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Aerobic oxidation of alcohols and alkenes over a novel lacunary phosphomolybdate anchored to zeolite H β †

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Lacunary phosphomolybdate anchored to zeolite H β was synthesized and characterised by various physicochemical techniques. The catalytic activity was evaluated for aerobic oxidation of benzyl alcohol and styrene. The catalyst was found to be efficient, especially in terms of selectivity for the desired benzaldehyde product (for benzyl alcohol – 90%, styrene – 72%), very high turnover number (alcohols > 3500, alkenes > 18 000) as well as recyclability. The viability of the catalyst was also extended to various alkenes and alcohols.

Introduction

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1.

One of the most significant reactions in organic chemistry¹ is oxidation reaction of alkenes and alcohols, which provide a variety of products; among them carbonyl compounds, epoxides, diols, and aldehydes are of much importance.² The oxygenated derivatives, especially carbonyl compounds, have widespread applications in dyestuff, perfumery and agro chemical industries.³ From the view point of growing environmental worries, catalytic methods utilizing green oxidant such as O₂ are highly desirable for sustainable chemistry.

One of the option is to use heterogeneous catalyst. Hence, the prospect of developing new catalytic methodology by supporting various species on supports, emerges as an attractive pathway and has opened the opportunity to create more active as well as selective catalytic systems.

Polyoxometalates (POMs) are very good alternative in terms of economic viability and easy to manufacture, where the homogenous form can be easily heterogenized. They are excellent candidates due to plethora of structural and compositional variability⁴ and the modification of properties can be basically accomplished by tuning the structural properties at the atomic or molecular level of parent POMs. Among various POMs, phosphomolybdates, have gained much importance due to their excellent redox properties. The lacunary phosphomolybdates can be synthesised by removing one or more molybdenum-oxygen (Mo-O) octahedral from the saturated Keggin anion framework leading to an increase in the overall anionic charge of the complex.⁵ The phosphomolybdates can be present in different type of species⁶ in the acidified aqueous solution, mainly due to hydrolytic decomposition because of kinetic instability and equilibrium rate.^{6,7} It was hence a challenging task to stabilize these species onto a suitable support.

Our group has successfully stabilized the mono-lacunary phosphomolybdate (PMo₁₁) species onto hydrous zirconia,⁸ alumina,⁹ MCM-41¹⁰ and evaluated the catalytic activity for solvent-free oxidation of styrene and benzyl alcohol. It is known that the 'support' not only provides a mechanical means but also modifies the overall catalytic properties of the material. Therefore, as an extension of our previous work, it was thought of interest to use zeolites as support and to explore the redox properties of the catalyst for oxidation reaction. Among zeolites, zeolite beta (H β) was selected due to following reasons: (1) zeolite beta shows typical characteristics of ideal support, (2) it is a high silica zeolite having large pores, (3) it has surface silanol groups as well as hydrophobic character and (4) it is a good candidate for catalysis due to inherent property of high thermal and chemical stability.

A series of catalysts containing 10–40% of PMo₁₁ and zeolite were synthesized. The 30% loaded catalyst was characterized by various physicochemical characterization techniques. The catalytic activity was evaluated for the aerobic oxidation of alcohols and alkenes, where benzyl alcohol and styrene were taken as test substrates for reaction optimization (Scheme 1). The conditions for maximum conversions were optimized by varying different reaction parameters such as % loading, amount of the catalyst, reaction time, and reaction temperature. Some important factors for the formation of a successful anchoring platform and better catalytic activity are the nature of support, structural porosity and high specific surface area. Hence, a comparative study was carried out between $PMo_{11}/MCM-41$ and the present catalyst to investigate the effect of support. The catalyst was regenerated and recycled up-to two

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Scheme 1 Reaction scheme for oxidation of benzyl alcohol and styrene.

cycles without significant decrease in the catalytic activity. The scope of reaction was extended to variety of substrates.

2. Experimental

2.1. Materials

All the chemicals used were of A. R. grade. Benzyl alcohol, cyclopentanol, cyclohexanol, 1-hexanol, 1-octanol, styrene, 4-methyl styrene, α -methyl styrene, *tert* butylhydroperoxide (70% aq. TBHP) and dichloromethane were obtained from Merck and used as received. The sodium form of zeolite β (Si/Al ratio 10) was used as received and was purchased from zeolites and Allied Products, Bombay, India.

2.2. Treatment of the support (zeolite-H β)

In order to convert sodium salt of zeolite (Na β) to NH₄⁺ form conventional ion exchange method¹¹ using a 10 wt%, 1 M NH₄Cl aqueous solution was used. The resulting NH₄⁺ form zeolite was then converted to acidic form (H⁺ type) by calcination in air for 6 h at 550 °C. The obtained material was designated as H β .

2.3. Synthesis of mono lacunary phosphomolybdate (PMo₁₁)

The mono lacunary phosphomolybdate $(Na_7[PMo_{11}O_{39}] \cdot 16H_2O)$ was synthesized by following method reported by us earlier.¹⁰

2.4. Synthesis of catalyst (anchoring of PMo_{11} to $H\beta$)

Impregnation method was used to synthesise a series of catalysts containing 10–40% of PMo₁₁ anchored to H β . One gram of support was impregnated with aq. solution of 0.1–0.4 g of PMo₁₁ (10–40 mL distilled water, respectively). The resultant material was dried at 100 °C for 10 h. The as synthesised catalysts were designated as 10% PMo₁₁/H β , 20% PMo₁₁/H β , 30% PMo₁₁/H β , and 40% PMo₁₁/H β , respectively.

2.5. Oxidation of benzyl alcohol and styrene with molecular oxygen

The oxidation reaction was performed in a batch-type reactor under atmospheric pressure. In a typical reaction appropriate amount of catalyst was added in a two-necked flask (50 mL) containing substrates (100 mmol) and 0.2 mmol *tert*butyl hydrogen peroxide (TBHP) in order to initiate the reaction. The reaction mixture was maintained at 80 °C for styrene and 90 °C for benzyl alcohol on REMI magnetic stirrer equipped with preheated oil bath at 600 rpm. The reaction was started by bubbling O_2 (analytical grade) into the liquid. Different reaction parameters were varied such as catalyst amount, reaction time and reaction temperature. After completion of reaction, the catalyst was removed by simple centrifugation. The products were analysed on a gas chromatograph (GC) using Rtx-5 capillary column after extraction with dichloromethane and drying with magnesium sulphate. Identification of the product was carried out by comparing it with authentic samples and then by gas chromatography-mass spectroscopy (GC-MS).

2.6. Characterization

TGA-DTA was obtained from Mettler Toledo Star SW 7.01 instrument up to 600 °C (scan rate-10 °C min; type of gasnitrogen and flow used-10 mL min⁻¹). FT-IR spectra were obtained from Perkin Elmer instrument (number of scans-4 and resolution-2 cm⁻¹) using the KBr wafer. The Raman spectra were recorded on a Bruker RFS 27, with resolution-2 cm⁻¹ and number of scans-4. Adsorption-desorption isotherms were recorded on a Micromeritics ASAP 2010 surface area analyser at -196 °C using BET method. The ³¹P MAS NMR spectra were recorded at 121.49 MHz by BRUKER Avance DSX-300 using a 7 mm rotor probe, spinning rate 5-7 kHz, Number of scans-6400 and Pulse width-4. 85% H₃PO₄ was used as an external standard and samples were kept in a desiccator over P2O5 until the NMR measurement. The XRD pattern was obtained on PHILIPS PW-1830 using Cu Ka radiation (1.54056 Å) and scanning angle from 0° to 60°. Elemental analyses (EDX) and SEM were carried out on JSM 5910 LV combined with an INCA instrument for EDX-SEM.

3. Result and discussion

3.1. Catalyst characterization

30% loaded PMo₁₁ on H β (30% PMo₁₁/H β) showed highest catalytic activity, as a result we have selected 30% PMo₁₁/H β for further detailed characterizations with various techniques.

TGA curves of zeolite support and catalysts are shown in Fig. 1. The initial weight loss of 16% from 30 to 200 °C for PMo₁₁ (Fig. 1a) may be due to the removal of adsorbed molecules of water. The final weight loss of 1.8% indicates the loss of water of crystallisation at around 275 °C. The zeolite support (Fig. 1b) showed a unique weight loss of 13–15% up to 250 °C, which is due to removal of physically adsorbed water molecules. Absence of further weight loss beyond 250 °C and up to 600 °C indicates retainment of zeolite H β framework. The TGA of 30% PMo₁₁/H β (Fig. 1c) shows initial weight loss of 11.2% up to 150 °C due to removal of physically adsorbed molecules of water. No substantial weight loss was observed up to 350 °C (2.6%), indicating catalyst stability up to 350 °C.

The DTA of PMo_{11} shows two endothermic peaks at 80 $^\circ C$ and 140 $^\circ C$ which may be due to loss of adsorbed water and



Fig. 1 TGA curves of (a) PMo_{11} , (b) $H\beta$ and (c) $30\% PMo_{11}/H\beta$.

water of crystallization (SM 1), respectively. In addition, a broad exothermic peak in the region 270–305 °C was also observed which may be due to the decomposition of PMo_{11} . DTA curve of 30% $PMo_{11}/H\beta$ (SM 1) shows a very broad endothermic range from 50 °C to 150 °C due to continuous loss of adsorbed water. A broad exothermic peak at 350 °C, was observed which may be due to decomposition of PMo_{11} . It can be concluded that thermal stability of PMo_{11} increases on anchoring PMo_{11} to the support. The TGA and DTA analyses are in agreement with one another.

The decrease in the specific surface area for 30% $PMo_{11}/H\beta$ (362 m² g⁻¹) as compared to that of H β (587.2 m² g⁻¹) is as expected and is the first indication of chemical interaction between available surface oxygen of PMo11 and HB. The nitrogen adsorption isotherms of support and catalyst are displayed in Fig. 2. The catalyst showed Type (IV) pattern with three different stages: monolayer formation by adsorption of nitrogen $(P/P_0 < 0.4)$ on the mesopore walls, a steep increase in adsorption $(P/P_0 = 0.4-0.8)$ due to capillary condensation with hysteresis loop, and multilayer adsorption on the outer surface of the particles. The pore size of $H\beta$ zeolite in the present case is around 2.5 nm. It is known that the size of lacunary PMo₁₁ is <1.0 nm, hence it can easily enter in the channels of H β . A decrease in the pore diameter was observed after anchoring PMo₁₁ on to the support due to the presence of PMo₁₁ inside the zeolite framework by pore filling as well as surface coverage.

The FT-IR spectrum of PMo_{11} (Fig. 3a) shows asymmetric stretching of P–O (1048 and 999 cm⁻¹), Mo=O (935 cm⁻¹) and Mo–O–Mo (906 and 855 cm⁻¹) and the reported values are in good agreement with reported litterarure.¹² The FT-IR spectra for H β and 30% $PMo_{11}/H\beta$ (Fig. 3c) shows broad band in the range 1060–1090 cm⁻¹ due to asymmetric stretching vibration O–T–O (v_{asym}), which is subject to change due to its sensitive to the silicon and aluminum ratio in the framework of zeolite. A characteristic of the pore opening is observed due to band at 455 cm⁻¹.¹¹ The bands of PMo_{11} at 1048 and 999 cm⁻¹ are not visible due to merging with the broad band of H β in the range 1060–1090 cm⁻¹. The shifting and broadening of Mo–O–Mo band from 905 to 920 (shift of 15 cm⁻¹) and from 855 to 890 cm⁻¹ (shift of 35 cm⁻¹) as well as disappearance of Mo=O



Fig. 2 Nitrogen sorption and pore size distribution of (a) H β and (b) 30% PMo_{11}/H β .

band (935 cm⁻¹) may be due to strong chemical interaction of terminal oxygen of PMo₁₁ with H β , which was further confirmed by FT-Raman analysis.

FT-Raman spectra of PMo₁₁ and 30% PMo₁₁/Hβ are displayed in Fig. 4. The FT-Raman spectrum of PMo₁₁ (Fig. 4a) shows typical bands at 947 $\nu_{\rm s}$ (Mo–O_d), 932 $\nu_{\rm as}$ (Mo–O_d), 891 and 550 $\nu_{\rm as}$ (Mo–O_b–Mo), 355 $\nu_{\rm as}$ (O_a–P–O_a) and 217 $\nu_{\rm s}$ (Mo–O_a), where



Fig. 3 FT-IR of (a) PMo₁₁, (b) Hβ, and (c) 30% PMo₁₁/Hβ.



Fig. 4 FT-Raman spectra of (a) PMo_{11} and (b) 30% $PMo_{11}/H\beta$.

O_a, O_b, O_c, and O_d are attributed to the oxygen atoms connected to phosphorus, oxygen atoms bridging two molybdenum (from two different triads for O_b and from the same triad for O_c), and to the terminal oxygen Mo=O, respectively.¹⁰ The FT-Raman spectrum of 30% PMo₁₁/Hβ (Fig. 4b) shows the retention of all the characteristic bands, however, slight decrease in intensity and shift in bands of v_s (Mo–O_d) – from 947 to 962 (shift of 15 cm⁻¹); v_{as} (Mo–O_d) – from 932 to 898 (shift of 34 cm⁻¹); v_{as} (Mo–O_b–Mo) – from 891 to 836 (shift of 55 cm⁻¹) and v_{as} (O_a–P–O_a) – from 355 to 323 (shift of 32 cm⁻¹), may be due to a strong hydrogen bonded interaction between the terminal oxygen of PMo₁₁ and hydroxyl group of Hβ this is further confirmed by solid state ³¹P-NMR.

³¹P MAS NMR is the most important method to study the structure, composition and chemical environment around phosphorus in POM compounds. The ³¹P MAS NMR spectra of PMo₁₁ (Fig. 5a) shows a very intense peak at 1.64 ppm which is in good agreement with the reported one.⁸ For catalyst, an intense de-shielded peak at 0.145 ppm (Fig. 5b) indicates the chemical interaction between PMo₁₁ and Hβ. However, two low



Fig. 5 31 P MAS NMR spectra of (a) PMo₁₁ and (b) 30% PMo₁₁/H β .

intensity peaks at 2.62 and -4.53 ppm are also observed, indicating high degree of adsorption as well as small fragmentation.^{5,13}

Fig. 6 shows XRD patterns of support H β and 30% PMo₁₁/H β . The characteristic crystalline peaks for PMo₁₁ is generally observed in the 2 θ range of 25 to 35. The XRD of catalyst is almost similar to that of the support H β with no separate crystalline peak of PMo₁₁. This shows a well dispersion of PMo₁₁ inside the framework of the zeolite support. This is in good agreement with the reported one.¹¹

SEM images of H β and 30% PMo₁₁/H β are shown in Fig. 7. The semi-crystalline nature of PMo₁₁ is distinctly visible in Fig. 7a, at 1000× magnification and there was no change in the surface morphology of the catalyst as compared to the support. The catalysts shows a uniform dispersion of PMo₁₁ in a noncrystalline form on the surface of the support. The framework of zeolite support is retained after incorporation of PMo₁₁, which is in good agreement with that of XRD spectra.

Thus, XRD and SEM confirm the uniform dispersion of PMo₁₁ and retainment of surface morphology of the support.

3.2. Catalytic oxidation reaction of benzyl alcohol and styrene

In order to ensure the catalytic activity for the oxidation of benzyl alcohol and styrene two reactions were carried out: (1) in presence of support H β as catalyst no conversion was found, (2) reactions were also carried out in the absence of catalyst which resulted in no oxidation reaction. In the present work, a detailed catalytic study was carried out for the oxidation of benzyl alcohol as well as styrene (Scheme 1) by varying different parameters like % loading, catalyst amount, reaction time and temperature to optimize the conditions for the maximum conversion.

The effect of % loading of PMo_{11} on the oxidation of benzyl alcohol using molecular oxygen under similar reaction conditions (benzyl alcohol – 100 mmol, TBHP – 0.2 mmol, amount of



Fig. 6 Power XRD pattern of (a) PMo_{11} , (b) $H\beta$ and (c) 30% $PMo_{11}/H\beta$.



Fig. 7 SEM images of (a) PMo_{11} (1000 \times magnification), (b) H β and (c and d) 30% PMo_{11}/H $\beta.$

catalyst – 25 mg (0.231 wt%), time – 24 h and temp – 90 °C) is shown in Fig. 8a. The conversion increases with increase in the % loading of PMo₁₁ from 10% to 20%. A significant increase in the conversion was observed on increasing the loading from 20% to 30%. The 30% loaded catalyst showed highest conversion 25.5%, however there was no significant change in the conversion on further increasing the loading to 40%. No change in conversion, at higher % loading might be possible due to agglomeration of the active species on the surface of support leading to low accessibility towards the active sites. It is also seen that at higher loading the selectivity for benzaldehyde decreases. Hence, 30% loading was selected for further study. The amount of catalyst has a significant effect on the oxidation of benzyl alcohol, hence the catalyst amount was increased from 10 mg (0.092 wt%) to 30 mg (0.2772 wt%) (Fig. 8b). Initially a sharp increase in conversion was observed on increasing the catalyst amount from 10 mg to 25 mg. On further, increasing the catalyst amount the conversion does not increase significantly. Therefore, 25 mg amount of catalyst (0.231 wt%), was found optimum for obtaining maximum conversion.

The effect of reaction time was carried out by observing change in % conversion at different time intervals. It was observed on increasing the reaction time, the % conversion also increases significantly (Fig. 8c). It is known that more reaction time is necessary to form a reactive intermediate (substrate + catalyst) which subsequently leads to the products. Maximum 25.5% conversion was observed at 24 h. However, when the reaction was allowed to continue till 25 h, no significant conversion was observed, but selectivity of benzaldehyde decreases. The maximum conversion was achieved at 24 h of reaction time.

The effect of temperature was investigated in the range 70–100 °C (Fig. 8d). At 90 °C an optimum of 25.5% conversion was achieved. On increasing the temperature further to 100 °C there was no significant increase in the conversion however, decrease in the selectivity of benzaldehyde was observed due to over-oxidation of benzaldehyde to benzoic acid at elevated temperature. Thus, 90 °C was considered optimised temperature for obtaining maximum conversion as well as selectivity for benzaldehyde.



Fig. 8 Reaction optimization: effect of (a) % loading, (b) catalyst amount, (c) reaction time and (d) reaction temperature. % Conversion is based on benzyl alcohol.

Following are the optimised conditions for obtaining maximum % conversion (25.5%) of benzyl alcohol to benzaldehyde (90% selectivity): loading of PMo_{11} – 30%, amount of catalyst – 25 mg (0.231 wt%), time – 24 h, temperature – 90 °C.

A detail study, similar to benzyl alcohol oxidation, was carried out for aerobic oxidation of styrene using 30% $PMo_{11}/H\beta$ by changing various reaction parameters such as % loading of PMo_{11} , catalyst amount, time and temperature to optimize the conditions using oxidant O_2 (Fig. 9). It is well known that oxidation of styrene gives styrene oxide as an intermediate product. However, in most of the cases, benzaldehyde was obtained as major product *via*. (i) direct oxidative cleavage of C=C bond of styrene and (ii) fast conversion of styrene oxide to benzaldehyde. Similarly, in the present case, benzaldehyde was characterized as the major (>72%) oxidation product along with styrene oxide, acetophenone, benzoic acid as minor products. All the reaction parameters play significant role in optimizing the best conversion of styrene and highest selectivity for benzaldehyde.

The optimum conditions for maximum % conversion (57%) of styrene to benzaldehyde (72% selectivity) are: loading of $PMo_{11} - 30\%$, amount of catalyst – 25 mg (0.227 wt%), time – 8 h, temperature – 90 °C.

3.3. Oxidation of different alcohols and alkenes

In order to explore the applicability of the method for a selective aerobic oxidation different alcohol and alkene substrates were studied (Table 1). The most common benzylic alcohols, and primary and secondary alcohols were used as a substrates oxidized to corresponding aldehydes or ketones with moderate to good activity and exceptional selectivity. The oxidation of secondary alcohol was much easier than primary alcohols (Table 1). The obtained trend was in agreement with the reported ones. In all cases we were able to obtain outstanding TONs. However, the present catalytic system is not applicable to less reactive long chain primary alcohols, like 1-octanol.

In the case of alkenes, styrene, 4-methyl styrene produced 72% benzaldehyde and 67% acetophenone, respectively. α -Methyl styrene exhibited good conversion (59%) and 70% selectivity for acetophenone. In all cases, excellent selectivity (60–70%) of desired product with very high TON was obtained.

3.4. Control experiments and heterogeneity test

The control experiments with H β and PMo₁₁ were performed under optimized conditions (Table 2). It is seen from Table 2 that the support is not active towards the oxidation reaction suggesting that the activity is mainly due to PMo₁₁. The same reaction was performed by taking the active amount of PMo₁₁. It was observed that the active species produced 25.2% conversion of benzyl alcohol with 91% selectivity of benzaldehyde. Similar obtained activity for supported catalysts indicate that PMo₁₁ is the real active species.

Heterogeneity test was carried out for the oxidation of benzyl alcohol.¹⁴ A test was performed by filtering the catalyst at 90 °C after 18 h and the filtrate was allowed to react up to 24 h. The reaction mixture of 18 h as well as the filtrate of 24 h were analysed by GC. No change in the conversion and selectivity was observed indicating that the catalyst falls into category C. Similar reactions were carried out for styrene oxidation. It also confirms that the reactions are not just auto-oxidation but the catalyst plays an important role for selective conversion of the substrates.



Fig. 9 Effect of (a) % PMo₁₁ loading, (b) catalyst amount, (c) reaction time and (d) temperature on styrene oxidation under aerobic conditions.

Table 1Oxidation of various alcohols and alkenes over supportedcatalysts, under optimized conditions a

Substrate	% Con.	Products	% Sele.	TON
ОН	25.5 ^{<i>a</i>}		90	9551
OH	21 ^{<i>a</i>}		>99	8580
ОН	20^a	0	>99	8171
ОН	9 ^{<i>a</i>}		>99	3745
ОН	NC ^a		_	_
	57 ^b		72	20 975
	59 ^b		70	22 099
	50 ^b		67	18 728

^{*a*} % Conversion is based on substrate: ^{*a*} alcohols, ^{*b*} alkenes – O_2 : 0.2 mmol TBHP, temp. – ^{*a*} 90 °C, ^{*b*} 80 °C; time – ^{*a*} 24 h, ^{*b*} 8 h; catalyst amount, ^{*a*} 0.231 wt%, ^{*b*} 0.227 wt%. TON was calculated from the formula, TON = moles of product/moles of catalyst.

A leaching test was carried out by taking 1 g of catalyst with 10 mL of distilled water and was refluxed for 24 h. Then, 1 mL of the supernatant liquid was reacted with 10% ascorbic acid solution. No blue colour was observed, indicating that there was no leaching. The same test was repeated by taking alcohols and the filtrate of the reaction in order to see the presence of any leached PMo₁₁. The absence of blue colour indicates no leaching.

3.5. Recycling study and characterization of regenerated catalyst

The oxidation of benzyl alcohol and styrene were performed over recycled catalysts (Table 3), under optimized conditions. The catalyst was removed by centrifugation; the first washing

 Table 2
 Control experiments over the catalyst and the support^a

Catalyst	Substrate	Conversion %	Selectivity ^c %
Нβ	Benzyl alcohol ^a	<1	100
	Styrene ^b	<1	100
PMo ₁₁	Benzyl alcohol ^a	25.2	91
	Styrene ^b	43	64
30% PMo ₁₁ /Hβ	Benzyl alcohol ^a	25.5	90
	Styrene ^b	57	72

 a % Conversion is based on substrate a alcohol, b alkene – O₂: 0.2 mmol TBHP, temp. – a 90 °C, b 80 °C; time – a 24 h, b 8 h; c selectivity for benzaldehyde.

was done by dichloromethane. Further successive washings were done by distilled water and dried at 100 °C, and the recovered catalyst was used for the next run. No considerable loss in the activity was detected up to two cycles (Table 3).

In order to see the need for reactivating the catalyst by washing and heating at 100 °C, we have carried out two experiments as follows: (1) separating the catalyst and adding a fresh one to the same solution and the reaction is further carried out for 10 h and it was observed that the conversion increases by 10%, with similar selectivity for benzaldehyde. This indicates that the catalyst may be poisoned by the product molecules blocking the active sites. (2) On adding fresh benzyl alcohol in the reaction mixture after 24 h without further catalyst washing, no increase in conversion was observed. This truly suggests that washing procedure reactivates the catalyst.

The reused catalyst was further characterized by EDX, FT-IR and SEM analysis. EDX elemental analysis performed on the fresh (fresh: P = 0.37%, Mo = 12.0%) and recycled catalyst (recycled: P = 0.33%, Mo = 11.3%) shows that all the elements in the recycled catalysts are retained. The FT-IR data for the fresh as well as the recycled catalysts are presented in Fig. 10. The FT-IR of fresh catalyst shows bands at 890 cm⁻¹ and 918 cm⁻¹ assigned to Mo–O–Mo stretches. Similar bands were observed for recycled 30% PMo₁₁/H β . No appreciable shift in the FT-IR band position of the regenerated catalyst compared to fresh 30% PMo₁₁/H β indicates the retention of structure of PMo₁₁ in the catalyst. Fig. 11 shows SEM images of the recycled as well as fresh catalyst. Even after three cycles the surface morphology of the catalyst is retained. The above studies show that there is no deactivation of the catalyst after reuse.

Table 3 Recycling studies under the optimised conditions"				
Cycle	Conversion ^{a,b} (%)	Selectivity ^{a,b,c} (%)	TON ^{<i>a,b</i>}	
Fresh	25.5/57	90/72	9551/20975	
1	25.0/55	89/68	9364/20306	
2	24 0/54	89/66	8989/19937	

^a % Conversion is based on substrate ^a benzyl alcohol, ^b styrene, O₂: 0.2 mmol TBHP, catalyst quantity ^a 0.231 wt%, ^b 0.227 wt%. ^c Selectivity for benzaldehyde.



Fig. 10 FT-IR spectra of fresh and recycled catalyst.



Fig. 11 SEM images of (a) fresh catalyst and (b) recycled catalyst.

3.6. Comparison of catalysts and effect of supports

It is recognised that the support type not only shows a mechanical role but also significantly modifies the catalytic activity of the catalyst. The difference in catalytic activity and product selectivity in oxidation reaction of benzyl alcohol may be due to the nature of supports such as structural mesoporosity and high specific surface area. Hence, the obtained results of 30% $PMo_{11}/H\beta$ were compared with 30% $PMo_{11}/MCM-41.^{10}$ It is seen that benzyl alcohol conversion is higher in the case of 30% $PMo_{11}/MCM-41$ (28%). This might be due to difference in the surface area of the catalysts where surface area of 30% $PMo_{11}/MCM-41$ (485 m² g⁻¹) is higher compared to 30% $PMo_{11}/H\beta$ (362 m² g⁻¹). Hence, the order of catalytic activity observed was 30% $PMo_{11}/MCM-41 > 30\%$ $PMo_{11}/H\beta$. 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 (90%) of benzaldehyde is attributed to acidity of the support. It is well known that MCM-41 and zeolite H β both exhibit acidic character, however H β (1.14 mmol g⁻¹) is much more acidic than MCM-41 (0.82 mmol g⁻¹).¹⁵ Similar trend was observed for oxidation of styrene (30% PMo₁₁/MCM-41 = 60% conversion, 30% PMo₁₁/H β = 57% conversion), however 30% PMo₁₁/H β

showed higher selectivity for benzaldehyde 72% as compared to 30% PMo_{11}/MCM -41 (70%). The observed difference in conversion as well as selectivity might due to difference in surface area, pore geometry of zeolite H β supercages.

3.7. Comparative study with reported catalysts

Table 5 comprises the catalytic activity of reported catalyst for oxidation of benzyl alcohol and styrene.^{8,16-19} The catalyst 2.5% Au–2.5% Pd/TiO₂ showed excellent conversion (90%) in presence of 0.2 MPa O₂ pressure in reactor at 100 °C and high turnover frequency (TOF).¹⁸ It is important to note that costly metals such as gold, Pd, and TiO₂ are used as a catalyst under 0.2 MPa pressure of O₂. Superiority of the present catalytic system lies in obtaining better conversion as well as selectivity under mild reaction conditions with very high TON (9551).

3.8. Reaction mechanism study

Three different oxidation processes were studied in order to study the reaction mechanism (Table 4), (1) TBHP as the only oxidant, (2) O_2 as the only oxidant and (3) using 0.2 mmol TBHP as initiator along with O_2 as the oxidant. Control experiments without a catalyst suggested that there was no conversion of substrates and that the reaction does not proceed through auto-oxidation.²⁰

In the first case (1) entirely polymeric product was obtained for styrene oxidation, however benzyl alcohol showed no conversion. On comparing the activities of (2) and (3) the conversions were almost doubled in the case of (3) with respect to (2). This is because O_2 is the only oxidant and it requires extended activation time, *i.e.* a larger induction period. Whereas, in the case of O_2 as the main oxidant and TBHP as an initiator, it forms species BuO'/OH which activates O_2 . From these observations, it was proposed that the reaction appears to be a radical mechanism and activation of catalyst was necessary for initiating the reaction, where TBHP acts as a radical initiator only (Scheme 2). Our group had earlier proposed a mechanism for aerobic oxidation of alkenes and alcohols,²¹ similarly in the present case also we expect the same mechanism.

Table 4 Effect of various oxidants on both the reactions^a

			Selectivity		
Substrate	Oxidant	Conversion	Benzaldehyde	Others	
Benzyl alcohol ^a	TBHP	<1	99	1	
	O_2	10	98	2	
	O ₂ /TBHP	25.5	90	10	
Styrene ^b	TBHP	39	3	97 ^c	
	O_2	30	58	42	
	$O_2/TBHP$	57	72	28	

 a Reaction conditions: reaction temp.: a 90 °C, b 80 °C, reaction time: a 24 h, b 8 h, catalyst amount 25 mg, TBHP: 0.2 mmol. c Polymer as the major product.

Table 5 Comparison of catalytic activity with the reported catalysts for oxidation of benzyl alcohol and styrene

Catalyst	Reaction conditions ^a	Solvent (mL)	% Conv.	Products (% select.)	TON	Ref.
TBA-SiW ₁₁ Ru ^c	$1:2:120:110^{b}$	3	36	65	340	16
Mo–V–O oxide d	$0.7:30:24:80^{b}$	1.6	22	>99	_	17
2.5% Au-2.5% Pd/TiO2 ^e	-:-:8:100	_	74.5	91.6		18
30% PMo ₁₁ /Hβ ^f	$100:25:24:90^b$	_	25.5	90	9551	This work
Mo-exchanged zeolite	$3:300:5:90^{g}$	10	15.7	34.8		19
20% PMo ₁₁ /ZrO ₂ ^f	$100:25:8:80^{ m g}$	_	21.7	93.9	11 329	8
$30\% \text{ PMo}_{11}/\text{H}\beta^f$	$100:25:8:80^{g}$	—	57	72	20 975	This work

^{*a*} % Conversion is based on substrate; benzyl alcohol: amount of catalysts (mg): time (h): temperature (°C). ^{*b*} Benzyl alcohol; solvent = ^{*c*} isobutyl acetate/ ^{*d*} toluene; ^{*e*} 0.2 MPa pO₂, ^{*f*} TBHP was used as an initiator, ^{*g*} styrene, product (benzaldehyde).



Scheme 2 Possible mechanism for oxidation of alcohols and alkenes over 30% $PMo_{11}/H\beta.$

4. Conclusion

In conclusion, a novel mono lacunary phosphomolybdate anchored to zeolite-H β was synthesized and efficiently characterized. Catalytic study was carried out for solvent free aerobic oxidation of benzyl alcohol and styrene. The applicability of the method was extended to different alkenes and alcohols. In all the cases a high TON >18 000 for alkenes and >3500 for alcohols was found. A basic comparative study on effect of support was carried out by comparing zeolite-H β based catalyst with mesoporous MCM-41 and it was found that acidity of supports play a role in selectivity of the desired product. The catalyst can be recovered after simple filtration and can be recycled without any significant change in the conversion.

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