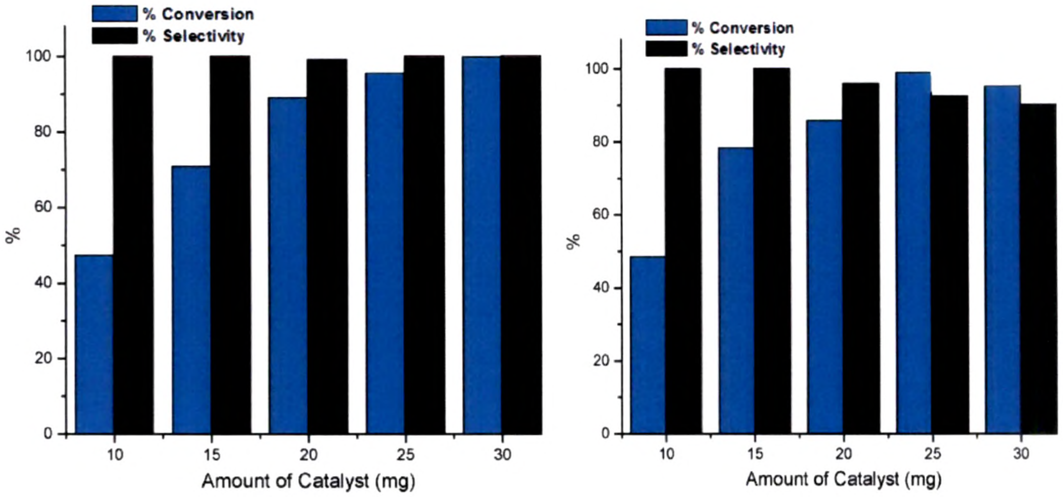


Figure 20. % Conversion is based on styrene; styrene = 10 mmol, H_2O_2= 30 mmol, Temp= 80°C, Time= 20h, PMo_{11}/ZrO_2 (Left) and PMo_{11}/Al_2O_3 (Right)

It is shown in the Figure 20 that the % conversion increases with an increase in the amount of catalysts from 10 mg to 25 mg. 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.

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 25 mg of the catalyst. The results are shown in Figure 21. It is seen from Figure 21 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.

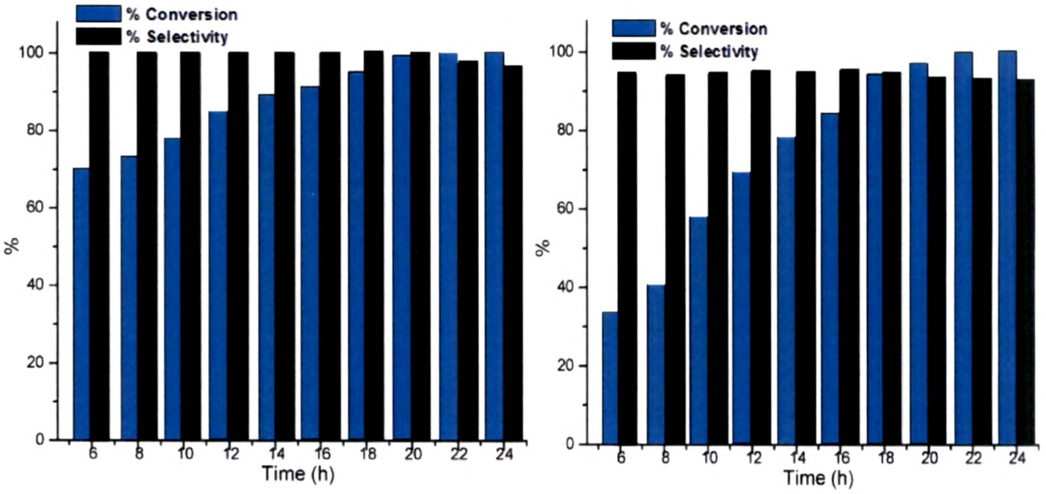


Figure 21. % Conversion is based on styrene; styrene = 10 mmol, H_2O_2= 30 mmol, Temp= 80°C, amount of catalyst= 25 mg, PMo_{11}/ZrO_2 (Left) and PMo_{11}/Al_2O_3 (Right)

The optimum conditions for 99.5 % conversion with >99 % selectivity for benzaldehyde with 20%-PMo_{11}/ZrO_2 and 99.2 % conversion with 92 % selectivity for benzaldehyde with 20%-PMo_{11}/Al_2O_3 are, styrene to H_2O_2 =1:3, catalyst amount = 25mg, temperature = 80^{o}C, time = 20 h .

In order to see the scope of the present catalytic system, oxidation of alkenes with H_2O_2 was also carried out over both supported catalysts under optimized condition and results are presented in Table 6.

Table 6 Oxidation of alkenes with H_2O_2 under optimized conditions

Alkenes	Conversion (%)	Products	Selectivity (%)	TON
[a]Styrene	99.5	Benzaldehyde	>99	5184
[a]α-methyl styrene	90.2	Acetophenone	>97	4699
[a]Cyclic olefins	Nc	-	-	-
[b]Styrene	99.2	Benzaldehyde	>92	5168
[b]α-methyl styrene	89.2	Acetophenone	>92	4647
[b]Cyclic olefins	Nc	-	-	-

% Conversion is based on alkene; alkene = 10 mmol, H_2O_2= 30 mmol, Temp= 80°C, Time= 20 h, amount of catalyst= 25 mg; [a]$(PMo_{11})_2/ZrO_2$, [b]$(PMo_{11})_2/Al_2O_3$

It is seen from Table 6 that, for PMo_{11}/ZrO_2 and PMo_{11}/Al_2O_3, almost similar conversion of styrene as well as substituted styrene is obtained, but at the same time significant difference in product selectivity was found. This may be due to nature of supports. In all cases, excellent selectivity of desired product with very high TON is obtained. Present catalytic systems are not applicable for oxidation of cyclic olefins.

Controlled experiment

The control experiments with ZrO_2, Al_2O_3 and PMo_{11} were also carried out under optimized conditions with benzyl alcohol as well as styrene (Table 7).

Table 7 Controlled experiments

Materials	Conversion (%)	Selectivity (%) Benzaldehyde
ZrO_2	-	-
Al_2O_3	-	-
PMo_{11}	$21^a/96^b$	93^a / 99^b

% Conversion is based on substrate; benzyl alcohol[a], styrene[b], substrate = 10mmol, H_2O_2= 30 mmol, Temp= [a]90, [b]80°C, Time= [a]24h, [b]20h, amount of active specie= 4.2 mg (PMo_{11}), 21.8 mg (Al_2O_3, ZrO_2).

It can be seen from Table 7 that ZrO_2 and Al_2O_3 are inactive toward the oxidation of styrene and oxidation of benzyl alcohol indicating the catalytic activity is due to only PMo_{11}. The same reaction was carried out by taking the active amount of PMo_{11} (4.2 mg). It was found that the active catalyst gives 21% conversion of benzyl alcohol with 93 % selectivity of benzaldehyde and 96% styrene conversion of with 99 % selectivity of benzaldehyde. Similar obtained activity for supported catalyst indicates that PMo_{11} is the real active species. Thus, we are successful in supporting PMo_{11} onto supports without any significant loss in activity and hence in overcoming the traditional problems of homogeneous catalysis.

Heterogeneity Test

Heterogeneity test was carried out for the oxidation of styrene (Figure 22a) and benzyl alcohol (Figure 22b) over PMo_{11}/Al_2O_3 as examples. For the rigorous proof of heterogeneity, a test was carried out by filtering catalyst from the reaction mixture at 80 °C after 2 h (for benzyl alcohol; 90 °C after 8 h) and the filtrate was allowed to react up to 4 h (for benzyl alcohol; 10 h).

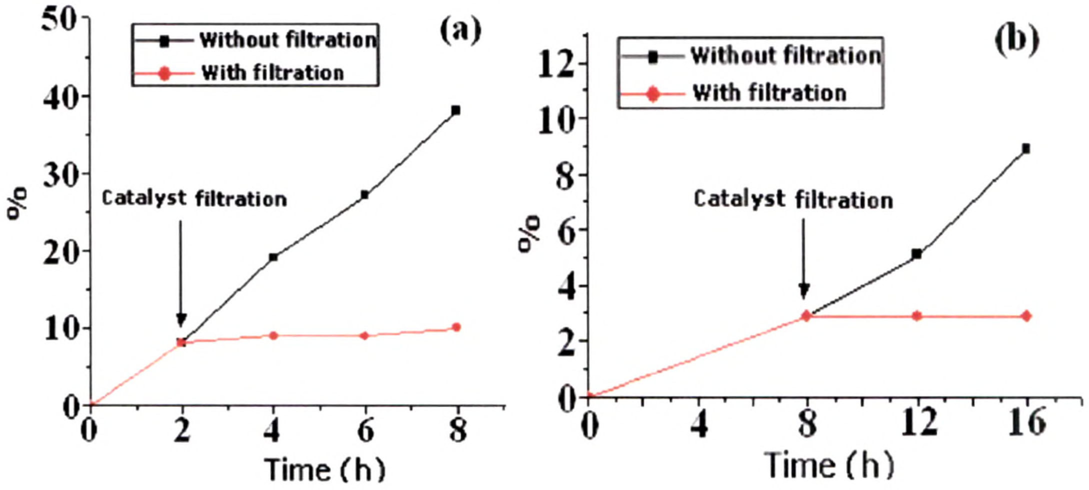


Figure 22. % Conversion is based on substrate (^{a}styrene/^{b}benzyl alcohol); amount of PMo_{11}/Al_2O_3 =25 mg; molar ratio of substrate to H_2O_2: 1:3, temperature ^{a}80 °C, ^{b}90 °C.

The reaction mixture of 2 h and the filtrate were analyzed by gas chromatography. No change in the % conversion as well as % selectivity was found indicating the present catalyst fall into category C 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.

Table 8 Oxidation of benzyl alcohol and styrene with fresh and regenerated catalysts

Catalyst	Cycle	Conversion (%)	Selectivity (%)
			Benzaldehyde
PMo_{11}/ZrO_2	Fresh	$99.5^a/24.5^b$	$99^a/93^b$
	1	$97.2^a/24.5^b$	$99^a/93^b$
	2	$96.9^a/24.3^b$	$99^a/93^b$
	3	$96.9^a/24.3^b$	$99^a/93^b$
	4	$96.7^a/24.3^b$	$99^a/92^b$
PMo_{11}/Al_2O_3	Fresh	$99.1^a/22^b$	$95^a/91^b$
	1	$99.0^a/21.6^b$	$95^a/90^b$
	2	$98.7^a/21^b$	$95^a/91^b$
	3	$98.7^a/21^b$	$95^a/91^b$
	4	$99.7^a/21^b$	$95^a/91^b$

% Conversion is based on substrate (^{a}styrene/ ^{b}benzyl alcohol); amount of catalyst = 25 mg; molar ratio of substrate to H_2O_2: 1:3, Time, ^{a}20 h, ^{b}24 h; temperature ^{a}80 °C, ^{b}90 °C

The catalysts remain insoluble under the present reaction conditions and were separated easily by simple filtration followed by washing with dichloromethane and dried at 100 °C. Oxidation of styrene and benzyl alcohol was carried out with the regenerated catalysts, under the optimized conditions. The data for the catalytic activity is represented in Table 8. It is seen from the table that there was no change in selectivity, however, a little decrease in conversion was observed. This shows that the catalysts are stable, regenerated and reused successfully up to four cycles.

Effect of supports

It is well know that support does not play always merely a mechanical role but it can also modify the catalytic properties of the catalysts. So, in order to see the effect of support, comparison of activity of 20% PMo_{11}/ZrO_2 and 20%PMo_{11}/Al_2O_3 was done for oxidation of alcohol and alkene under optimized conditions and results are presented in Table 9.

On comparing catalytic activity of 20% PMo_{11}/ZrO_2 and 20% PMo_{11}/Al_2O_3 for oxidation of styrene (with H_2O_2 and O_2), no remarkable difference in conversion was observed. However, in case of benzyl alcohol oxidation, 20% PMo_{11}/ZrO_2 showed better conversion of styrene with H_2O_2 as compare to that of 20%PMo_{11}/Al_2O_3. However, significant difference in selectivity of benzaldehyde was observed for all the case. It is well known that the products distribution is affected by acidity of the catalyst. Generally, oxidation of benzyl alcohol gives benzaldehyde (major), with over oxidation product benzoic acid (minor). These types of over oxidation reactions are directly promoted by acidity of the catalyst. So, observed result i.e. lower selectivity of benzaldehyde in case of PMo_{11}/ZrO_2 is attributed to acidity of ZrO_2.

Similarly, oxidation of styrene gives styrene oxide as an intermediate product. However, in most of the cases, stable 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. Formation of benzaldehyde is encouraged by acidity for both these routes. Thus, because of acidity of ZrO_2, in case of PMo_{11}/ZrO_2 selectivity towards benzaldehyde is greater as compare to PMo_{11}/Al_2O_3.

Table 9 Oxidation of benzyl alcohol and styrene using different oxidants

Catalyst	Oxidant	Conversion (%)	Selectivity (%)	TON
PMo_{11}/ZrO_2	$^xH_2O_2$	$24.5^a/99.5^b$	$93^a/99^b$	$1253^a/5184^b$
	$^yO_2$	$23.1^a/21.7^b$	$92^a/99^b$	$11814^a/11329^b$
PMo_{11}/Al_2O_3	$^xH_2O_2$	$22.0^a/99.2^b$	$91^a/92^b$	$1125^a/5168^b$
	$^yO_2$	$23.0^a/20.2^b$	$95^a/89^b$	$11763^a/10546^b$

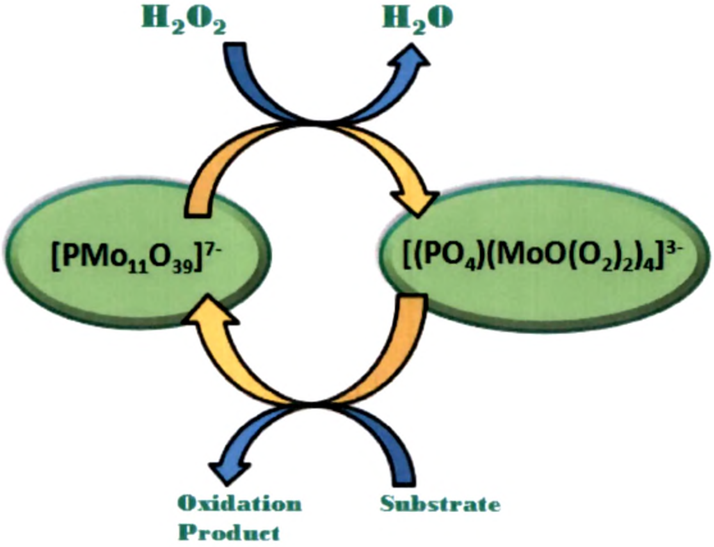
% Conversion is based on substrate (^{a}benzyl alcohol/^{b}styrene); amount of catalyst = 25 mg; temperature ^{a}90 °C, ^{b}80 °C

^{x}Reaction conditions; molar ratio of substrate to H_2O_2= 10: 30 mmol, Time, ^{a}24 h, ^{b}20 h; ^{y}Reaction conditions; substrate = 10 mmol, O_2, TBHP= 0.2 %, Time, ^{a}24 h, ^{b}8 h;

Comparison of different oxidants

It is seen from Table 9 that for both catalysts higher TON i.e. high mole conversion of substrate was observed with O_2 as compare to that of H_2O_2. The difference in conversion can be explained on the basis of the reactivity of oxidants. In case of H_2O_2 the activation of the metal centre takes place through the formation of $[PO_4\{MoO(O_2)_2\}_4]^{3-}$ intermediate *in situ* from $Na_7PMo_{11}O_{39}$. The formed active peroxo intermediate oxidizes the alkenes. The same mechanism is expected in case of molecular oxygen except that molecular oxygen directly attacks the vacant site (*i.e. cis* Mo(=O_2) components) to form the active metal oxo intermediate. Thus, the activation of the catalyst requires more time in the case of H_2O_2 as compared to that of direct involvement of molecular oxygen. Hence, higher TON is expected in the case of molecular oxygen. The obtained results are in good agreement with the proposed explanation. However, in all cases, benzaldehyde was observed as major product with >90 % selectivity.

Probable reaction mechanism



Scheme 3. Hypothetic mechanism of oxidation over supported catalysts with H_2O_2

The reaction mechanism of oxidation of styrene or benzyl alcohol over supported catalysts using H_2O_2 as an oxidant (Scheme 3) is very similar to reported mechanism of the catalytic oxidation of benzyl alcohol over $[PW_{11}O_{39}]^{7-}$ [30]. They reported $[PW_{11}O_{39}]^{7-}$ react with H_2O_2 and the active species $[(PO_4)\{WO(O_2)_2\}_4]^{3-}$ is formed. This active species is responsible for oxidation of substrate. In the present case, we are expecting similar mechanism with $[(PO_4)\{MoO(O_2)_2\}_4]^{3-}$ as an active species.

Kinetics of oxidation of styrene with H_2O_2

A detailed study on the kinetic behavior was carried out for both the catalysts. In all the experiments, reaction mixtures were analyzed at fixed interval of time using Gas Chromatograph (Nucon 5700 model) using BP-1 capillary column (30m, 0.25mm id).

Determination of Order as well as Rate of Reaction

The plot of ln C/C_o *vs* time (Figure 23) shows a linear relationship of styrene consumption with respect to time. With increase in reaction time there is a gradual and linear decrease in the styrene concentration for both the catalysts. These observations indicate the oxidation of styrene follows first order dependence with respect to time. The only difference was the rate of reaction was faster for 20% PMo_{11}/ZrO_2 as compared to that of 20% PMo_{11}/Al_2O_3.

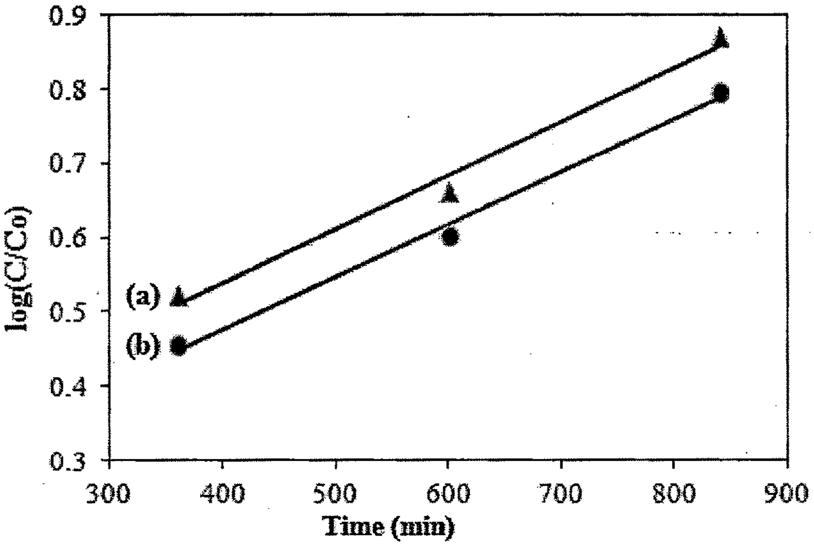


Figure 23. Consumption of styrene as a function of time; (a) 20%-PMo_{11}/ZrO_2 (b) 20 %-PMo_{11}/Al_2O_3; Catalyst concentration 1.35 x 10^{-3} mmol; T = 80°C

This was further supported by the study of effect of catalyst concentration on the rate of oxidation of styrene. The catalyst concentration was varied form 0.8 x 10^{-3} to 2 x 10^{-3} mmol at fixed substrate concentration of 10mmol and at temperature 80°C. The plot of rate (k) *vs* catalyst concentration (Figure 24) also shows a linear relationship for both the catalysts.

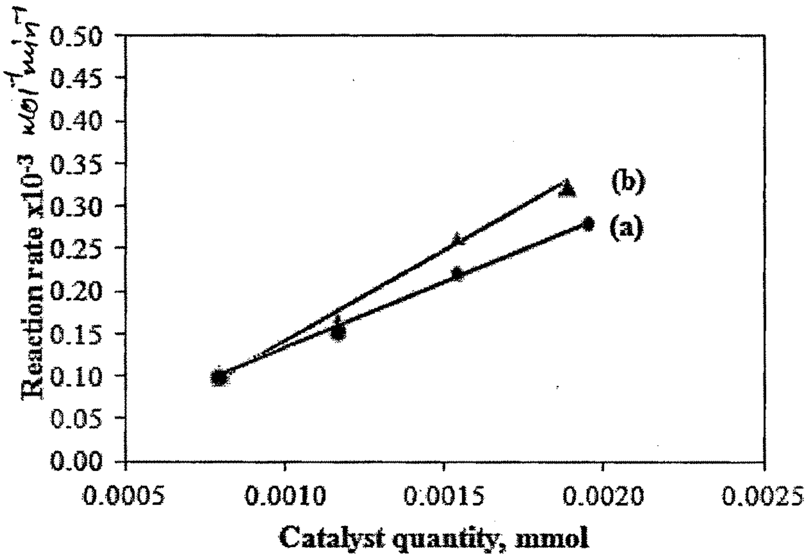


Figure 24. Effect of catalyst concentration on the rate of oxidation of styrene, (a) 20% PMo_{11}/ZrO_2 (b) 20 % PMo_{11}/Al_2O_3

The above study confirms that the initial rates of oxidation of styrene follow first order with respect to substrate as well as catalyst for 20% PMo_{11}/ZrO_2 as well as 20% PMo_{11}/Al_2O_3.

Based on the above results, the rate law was also deduced for both the catalysts and was found to obey the following equation [Eq (1)].

$$\frac{-d\,[BA]}{dt} = k\,[Sty]\,[Cat] \qquad (1)$$

Effect of temperature

As most of the oxidation reactions are temperature sensitive, the effect of temperature on oxidation of styrene was also studied by varying the temperature between 333 - 353 K, keeping the styrene: H_2O_2 ratio of 1:3 and catalyst concentration of 1.35×10^3 mmol. As the temperature increases from 333 to 353 K, the conversion of styrene also increases drastically for both the catalysts. This may be due to the activation of the catalytic species with temperature.

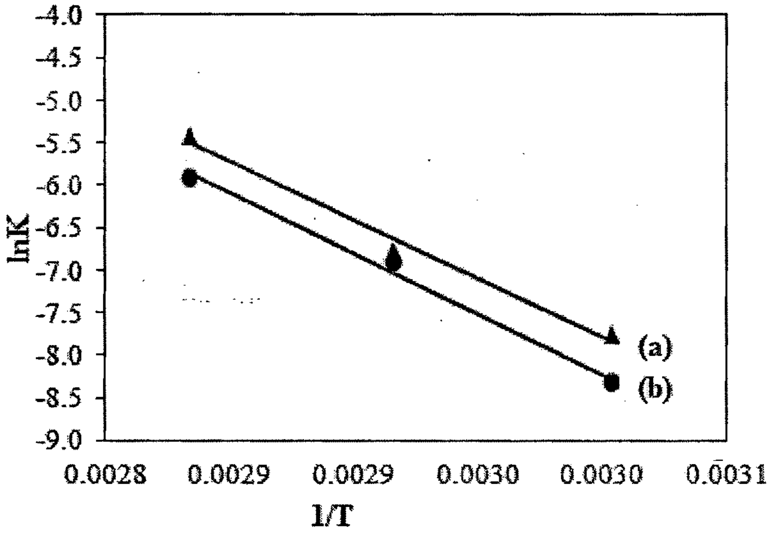


Figure 25. Arrhenius Plot; (a) 20% PMo_{11}/ZrO_2 and (b) 20% PMo_{11}/Al_2O_3. Concentration of catalysts 1.35×10^3 mmol,

The graph of ln *k* vs. 1/T was plotted (Figure 25) and the value of activation energy (E_a) was determined from the plot. From the value of activation energy (E_a), the pre-exponential factor (A) was determined using Arrhenius Equation Eq (2) and the values are reported in Table 10.

$$k = A\,e^{-Ea/RT} \qquad (2)$$

where, Ea= Activation energy

A = Pre-exponential Factor

k = Rate Constant

Table 10. Kinetic and Thermodynamic parameters for oxidation of styrene over supported catalysts

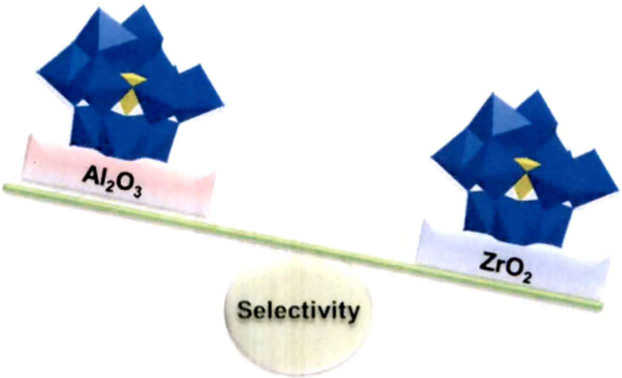
Catalyst	Rate consant k X 10^{-4} (m^{-1})	Activation energy (E_a) (kJ/mol)	Pre-exponential factor (A)
20% PMo_{11}/ZrO_2	1.77	113	2.7×10^{14}
20% PMo_{11}/Al_2O_3	1.89	118	8.5×10^{14}

It is also known that when the energy of activation is <25kJ/mol, the reaction may be governed by diffusion, especially low values of the activation energy (12-16kJ/mol) indicate the diffusion controlled process. In the present case, the values of activation energies are >25 kJ/mol, hence we may infer that the present catalysis is due to weak chemisorptions of species on the surface of the catalysts rather than diffusion controlled process.

As seen from Table 10, 20% PMo_{11}/ZrO_2 has a lower Ea value and slightly higher rate constant (k) value as compared to 20% PMo_{11}/Al_2O_3. From the view point of selectivity for benzaldehyde as well as kinetic parameters ZrO_2 was found to be a better support.

CONCLUSIONS

1. We have designed active, selective, recyclable and sustainable heterogeneous catalysts comprising PMo_{11} and ZrO_2 and Al_2O_3.
2. We are successful in supporting PMo_{11} onto ZrO_2 and Al_2O_3 without any significant loss in activity and hence in overcoming the traditional problems of homogeneous catalysis.
3. The catalysts have been proved to be successful for oxidation reactions with O_2 and H_2O_2 under solvent free mild conditions.
4. In case of oxidation of benzyl alcohol, 22-23% conversion with 92-94% selectivity for benzaldehyde with O_2 and 22-24% conversion with 91-93 % selectivity for benzaldehyde with H_2O_2 was obtained in 24h.
5. In case of oxidation of styrene, 20-21 % conversion with 89-94 % selectivity for benzaldehyde with O_2 in 8h and 99 % conversion with 92-99 % selectivity for benzaldehyde with H_2O_2 was obtained in 20 h.
6. In all cases, very good selectivity of desire products and TON was obtained. At the same time, present catalytic systems are not applicable for oxidation of cyclic olefins and long chain (C8 onwards) alcohols with both oxidants.
7. O_2 was found to be a better oxidant than H_2O_2.
8. The catalysts were regenerated and reused successfully upto 4 cycles. FT-IR and XRD study of reused catalysts shows no structural changes indicating catalytic systems are stable.
9. Based on the catalytic and kinetic studies ZrO_2 is a better support as compared to Al_2O_3.



10. The present heterogeneous catalysts are promising sustainable alternative to the traditional catalysts for solvent free liquid phase oxidation of alkenes and alcohols under mild reaction conditions.

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