



## Supported 12-molybdophosphoricacid: Characterization and non-solvent liquid phase oxidation of styrene

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### ARTICLE INFO

#### Article history:

Received 20 March 2008  
Received in revised form  
30 September 2008  
Accepted 1 October 2008  
Available online 14 October 2008

#### Keywords:

12-Molybdophosphoricacid  
Alumina  
Oxidation  
Styrene  
Epoxide

### ABSTRACT

A series of solid catalysts comprising 12-molybdophosphoricacid (PM) and neutral alumina were synthesized by impregnation. The support, fresh as well as calcinated catalysts were characterized by various physical–chemical techniques. Further, the structure of PM onto the surface of the support was confirmed by  $^{31}\text{P}$  MAS NMR and XPS. Non-solvent liquid phase oxidation of styrene was carried out with 30% aqueous  $\text{H}_2\text{O}_2$  as an oxidant by varying different parameters over fresh catalysts. The catalytic activity of calcinated catalysts were also evaluated by carrying out same oxidation reaction under optimized conditions. As solid catalysts, they show high conversion of styrene with good selectivity towards benzaldehyde and styrene epoxide.

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### 1. Introduction

Catalytic oxidation of alkenes into more valuable epoxides as well as oxygen containing carbonyl compounds is one of the important synthetic reaction. Epoxides and carbonyl compounds have industrial significance. Epoxides are mainly used as intermediates in the manufacture of bulk chemicals and industrial feedstock. Carbonyl compounds are widely used as solvents, perfumes, and flavouring agents or as intermediates in the manufacture of plastics, dyes, and pharmaceuticals.

Traditionally, oxidation was carried out using powerful oxidizing agents like  $\text{KMnO}_4$  and  $\text{CrO}_3$ , in stoichiometric quantities. Environmental concerns have forced the chemical industries to re-evaluate many of its processes to reduce or eliminate the formation of by-products. As a result the oxidation reactions involving catalytic amount of the oxidizing agents or liquid phase catalytic oxidation have come into prominence. In this context, heteropolyacids (HPAs), especially 12-molybdophosphoricacid has been gaining importance due to their redox properties [1–6].

In 1983, Venturello et al. [7] reported epoxidation of alkenes over tungstate and phosphate salts in the presence of a phase transfer catalyst (PTC) such as cetyl pyridinium chloride (CPC). Later

on, in 1987, Ishii et al. carried out epoxidation of relatively electron poor terminal olefins with HPAs and more environmentally and economically significant oxidant,  $\text{H}_2\text{O}_2$ .  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  has been used in the presence of a PTC such as CPC or Arquad [8]. After Ishii and co-workers' work, HPAs have been used as a catalytic system in the presence of CPC for oxidation of a large number of organic substrates [9–15]. Furthermore, different salts of HPAs [16–20] and transition metal substituted HPAs [21–25] have been synthesized and used in biphasic medium with different organic solvents. Some research groups have also used supported HPAs [26–30] for several organic conversions. Almost all reported oxidation reactions have been carried out in organic solvents. It would be interesting if oxidation reactions could be carried out without any PTC or organic solvents. In the present paper, first time we are reporting the results for solvent free oxidation of styrene using environmentally benign oxidant,  $\text{H}_2\text{O}_2$ , over supported HPAs. In the present paper we have made use of neutral alumina as the support. It is available in three different pH ranges: basic, acidic and neutral. Neutral alumina at pH of 6–8 is best as a support.

A series of catalysts containing 10–70% of 12-molybdophosphoricacid (PM) onto neutral alumina (A), have been synthesized. The support and new amorphous supported catalysts have been characterized by various thermal and spectral techniques like thermogravimetric analysis–differential thermal analysis (TGA–DTA), differential scanning calorimetry (DSC), Fourier transform infra red (FTIR), Raman, diffuse reflectance spectroscopy (DRS), surface area measurement (BET method) and X-ray diffraction (XRD). Further,

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the surface morphology of support and catalyst was studied by scanning electron microscopy (SEM). Any change in oxidation of P, as well as Mo after supporting onto the support was determined by magic angle spinning nuclear magnetic resonance ( $^{31}\text{P}$  MAS NMR) and X-ray photoelectron spectroscopy (XPS). The catalytic activity was evaluated for the non-solvent liquid phase oxidation of styrene with aqueous 30%  $\text{H}_2\text{O}_2$ . The conditions for maximum conversion as well as selectivity for desired products have been optimized by varying different parameters such as temperature, molar ratio of styrene to  $\text{H}_2\text{O}_2$ , amount of the catalyst and reaction time. The best catalyst of the series was calcinated at 300 and 400 °C for 5 h in air and characterized by FTIR, Raman, DRS and XRD to see any structural change. The activity of the calcinated catalysts has also been evaluated by carrying out same oxidation reaction under optimized conditions.

## 2. Experimental

### 2.1. Materials

All the chemicals used were of A.R. grade.  $\text{H}_3\text{PMo}_{12}\text{O}_{40}\cdot n\text{H}_2\text{O}$  (Loba chemie, Mumbai), neutral active  $\text{Al}_2\text{O}_3$  (Activity I–II, according to Brockmann), styrene and 30% aqueous  $\text{H}_2\text{O}_2$  were used as received from Merck.

### 2.2. Synthesis of the catalyst ( $\text{H}_3\text{PMo}_{12}\text{O}_{40}\cdot n\text{H}_2\text{O}$ supported onto neutral alumina)

A series of catalyst containing 10–70% of PM supported onto A was synthesized by wet impregnation. 1 g of A was impregnated with an aqueous solution of PM (0.1/10–0.7/70 g/ml of conductivity water) with stirring for 35 h and dried at 100 °C for 10 h. The obtained materials were designated as  $\text{APM}_1$ ,  $\text{APM}_2$ ,  $\text{APM}_3$ ,  $\text{APM}_4$ ,  $\text{APM}_5$  and  $\text{APM}_7$ . The best catalyst of the series,  $\text{APM}_3$ , was calcinated at 300 and 400 °C for 5 h and designated as  $\text{APM}_{33}$  and  $\text{APM}_{34}$ , respectively.

### 2.3. Characterization

Ion exchange capacity was determined by column method using the following formula:

$$\text{IEC (mequiv./g)} = \frac{\text{normality of NaOH (N)} \times \text{volume of NaOH (ml)}}{\text{gram of material (g)}}$$

The TGA–DTA and DSC of the samples were carried out on a TA Instrument (Q 50) and on DSC–Perkin Elmer instrument (DSC 7) in the temperature range 50–600 °C under nitrogen atmosphere with a flow rate of 2 ml/min and a heating rate of 10 and 20 °C/min. The FTIR spectra of the samples were obtained by using KBr wafer on Shimadzu Photometer instrument at room temperature. The Raman spectra were recorded on a FT-Raman Spectrophotometer, Model Bruker FRA 106. The DRS of samples were recorded on a Jasco DR-UV-VIS spectrophotometer (model V-560) instrument using barium sulphate as a reference. The specific surface area was calculated from adsorption–desorption isotherms using BET method on a Carlo-Erba sorptometer (Model: Series 1800) surface area analyzer at –196 °C. The powder XRD pattern was obtained by using the instrument Philips Diffractometer (Model PW – 1830). The conditions used were  $\text{Cu K}\alpha$  radiation (1.5417 Å). The surface morphology of the support and supported catalyst was studied by SEM using a JEOL SEM instrument (Model-JSM-5610LV) with scanning electron electrode at 15 kV. Scanning was done at 1 mm range and images were taken at a magnification of 100× for catalyst.  $^{31}\text{P}$  MAS NMR spectra were recorded on a Bruker Avance DSX - 300 NMR spectrometer at 121.48 MHz using a 7 mm rotor probe with

85% phosphoric acid as an external standard. The spinning rate was 4–5 kHz. XPS were recorded using an ESCA-3000 (VG Scientific Ltd., England) with a 9 channeltron CLAM4 analyzer under a vacuum of  $1 \times 10^{-8}$  Torr, using  $\text{Mg K}\alpha$  radiation and a constant pass energy of 50 eV. The binding energy values were charge-corrected to the C 1s signal (284.6 eV).

### 2.4. Catalytic reaction

The oxidation reaction of styrene was carried out in a three neck round bottom flask provided with a double walled condenser containing catalyst, styrene and  $\text{H}_2\text{O}_2$  at 80 °C with constant stirring for 48 h. The temperature was maintained at 80 °C in an oil bath. Same reaction was carried out by varying different parameters such as molar ratio of styrene to  $\text{H}_2\text{O}_2$ , amount of the catalyst, reaction time and temperature. 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 (GC) using SE-30 column. Product was identified by comparison with the authentic samples and finally by gas chromatography–mass spectroscopy (GC–MS).

## 3. Results and discussion

### 3.1. Characterization

The initial pH of the original solution was 2.5. The pH changes to 2.6 after the contact with neutral alumina. Almost the same value of pH indicates that the  $\text{PMo}_{12}\text{O}_{40}^{3-}$  species does not depolymerize to  $\text{PMo}_{11}\text{O}_{39}^{7-}$  when supported onto neutral alumina. Ion Exchange Capacity (IEC) gives the measurement of Bronsted acidity only. The IEC values for alumina is zero while that for  $\text{APM}_3$  is 0.28 meq/g.

Any leaching of the active species from the support makes the catalyst unattractive and hence it is necessary to study the stability as well as leaching of PM from the support. HPA can be quantitatively characterized by the heteropoly blue colour, which is observed when it reacted with a mild reducing agent such as ascorbic acid [31]. In the present study, this method was used for determining the leaching of PM from the support.

Standard samples containing 1–5% of PM in water were prepared. To 10 ml of the above samples, 1 ml of 10% ascorbic acid was added. The mixture was diluted to 25 ml. The resultant solution was scanned at a  $\lambda_{\text{max}}$  of 785  $\text{cm}^{-1}$  for its absorbance values. A standard calibration curve was obtained by plotting values of absorbance against % concentration. 1 g of supported catalyst with 10 ml conductivity water was refluxed for 48 h. Then 1 ml of the supernatant solution was treated with 10% ascorbic acid. Development of blue colour was not observed indicating that there was no leaching. The same procedure was repeated with styrene and the filtrate of the reaction mixture after completion of reaction in order to check the presence of any leached PM. The absence of blue colour indicates no leaching of PM. The above study indicates the presence of chemical interaction between PM and the support, A. It also confirms the stability of catalysts under reaction conditions.

TGA–DTA (Fig. 1) and DSC (Fig. 2) show that parent PM is less stable (430 °C) as compared to supported PM (475 °C). This shows that supporting of PM on the surface of neutral alumina increases the thermal stability of PM. An increase in thermal stability indicates the presence of chemical interaction, preferably H-bonding, between PM and support.

The FTIR spectra of A, PM,  $\text{APM}_3$ ,  $\text{APM}_{33}$  and  $\text{APM}_{34}$  are presented in Fig. 3. The main characteristic bands of PM are observed at: 1070  $\text{cm}^{-1}$  ( $\text{P}-\text{O}_a$ ), 965  $\text{cm}^{-1}$  ( $\text{Mo}=\text{O}_d$ ), 870  $\text{cm}^{-1}$  ( $\text{Mo}-\text{O}_b-\text{Mo}$ ) and 790  $\text{cm}^{-1}$  ( $\text{Mo}-\text{O}_c-\text{Mo}$ ), where  $\text{O}_a$  is connecting X and M ( $\text{X}-\text{O}_a-\text{M}$ ),  $\text{O}_b$  is connecting the two  $\text{M}_3\text{O}_{13}$  units by corner

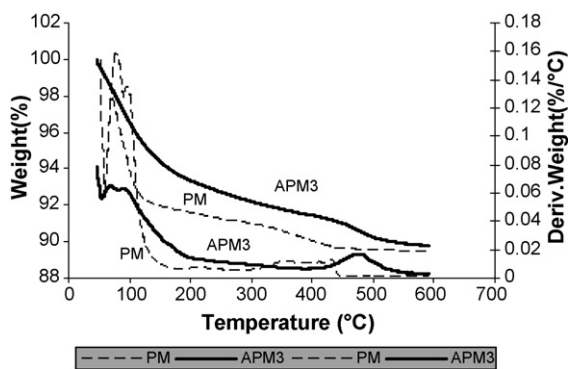


Fig. 1. TGA-DTA thermograms for PM and APM<sub>3</sub>.

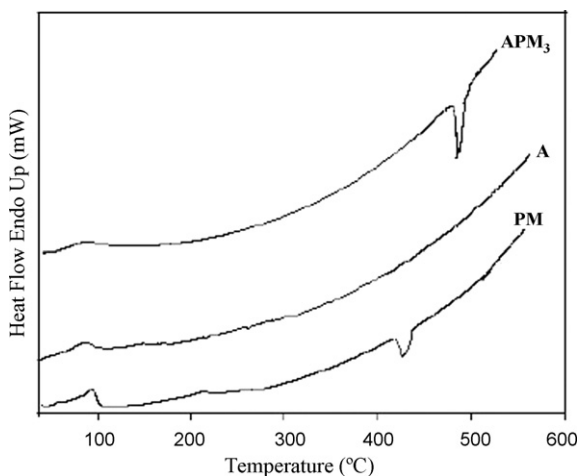


Fig. 2. DSC of A, PM and APM<sub>3</sub>.

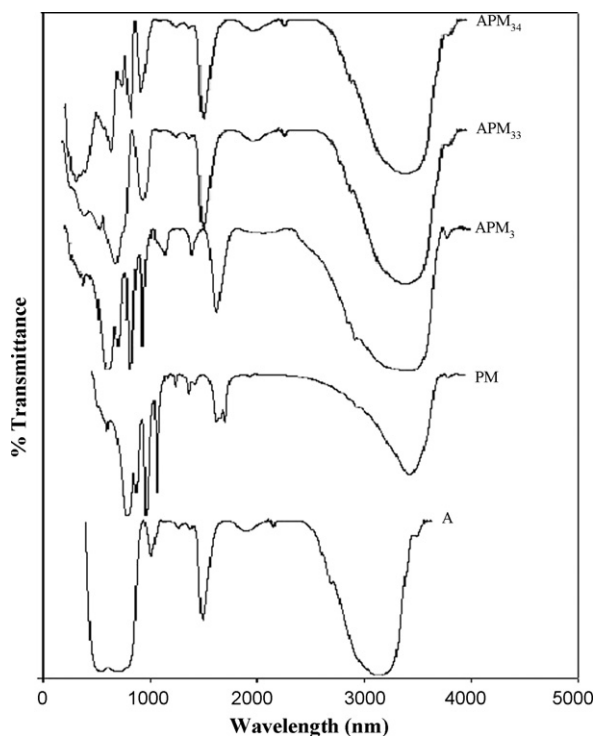


Fig. 3. FTIR of A, PM, APM<sub>3</sub>, APM<sub>33</sub> and APM<sub>34</sub>.

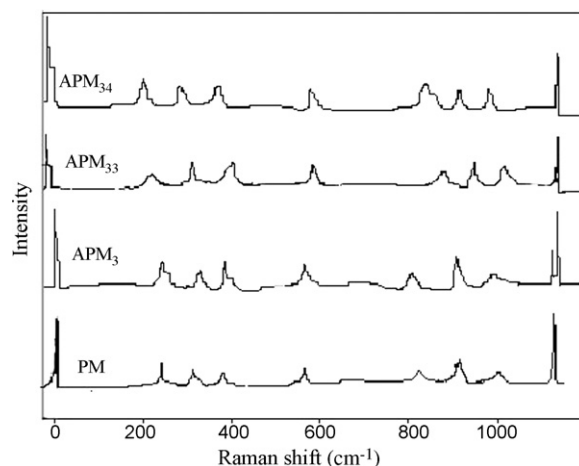


Fig. 4. Raman spectra of PM, APM<sub>3</sub>, APM<sub>33</sub> and APM<sub>34</sub>.

sharing (M–O<sub>b</sub>–M), O<sub>c</sub> is connecting two M<sub>3</sub>O<sub>13</sub> units by edge sharing (M–O<sub>c</sub>–M) and O<sub>d</sub> is the terminal oxygen (M–O<sub>d</sub>) [32]. The observed FTIR frequencies are in good agreement with the reported values. The presence of same bands in APM<sub>3</sub>, APM<sub>33</sub> and APM<sub>34</sub> confirm that PM keeps its Keggin structure undegraded after supporting onto the support up to 400 °C [33,34].

The Raman spectra of PM, APM<sub>3</sub>, APM<sub>33</sub> and APM<sub>34</sub> are shown in Fig. 4. The bands in parent PM at 997, 900, 870, 605, 374, 350 and 248 cm<sup>-1</sup> corresponds to  $\nu_s$  Mo=O<sub>d</sub>,  $\nu_{as}$  Mo–O<sub>b</sub>–Mo,  $\nu_{as}$  Mo–O<sub>b</sub>–Mo,  $\nu_s$  Mo–O–Mo,  $\nu_{as}$  O<sub>a</sub>–P–O<sub>a</sub>,  $\nu_{as}$  O<sub>a</sub>–P–O<sub>a</sub> and  $\nu_s$  Mo–O<sub>a</sub>. The presence of these bands in catalysts (fresh and calcined) again confirm the presence of undegraded PM onto the surface of the support [33,35].

The DRS gives information about the non-reduced heteropolyanion due to charge transfer from oxygen to metal. The  $\lambda_{max}$  of APM<sub>3</sub>, APM<sub>33</sub> and APM<sub>34</sub>, is same as that for PM (Fig. 5) and is in good agreement as reported earlier [34]. This confirms the presence of the undegraded PM species in all catalysts. In other words, the Keggin structure remain unaltered up to 400 °C. Further, DRS of the support was also carried out and no absorbance band was observed in the same region.

The values of surface area for support as well as fresh catalysts are listed in Table 1. It is known [36] that there may be decrease in surface area in case of the supported catalyst in which oxides are used as supports. The obtained values are in good agreement. With

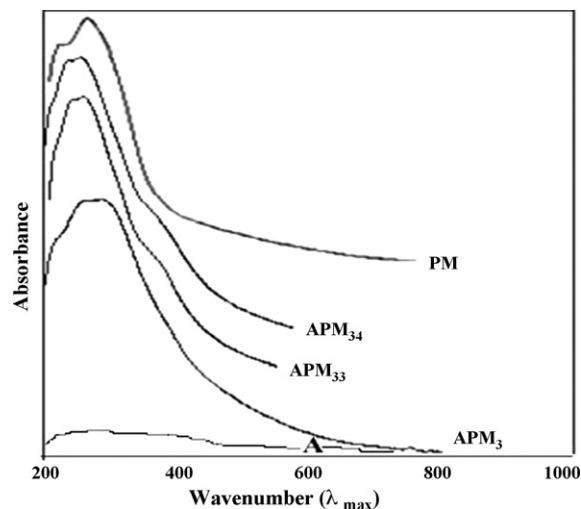


Fig. 5. DRS of A, PM, APM<sub>3</sub>, APM<sub>33</sub> and APM<sub>34</sub>.

**Table 1**  
Surface area of support and catalysts.

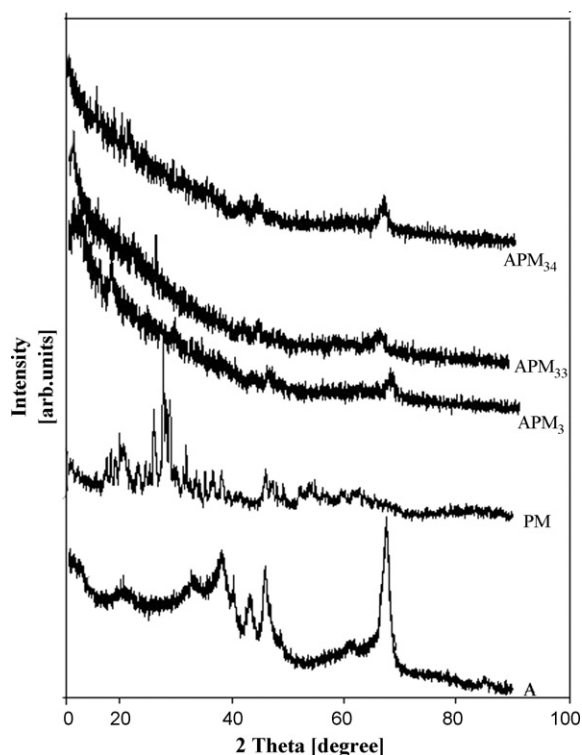
Catalyst	Total surface area (m <sup>2</sup> /g)
A	81.0
APM <sub>1</sub>	80.8
APM <sub>2</sub>	78.7
APM <sub>3</sub>	75.9
APM <sub>4</sub>	75.0
APM <sub>5</sub>	75.4
APM <sub>7</sub>	75.5

increase in loading of PM, the surface area decreases however the increase is not significant. Almost the same values of surface area may be due to the stabilization/blocking of the sites.

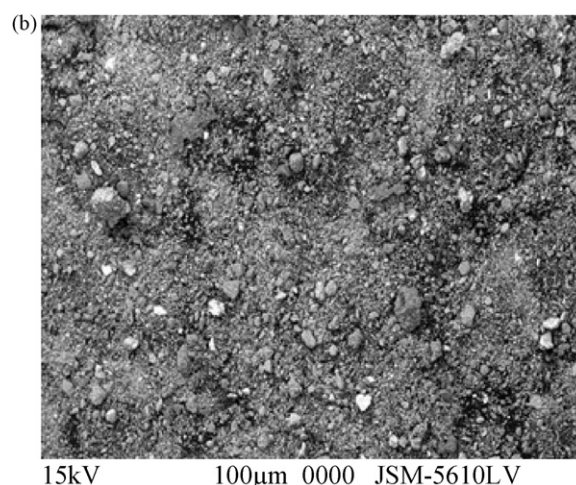
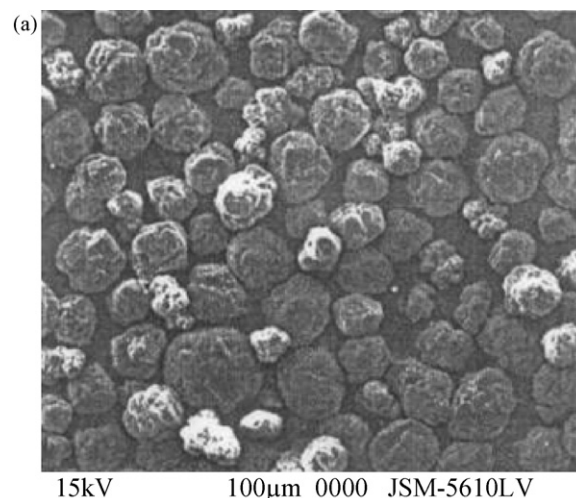
XRD pattern of A, PM, APM<sub>3</sub>, APM<sub>33</sub> and APM<sub>34</sub> are presented in Fig. 6. The XRD of APM<sub>3</sub>, APM<sub>33</sub> and APM<sub>34</sub> shows no characteristic diffraction line of PM and A indicating a very high dispersion of solute in a non-crystalline form on the surface of the support.

The SEM images of A and APM<sub>3</sub> at a magnification of 100× are reported in Fig. 7. It is seen from the figure that the surface of the support is distinctly altered. SEM of APM<sub>3</sub> in Fig. 7(b) shows a uniform dispersion of particles. Thus XRD and SEM are in good agreement with each other and confirm the uniform as well as high dispersion of PM in a non-crystalline form onto the surface of the support.

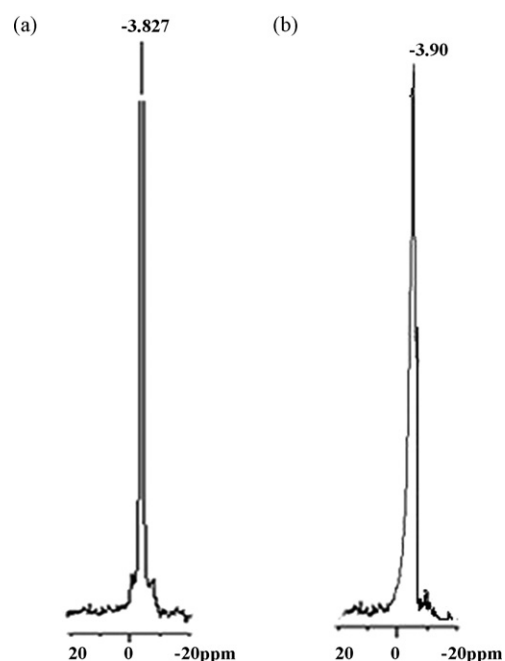
The solid-state <sup>31</sup>P (MAS) NMR of PM and APM<sub>3</sub> are shown in Fig. 8. The <sup>31</sup>P NMR spectra of PM in Fig. 8(a) shows chemical shift at −3.827 ppm which is in good agreement with the reported value corresponding to α-PMO<sub>12</sub> [33,34]. The <sup>31</sup>P NMR spectra of APM<sub>3</sub>, Fig. 8(b), show a single peak at −3.90 ppm corresponds to the weakly interacting intact molybdophosphoric acid species [34]. The absence of any peak at −10.7 ppm and −1.2 ppm confirm the absence of any partially reduced PM [34,37] as well as lacunary anion (PM<sub>11</sub>O<sub>39</sub>) [37]. No appreciable change in the value of chemical shift indicates that the PM Keggin structure remains intact on



**Fig. 6.** XRD of A, PM, APM<sub>3</sub>, APM<sub>33</sub> and APM<sub>34</sub>.



**Fig. 7.** SEM of A (a) and APM<sub>3</sub> (b) at a magnification of 100×.



**Fig. 8.** Solid-state <sup>31</sup>P (MAS) NMR of (a) PM and (b) APM<sub>3</sub>.

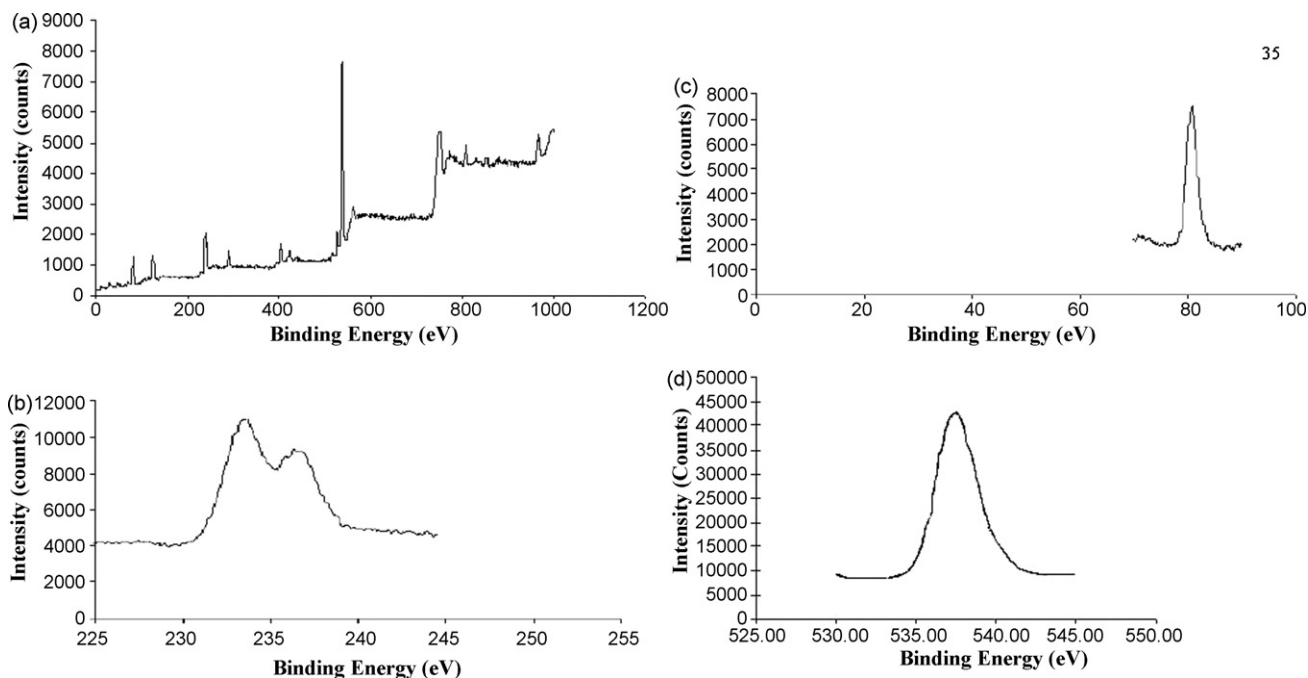


Fig. 9. XPS of APM<sub>3</sub>: (a) full range spectra, (b) Mo 4d, (c) Al 2p and (d) O 1s.

Table 2

Core electron binding energies for different elements in the supported PM.

XPS (core level)	Energy level	B.E. (eV)	
		Standard	Observed
Al (Al <sub>2</sub> O <sub>3</sub> )	2p	75.6	75.9
O (MoO <sub>3</sub> )	1s	531	532.2
Mo (MoO <sub>3</sub> )	4d <sub>5/2</sub>	227.7	227.4
Mo (MoO <sub>3</sub> )	4d <sub>3/2</sub>	230.9	229.9

the surface of the support. The observed line broadening for APM<sub>3</sub> may be due to the supporting of PM onto support. The values of resonance are in good agreement with the values reported earlier [33–34].

The XPS of APM<sub>3</sub> are presented in Fig. 9. The observed and theoretical values of binding energy (B.E.) for Al 2p, O 1s and Mo 4d are presented in Table 2. It is well known that as the Al<sub>2</sub>O<sub>3</sub> contains strong Lewis acidity, it will withdraw some of the charge density from PM when supported onto alumina. As a result, there is an increase in B.E. of Al<sub>2</sub>O<sub>3</sub>. Further, the B.E. of O 1s is shifted to the higher value and the band becomes broader indicating the presence of different types of oxygen atoms in the heteropolyanion. The observed B.E. for Mo 4d is almost same as theoretical value and

confirms the presence of Mo as Mo<sup>6+</sup>. The study confirms that the surface of Al<sub>2</sub>O<sub>3</sub> is composed of intact heteropolyanion species.

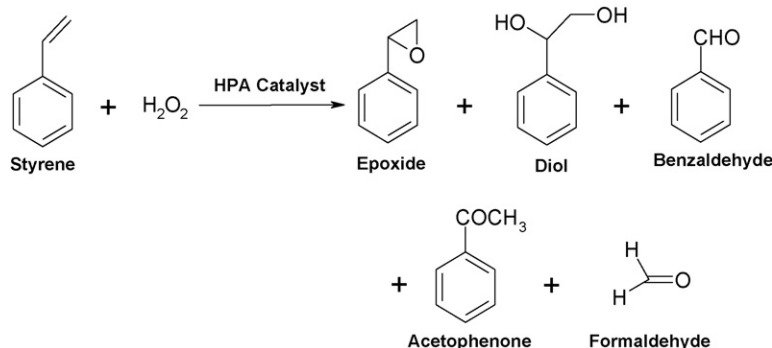
### 3.2. Catalytic reaction

Oxidation of styrene involves the formation of five products: (a) epoxide, (b) diol, (c) benzaldehyde, (d) acetophenone, and (e) formaldehyde (Scheme 1).

To ensure the catalytic activity, the same reaction was carried out without catalyst. It was found that no oxidation takes place. The support, A was also used as catalyst for oxidation of styrene and conversion was found to be zero.

#### 3.2.1. Effect of % loading of PM and temperature

The oxidation of styrene was carried out with H<sub>2</sub>O<sub>2</sub> in 1:3 molar ratio by using 25 mg of fresh catalysts for 48 h at two temperatures, 40 and 80 °C. At 40 °C, the conversion is found to be zero. The results obtained at 80 °C are presented in Fig. 10. Figure shows a sharp increase in the conversion with increase in the % loading of PM from 10 to 30% on the support. On increasing the % loading from 20 to 40% the conversion increases. It is seen from Table 1 that the surface area decreases from APM<sub>2</sub> to APM<sub>4</sub> and hence the catalytic activity should decrease but the obtained results are controversy.



Scheme 1. Products for oxidation of styrene with H<sub>2</sub>O<sub>2</sub>.

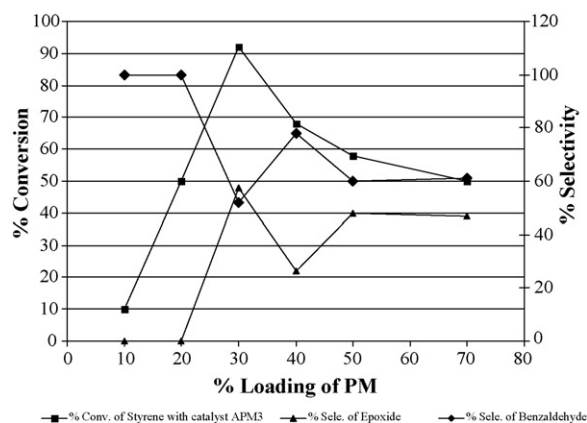


Fig. 10. % conversion and % selectivity with different % loading.

Hence, the catalytic activity cannot be correlated with surface area. It can be concluded that the present catalytic system is not a surface type heterogeneous catalyst in which the catalytic activity is directly proportional to surface area but it is a pseudoliquid type heterogeneous catalyst [38]. So, further detailed study was carried out at 80 °C over APM<sub>3</sub>.

### 3.2.2. Effect of mole ratio of styrene to H<sub>2</sub>O<sub>2</sub>

The reaction was carried out by varying mole ratio of styrene to H<sub>2</sub>O<sub>2</sub> with 25 mg of the catalyst for 48 h at 80 °C. The obtained results are reported in Table 3. It is seen from Table 3 that with increase in the concentration of H<sub>2</sub>O<sub>2</sub>, there is a drastic change in the % conversion with change in % selectivity of the products. The increase in % conversion may be due to increase in concentration of H<sub>2</sub>O<sub>2</sub>. The % conversion of styrene is 92% and the product selectivity for benzaldehyde and styrene epoxide is 52 and 48%, respectively when mole ratio of styrene to H<sub>2</sub>O<sub>2</sub> is 1:3.

### 3.2.3. Effect of the amount of catalyst

The reaction was carried out with different amount of catalyst with mole ratio of 1:3 for 48 h at 80 °C. The % conversion and % selectivity is reported in Table 4. It can be seen from Table 4 that the % conversion is almost constant with increase in amount of catalyst. The effect of amount of the catalyst was studied keeping all other parameters (temperature, reaction time, mole ratio of substrate: H<sub>2</sub>O<sub>2</sub>) constant. Under these conditions, no increase in the conversion with increase in amount of the catalyst indicates the attainment of the maximum equilibrium. So the obtained results are as expected.

### 3.2.4. Effect of reaction time

Oxidation of styrene with H<sub>2</sub>O<sub>2</sub> 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 Table 5. It is seen from Table 5 that with

Table 3  
% conversion and % selectivity with different molar ratio of styrene to H<sub>2</sub>O<sub>2</sub>.

Molar ratio	% conversion	% selectivity	
		Benzaldehyde	Epoxide
1:1	76	53	47
1:2	81	65	34
1:3	92	52	48
1:4	93	54	46
1:5	93.2	53	47
1:6	96.4	53	47

% conversion is based on styrene; time = 48 h; temperature = 80 °C; amount of catalyst = 25 mg.

Table 4  
% conversion and % selectivity with different amount of catalyst.

Amount of catalyst (mg)	% conversion	% selectivity	
		Benzaldehyde	Epoxide
25	92	52	48
50	91	65	35
75	92	52	48
100	90	52	48
125	91	54	46
150	92	53	47

% conversion is based on styrene; time = 48 h; temperature = 80 °C; mole ratio of styrene to H<sub>2</sub>O<sub>2</sub> = 1:3.

Table 5  
% conversion and % selectivity by varying reaction time.

Time (h)	% conversion	% selectivity	
		Benzaldehyde	Epoxide
12	61	56	46
24	71	69	31
36	74	64	36
48	92	52	48
60	93	52	48

% conversion is based on styrene; amount of catalyst = 25 mg; temperature = 80 °C; mole ratio of styrene to H<sub>2</sub>O<sub>2</sub> = 1:3.

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.

The optimum conditions for 92% conversion of styrene and maximum % selectivity towards benzaldehyde and styrene epoxide results with the mole ratio of styrene to H<sub>2</sub>O<sub>2</sub> as 1:3, with 25 mg of catalyst and 48 h reaction time at 80 °C.

### 3.2.5. Effect of calcination

The % conversion and % selectivity of different products with calcinated catalysts under optimized conditions are presented in Table 6. The decrease in % conversion and increase in % selectivity towards benzaldehyde for calcined catalysts may be explained on the base of Lewis acidity. It is known that on calcinations the Lewis acidity of alumina increases. An increase in Lewis acidity means more electrons are available for oxidation, responsible for fast conversion of benzaldehyde. In oxidation of styrene, epoxide is formed as an intermediate product which is then converted to benzaldehyde. In order to obtain epoxide selectively the reaction must be slow and controlled one. In case of H<sub>2</sub>O<sub>2</sub>, the reaction progresses towards the formation of benzaldehyde, as the reaction is a fast and exothermic reaction.

### 3.3. Recycling and repeated use of catalyst

The amount of catalyst is very small (25 mg). Hence, the recycling of the catalyst was not very efficient. There is difficulty in collection of the catalyst due to the loss during filtration. But if large

Table 6  
% conversion and % selectivity with calcinated materials in optimized condition.

Name of catalyst	% conversion	% selectivity	
		Benzaldehyde	Epoxide
APM <sub>3</sub>	92	52	48
APM <sub>33</sub>	90	63	37
APM <sub>34</sub>	81.1	70	30

% conversion is based on styrene; amount of catalyst = 25 mg; temperature = 80 °C; mole ratio of styrene to H<sub>2</sub>O<sub>2</sub> = 1:3.

amount of catalyst is used, the recycling of the catalyst was significant with almost the same catalytic activity with a 2% decrease in the % conversion. The distribution for the selectivity of the products remains the same.

#### 4. Conclusion

TGA–DTA and DSC confirm the stability of catalyst up to 475 °C. FTIR, DRS, NMR and XPS indicate that the Keggin structure of PM does not get destructed after supporting on the surface of A. XRD shows that the catalyst is amorphous and PM is uniformly dispersed on the surface of A.

<sup>31</sup>P MAS solid-state NMR and XPS study confirm that PM anion keeps its Keggin type structure intact when supported onto A.

The reaction is not a typical surface type heterogeneous reaction but is a pseudoliquid type reaction.

The present contribution reports solvent free liquid phase styrene oxidation at lower temperature, which is the first report made ever. The catalyst gives 92% conversion with 52 and 48% selectivity for benzaldehyde and epoxide, respectively.

The present catalysts is promising cleaner alternative to the traditional liquid phase oxidation reactions.

#### Acknowledgement

One of the authors, Mr. Pankaj Sharma, is thankful to UGC, New Delhi, for the financial support.

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