Supported polyperoxometallates: Highly selective catalyst for oxidation of alcohols to aldehydes

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Abstract

A new highly selective heterogeneous catalyst is developed from phosphomolybdic acid for the oxidation of alcohols by supporting polyoxo-molybdate anions on vanadium–aluminum mixed oxide. The Keggin anion was found to be stable on the surface of vanadium–aluminum mixed oxide unlike alumina. It was further observed to undergo degradation with peroxide, to form surface bound polyperoxomolybdate species. In order to examine its usefulness, the catalyst was screened for the oxidation of variety of alcohols, using hydrogen peroxide under solid–liquid–liquid phase transfer conditions to yield corresponding aldehydes with almost 100% selectivity. In all the substrates examined, no traceable amount of over oxidised product was detected.
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Keywords: Phosphomolybdic acid; Heteropoly Keggin anion; Polyperoxomolybdate Venturello species; Selective oxidation; Alcohol; Active methylene group; Vanadium–aluminum mixed oxide; S-L-L PTC

1. Introduction

Selective oxidation of alcohols is of great significance to the synthetic organic community [1–4]. The known chemical methodologies for this transformation use either conventional mineral oxidants in stoichiometric amounts [5–8] or environmentally benign oxidizing agents like molecular oxygen, hydrogen peroxide catalysed by transition metal compounds [9–20]. The former method generates considerable amount of inorganic waste, and is therefore environmentally not very attractive. Consequently, one of the preferred solutions is to use hydrogen peroxide as an oxygen donor in catalytic oxygen transfer reactions. Over the last few years, smart catalytic oxidations have proved to be the promising ones as exemplified by numerous examples [21–30], however most of the catalyst systems are based on noble metals like Pt, Pd and Ru, which are expensive and difficult to make. In this context, the polyoxometallates (POM) are definitely very attractive and challenging when looking for the economically viable and easy to manufacture alternatives of heterogeneous nature. The POM catalysts, which include early transition metal ions with d^0 configuration, e.g. Mo(VI) and W(VI) have been recognised as potential redox catalysts, exemplified by the oxidations of the various substrates such as benzyl alcohol, sulfides, hydrodesulfurisation of thiophene, isobutane and oxidative dehydrogenation of isobutyric acid [31–36]. This is the first report on heterogeneous POM stabilized on the vanadium–aluminum mixed oxide surface and its application in oxidation of alcohols, the key subject of this communication. All earlier attempts have led to unstable heteropoly anions on the surface of alumina because of the formation of aluminum phosphate. The new catalytic protocol developed was found to be highly efficient for the selective oxidation of the alcohols to aldehydes. To the best of our knowledge, this class of supported POM anions have never been used as heterogeneous catalyst for the oxidation of alcohols using H_2O_2. This paper also describes other interesting aspects such as substrate scope and recycling of the catalyst.

2. Experimental section

2.1. Chemicals

All the chemicals were of AR grade and used without further purification. Cetyl trimethyl ammonium bromide (CTMABr),

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tetrabutyl ammonium bromide (TBAB) and tetrabutyl ammonium hydrogen sulfate (TBAHS) were procured from BDH Laboratory Supplies, England. Phosphomolybdic acid (PMA) and ammonium metavanadate were obtained from Central Drug House, New Delhi. Oxalic acid and neutral alumina were acquired from Qualigens Fine Chemicals, India and all alcoholic substrates were obtained from Merck-Schuchardt, Germany. Hydrogen peroxide (50%, w/v) obtained from Merck India Ltd., was stored under refrigeration. The exact concentration of the H_2O_2 was determined by iodometric titration [37].

2.2. Catalyst synthesis

Twenty percent (w/w) phosphomolybdic acid/vanadium–aluminum mixed oxide (PMA/VAMO) was synthesised in our laboratory. The VAMO support was prepared by dispersing fine crystallites of vanadium oxide (VO) on the surface of alumina (15%, w/w) by employing wet impregnation method, followed by drying at $120\,^{\circ}C$ and subsequent calcination at $450\,^{\circ}C$ for 5 h. The solution of ammonium metavanadate in 2 M oxalic acid was used as a VO precursor. The required quantity of PMA, dissolved in methanol was used to anchor Keggin ion on the surface of VAMO via incipient wetness method followed by drying at $120\,^{\circ}C$ for 8 h and subsequent calcination at $450\,^{\circ}C$ for 4 h in the flow of air.

2.3. Catalyst characterisation

The PMA/VAMO was characterised by X-ray diffraction, framework IR analysis and H_2 temperature-programmed reduction (TPR) analysis. X-ray scattering measurements were made with Cu Kα radiation on a SIEMENS D 5000 diffractometer equipped with reflection geometry, a NaI scintillation counter, a curved graphite crystal monochromator and a nickel filter. The scattered intensities were collected from 2° to 40° (2θ) by scanning at 0.030° (2θ) steps with a counting time of 0.5 s at each step. Framework IR spectra were recorded on a Perkin-Elmer Spectrum-one spectrophotometer equipped with DRS system. H_2 temperature-programmed reduction experiments were carried out on a Thermoquest TPDRO 1100. Samples were tested by increasing the temperature from 50 to $800\,^{\circ}C$, at a heating ramp of $10\,^{\circ}C\,min^{-1}$. A mixture of 5 vol.% H_2 in Ar, at a flow rate of $30\,ml\,min^{-1}$ was used to reduce the catalyst samples with continuous temperature ramp. The temperature was then kept constant at $800\,^{\circ}C$ until the signal of the hydrogen consumption returned to the initial values.

2.4. Evaluation of the catalyst stability

2.4.1. Heteropoly blue colour test
The suspension of PMA/VAMO (2 g) in methanol (25 ml) was refluxed with vigorous stirring for 1 h. An aliquot was removed and 10% ascorbic acid (2 ml) was added.

2.4.2. Benzyl alcohol oxidation
H_2O_2 (0.5 mmol/min) was slowly added to the reaction mixture that consisted of benzyl alcohol (0.02 mol), CTABr (0.5 g)

in toluene (40 ml). Keeping the PMA/VAMO catalyst loading of $0.025\,g/cm^3$, the reaction was carried out at $65\,^{\circ}C$, for 1 h. The reaction mixture was filtered hot to separate the catalyst particles. The reaction was further continued at the same temperature for the next 30 min in the absence of solid catalyst particles.

PMA/VAMO catalyst (0.5 g) was stirred in water ($10\,cm^3$) for 1 h at $65\,^{\circ}C$. The catalyst was filtered and to the hot filtrate, benzyl alcohol (0.02 mol), toluene ($25\,cm^3$), CTABr (0.5 g) and H_2O_2 (0.5 mmol/min) were added and the reaction mixture was heated at $65\,^{\circ}C$, for 1 h.

2.4.3. UV–vis spectroscopic analysis
Following mixtures were prepared and subjected to stirring for 1 h at $60\,^{\circ}C$

   (i) PMA (0.1 g) in methanol ($10\,cm^3$).
  (ii) PMA (0.1 g) in water ($10\,cm^3$).
 (iii) PMA/VAMO (0.5 g) in methanol ($10\,cm^3$).
 (iv) PMA/VAMO (0.5 g) in water ($10\,cm^3$).
  (v) PMA/Al_2O_3 (0.5 g) in methanol ($10\,cm^3$).
 (vi) PMA/Al_2O_3 (0.5 g) in water ($10\,cm^3$).

The aliquots were withdrawn and the spectra of the solutions were obtained with a Perkin-Elmer Lambda 35 UV-VIS spectrophotometer using quartz cells in the range of 200–600 nm.

2.4.4. Nuclear magnetic resonance
The solutions obtained from above experiments were analysed by ^{31}P NMR utilizing Bruker 400 equipment. Phosphoric acid 85% was employed as external reference.

2.5. Reaction methodology

The preliminary evaluation of PMA/VAMO as the catalyst was carried out using benzyl alcohol as a substrate and H_2O_2 as an oxidising agent. Due to decomposition of H_2O_2 the oxidation methodology was designed in semi-batch process instead of batch type process. The optimum reaction conditions were established. All the other substrates were oxidised under the same experimental conditions. The reactions were performed in a mechanically agitated glass contactor equipped with a reflux condenser. The organic phase containing the required amount of the substrate, catalyst, CTABr in toluene as a solvent was stirred at speeds higher than 700 rpm. Desired amount of H_2O_2 was then added with the help of a peristaltic pump, at the rate of 0.5 mmol/min. The reaction was performed in a water bath where the desired temperatures were properly maintained.

2.6. Method of analysis

Samples (organic phase) were withdrawn periodically from the reaction mixture and filtered before being analysed by HP 6890N gas chromatograph equipped with autosampler 7683 series injector and HP chemstation. A ($30\,m \times 0.32\,mm$ i.d. $\times 0.25\,\mu m$) column packed with DB-5 (5% polyphenyl + 95% polymethyl siloxane) was used for analysis (injector/detector temperature $250\,^{\circ}C$, oven $60\,^{\circ}C$–2

min–10 °C min^{-1}–250 °C–5 min). 3-Pyridyl methanol was analysed by Water's Aliance HPLC system equipped with 2695 sample handling unit and 2487 UV detector. Purosphere star (250 mm × 4.6 mm × 5 μm) column was used with 0.02 mol Na_2HPO_4 (pH 7) buffer: acetonitrile (90:10) mixture as a mobile phase. Synthetic mixtures were prepared and used for calibration and quantification. Their structures were confirmed by GC–MS and LC–MS.

3. Results and discussion

3.1. Catalyst characterisation

X-ray powder diffraction patterns of PMA, V_2O_5, VAMO and PMA/VAMO are shown in Fig. 1. The XRD pattern of V_2O_5 showed very sharp peaks. VAMO sample with V_2O_5 content of 15 wt.% calcined at 450 °C showed small XRD peaks at 14.4 and 28.2 Å, indicating either the absence of free V_2O_5 species or its presence in the form of small crystallites. The X-ray diffractogram of PMA/VAMO was similar to that of PMA, wherein identical sharp XRD peaks suggest that in the supported form heteropoly Keggin anion remains intact and is present in the crystalline form. No XRD peaks were observed for orthorhombic
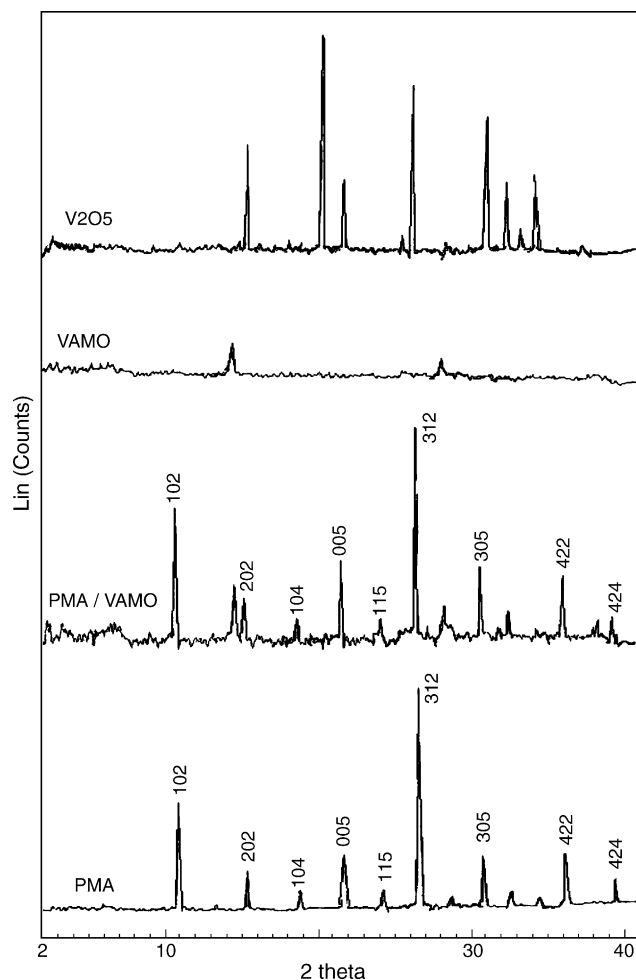

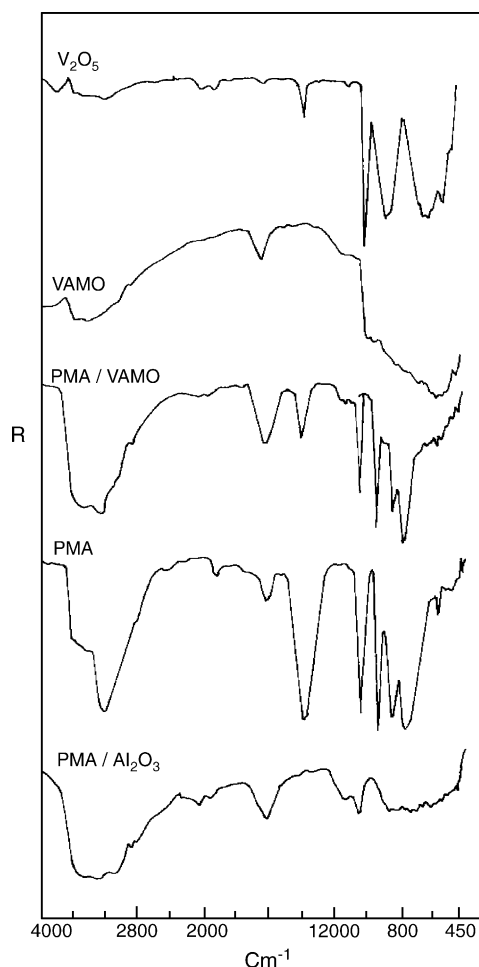Fig. 1. X-ray diffraction patterns of PMA, PMA/VAMO, VAMO and V_2O_5.

Fig. 2. IR spectra of V_2O_5, VAMO, PMA/VAMO, PMA, and PMA/Al_2O_3.

α-MoO_3 or monoclinic β-MoO_3 species or any other anhydrous form, which generally appears on thermal destruction of heteropoly Keggin anion.

PMA/VAMO exhibits characteristic absorption bands at 1063, 966, 867, 800 cm^{-1} in the IR spectrum (Fig. 2), which are assigned to the ν(P–O), ν(Mo–O_t) (O_t refers to the terminal oxygens), ν(Mo–O_c–Mo) (O_c refers to the corner oxygens) and ν(Mo–O_e–Mo) (O_e refers to the edge oxygens) respectively [38]. IR spectrum of pure vanadia gives a sharp band at 1020 cm^{-1}, generally associated V=O stretching mode of vanadium oxide. The IR spectrum of VAMO support also reveals this band. In the IR spectrum of PMA/VAMO, the absence of absorption band at 1020 cm^{-1} and a significant reduction in the absorption intensity of P–O stretching vibration band at 1063 cm^{-1} was observed. This indicates that there is no free V_2O_5 and probable interaction of Keggin anion with the surface bound VO species. Appearance of the absorption bands at lower frequencies in the IR spectrum of PMA/VAMO, which is characteristic of Keggin ion interactions with support is another sign of the VO–Keggin ion interaction. This VO–Keggin ion interaction is believed to stabilize the POMs on the VAMO surface. In the case of alumina it was shown that POMs were decomposed during the preparation, a process investigated by
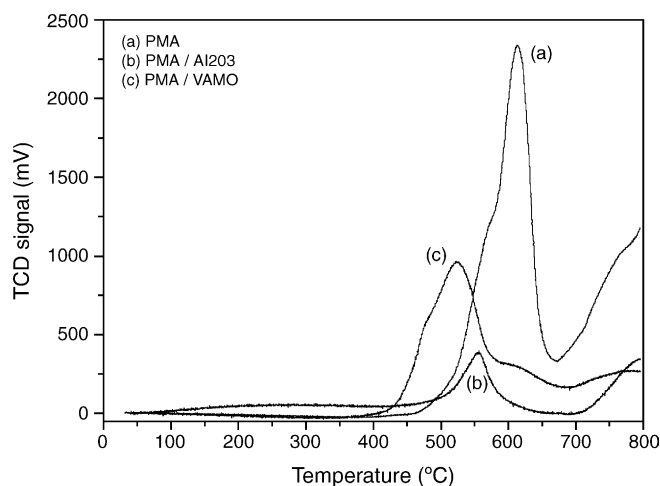
Fig. 3. H$_2$ TPR profiles of PMA, PMA/Al$_2$O$_3$, PMA/VAMO.

Fig. 4. Evaluation of PMA stability on VAMO.

liquid ^{95}Mo NMR studies [39–40]. This is also evident from the IR spectrum of PMA/Al$_2$O$_3$.

In order to assess the oxidative activity of PMA/VAMO catalyst, wherein supported Keggin anion is intact and found to be interacting with the surface bound V$_2$O$_5$ species, H$_2$ temperature-programmed reduction (TPR) studies were carried out. TPR profiles of the PMA in the pure form, PMA/VAMO and PMA/Al$_2$O$_3$ are shown in Fig. 3. H$_2$ TPR data of pure PMA showed a single peak at 614 °C with a distinctive shoulder at 582 °C associated with the release of oxygen upon the reaction with hydrogen under high temperature (curve a). H$_2$ TPR profile of PMA/VAMO revealed a peak with maxima at 525 °C associated with shoulder at 486 °C (curve c). This significant shift observed in the peak maxima, could be due to a better dispersion and thus accessibility of the POM species. The absence of small peaks usually associated with the reduction of the VO to V^{4+} and V^{3+} oxidation states [41] certainly confirms a significant interaction between Keggin anion and surface VO species, and the absence of dispersed V$_2$O$_5$ species.

3.2. Evaluation of the catalyst stability

The catalyst stability was assessed to establish the interaction between the POM anion and VAMO surface, mainly to ascertain whether the former is physically adsorbed or chemically bonded on the surface. The characteristic heteropoly blue colour test clearly indicated the Keggin anion to be chemically bonded to the surface [42]. However, oxidising benzyl alcohol in the presence of PMA/VAMO for 1 h generated the more convincing proof of non-leaching of Keggin anion. After 1 h the catalyst was removed by filtration. The reaction was continued further and it was observed that the reaction stopped in the absence of solid catalyst particles (Fig. 4). To reconfirm that POMs were not present in the aqueous phase in dissolved state, the PMA/VAMO catalyst was subjected to vigorous stripping in water for 1 h. The catalyst was filtered and the filtrate was used as the reaction medium. No noticeable transforma-
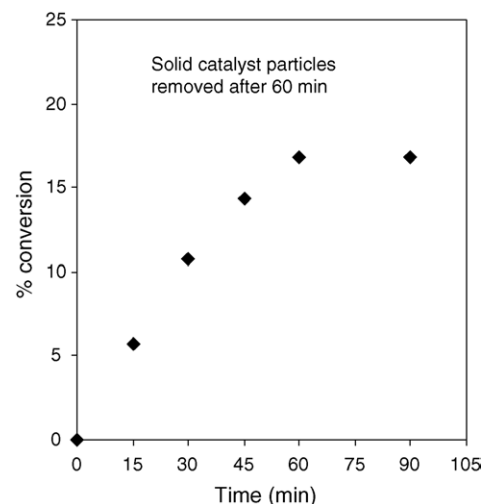
tion of alcohol confirmed the heterogeneous behaviour of the catalyst.

Authentic solution of PMA in methanol shows an absorption band with a maximum at 310 nm belonging to the oxygen–metal charge transfer. Likewise, the solutions obtained from PMA/VAMO and PMA/Al$_2$O$_3$ stripping experiments were monitored. Here also, no absorption bands were observed belonging to the oxygen–metal charge transfer (Fig. 5). The ^{31}P chemical shift (δ) in authentic PMA solution in
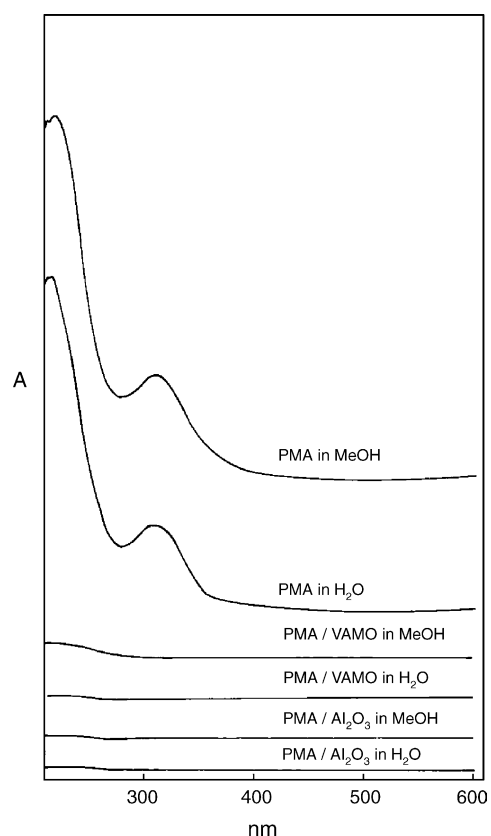

Fig. 5. UV spectra of PMA, PMA/VAMO and PMA/Al$_2$O$_3$.

methanol at -3.7 ppm for correlated with the P–O_a bond strength (Fig. 6). Absence of any chemical shift in the ^{31}P NMR spectra of solutions obtained from stripping experiments substantially confirms that the PMA/VAMO is a very stable catalyst and Keggin anion does not leach from the surface.

3.3. Oxidation of alcohols by PMA/VAMO

Preliminary experiments performed to investigate the influence of the VAMO support on the catalytic activity of PMA/VAMO and the role of V in VAMO. The oxidation of benzyl alcohol (model substrate) was tested in presence of the VAMO support, to give no oxidation of benzyl alcohol, thus clarifying that the support has no influence on the catalytic activity and concluding the use of PMA/VAMO as essential. Further, the oxidation of benzyl alcohol was also tested in the absence of CTABr and it was observed that the reaction did not proceed which implies the use of CTABr is necessary. However, the above mentioned evaluation tests rule out the possibility of any homogeneous catalysis as there were no dissolved polyoxomolybdate species detected either in organic or aqueous phase. The scope of PMA/VAMO to act as an oxidising catalyst was examined against a wide array of alcohols that include benzylic, heterocyclic, alicyclic and aliphatic alcohols. As depicted in Table 1, all the reactions exhibited almost 100% selectivity with no observable over oxidation to carboxylic acids. For verification of the reaction selectivity towards aldehyde and to check for any possible carboxylic acid adsorption on the catalyst surface, a control experiment of anisyl alcohol oxidation was performed under identical reaction conditions. The catalyst was recovered and stirred in methanol for 1 h. The mixture was found to contain anisaldehyde and no carboxylic acid. Oxidation of cinnamyl alcohol to cinnamaldehyde was used as the test reaction to judge the catalytic performance of PMA/VAMO and compare with the state-of the-art catalysts (Table 2). However the comparison was only semiquantitative, since in many cases the reaction conditions applied are far from optimum. In the oxidation of α,β-unsaturated alcohols, C=C double bond remained intact without any intramolecular hydrogen transfer (entry 2). The reactivity of *p*-nitro benzyl alcohol was comparatively higher than that of *o*-nitro benzyl alcohol, which can be attributed to the intramolecular hydrogen bonding in the latter. The reactivity of *p*-nitro benzyl alcohol oxidation was, however, observed to be slightly higher than that of benzyl alcohol under identical experimental conditions (entry 7,8). Similar reactivity patterns have been reported with other catalyst e.g. dinuclear manganese (IV) complexes [47]. Excellent conversion was seen in the case of alcohol having a heterocyclic unit, e.g. pyridine-3-methanol. However, due to its poor solubility in toluene, acetonitrile was used as a reaction solvent (entry 12). This result is indicative of the better efficacy of our catalyst to perform oxidation of heterocyclic alcohols in comparison with previously reported monomeric transition metal complex catalysts. The findings that this catalyst system also oxidised diphenylmethane to benzophenone (entry 5) further enhanced the scope of the heterogeneous PMA/VAMO.
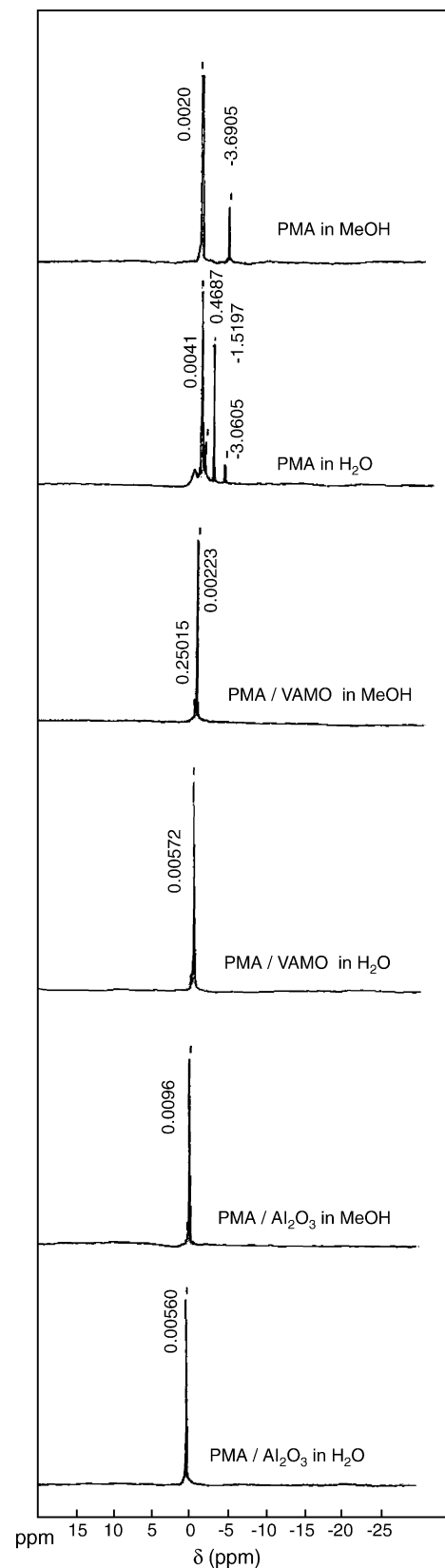

Fig. 6. ^{31}P NMR spectra of PMA, PMA/VAMO and PMA/Al$_2$O$_3$.

3.4. Mechanistic aspects

In the oxidation of substituted benzylic alcohols the use of PMA/VAMO, H_2O_2 and CTABr was found to be essential. The control experiments were performed to identify the function of CTABr. The possibility of free radical mechanism was investigated. The oxidation of anisyl alcohol using CTABr without PMA/VAMO was tested under identical conditions. However, the reaction did not take place, suggesting the role of CTAB as the phase transfer agent. In the other control experiments, TBAB and TBAHS were used as the phase transfer agents in oxidation of anisyl alcohol and 74% conversion of anisyl alcohol was obtained in 2 h. The substitution of Br^- with HSO_4^- did not affect the reaction rate. Both experiments ascertain the function of CTABr as phase transfer agent. The observation was analogous to the genesis of Ishii–Venturello chemistry that involves the use of HPA, H_2O_2 and CTABr and we believe that in our case also this mechanism is operative [48–50]. It involves var-

Table 1
Oxidation of alcohols using PMA/VAMO catalyst

No.	Substrate	Product	% Conversion of alcohol[a]	% Selectivity of aldehyde	TOF (h^{-1})
1	CH$_3$O—C$_6$H$_4$—CH$_2$OH	CH$_3$O—C$_6$H$_4$—CHO	98	100	88
2	C$_6$H$_5$—CH=CH—CH$_2$OH	C$_6$H$_5$—CH=CH—CHO	97	100	87
3	H$_3$C—C$_6$H$_4$—CH$_2$OH	H$_3$C—C$_6$H$_4$—CHO	96	100	86
4	Cl—C$_6$H$_4$—CH$_2$OH	Cl—C$_6$H$_4$—CHO	79	100	71
5	C$_6$H$_5$—CH$_2$—C$_6$H$_5$	C$_6$H$_5$—CO—C$_6$H$_5$	79	100	78
6	cyclohexanol OH	cyclohexanone O	70	100	63
7	O$_2$N—C$_6$H$_4$—CH$_2$OH	O$_2$N—C$_6$H$_4$—CHO	59	100	53
8	C$_6$H$_5$—CH$_2$OH	C$_6$H$_5$—CHO	32	100	29
9	o-NO$_2$-C$_6$H$_4$—CH$_2$OH	o-NO$_2$-C$_6$H$_4$—CHO	26	100	24
10	C$_6$H$_5$—CH$_2$OH[b] *	C$_6$H$_5$—CHO	54	100	49
11	C$_6$H$_5$—CH$_2$OH[c] **	C$_6$H$_5$—CHO	93	100	84
12	pyridine-3-CH$_2$OH[b] *	pyridine-3-CHO	94	100	84

Reaction conditions—alcohol: 0.02 mol; toluene: 40 cm^3; catalyst loading: 0.025 g/cm^3; CTABr: 1.4 mmol; H_2O_2: 0.5 mmol/min; temperature: 65 °C; time: 2 h.

[a] % Conversions based on GC analysis.
[b] Acetonitrile was used instead of toluene.
[c] Toluene at reflux temperature.

Table 2
A comparison of oxidation of cinnamyl alcohol to cinnamaldehyde

| Catalyst	T (K)	Solvent	Oxidizing agent	TOF (h^{-1})	Y (%)	S (%)	Ref.
$[N(C_6H_{13})_4]_3[PO_4\{WO(O_2)_2\}_4]$	Room temperature	Benzene	H_2O_2	373	38	–	[43]
5% Pt–0.8% Bi/Al$_2$O$_3$	313	H_2O + detergent	O_2	144	94	98	[16]
PMA/VAMO	333	PhCH$_3$	H_2O_2	87	97	100	–
0.3% Pd/hydroxyapatite	363	PhCF$_3$	O_2	72	87	–	[16]
RuCo$_{1.5}$O$_x$	383	PhCH$_3$	O_2	38	90	94	[16]
4-Benzoyloxy-TEMPO	300	PhCH$_3$	O_2	28	85	85	[16]
1.4% Ru/Al$_2$O$_3$	356	PhCF$_3$	O_2	27	98	98	[16]
Pd$_{2060}$(NO$_3$)$_{360}$(OAc)$_{360}$O$_{80}$/TiO$_2$	333	AcOH	O_2	19	91	98	[16]
RuO$_2$·xH$_2$O	383	PhCH$_3$	O_2	5	79	79	[16]
$[PPh_4]_2[MoO_3(O_2)_4]$	Room temperature	MDC	H_2O_2	–	45	–	[44]
Diphenyl selenide	Reflux	Benzene	t-BuOOH	–	87	–	[45]
RuCl$_2$(PPh$_3$)$_3$	298	MDC	Me$_3$SiOOSiMe$_3$	–	80	–	[46]
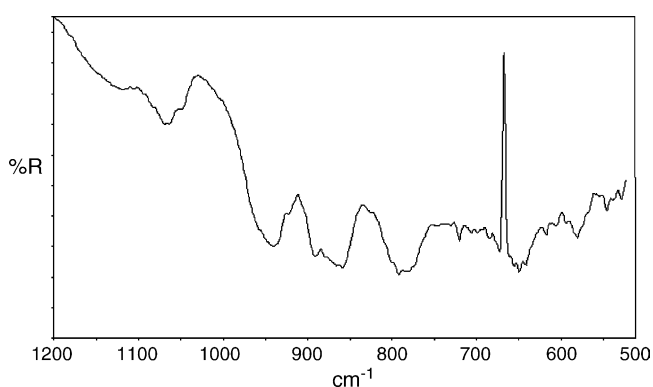
Fig. 7. IR spectra of recovered catalyst, PMA/VAMO.

ious dinuclear and tetranuclear metal peroxo species, of which the latter was found to play a key role. The experimental evidence of formation of Mo analogs of Venturello peroxo complexes was obtained by IR analysis. The control experiment was performed in the absence of alcoholic substrate and the IR spectrum of recovered PMA/VAMO catalyst in wet condition was obtained (Fig. 7). The characteristic bands obtained at 940, 890, 856, 791, 655–641, 580, 514 cm^{-1} are in agreement to the reported spectroscopic data for peroxo complexes isolated as salts [51–52]. Analogous to homogeneous Ishii–Venturello chemistry, it is pro-

posed that the supported POM Keggin anion $[PMo_{12}O_{40}]^{3-}$ forms the polyperoxometallate (PPOM) species (Fig. 8). As depicted in plausible Scheme 1, the sequence starts with the co-ordination of alcohol (by hydride abstraction) to the unsaturated (penta-coordinate) Mo(VI) species in tetranuclear PPOM anion to give an alcoholate intermediate. The latter on binding with another molecule of alcohol gives two molecules of aldehyde, water and the subsequent peroxo species $[P_qMo_rO=(O_2)_t]^{x-}$, which on interaction with H_2O_2 again regenerates the surface bound $[PO_4[MoO(O_2)_2]_4]^{3-}$. The formation of this tetranuclear metal peroxo species is in agreement with the observed catalyst recyclability.

3.5. Reusability of PMA/VAMO

The reusability of PMA/VAMO was established by carrying out repeated oxidation of p-methoxy benzyl alcohol with recovered catalyst (Fig. 9). After the first use the catalyst was filtered, washed with methanol and subsequently heated at 250 °C for 2 h, before reusing it in subsequent batches. With fresh catalyst, the conversion of p-methoxy benzyl alcohol was 87%, however it went down to 83% during the third run. The interesting part was the selectivity towards anisaldehyde that remained almost 100% during each run. The decrease in conversion could be attributed to the observed losses due to attrition, during filtration of the
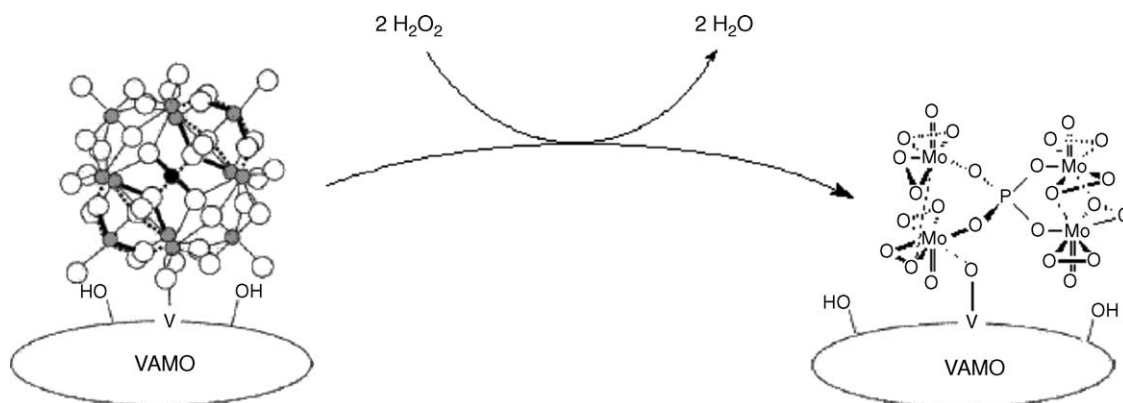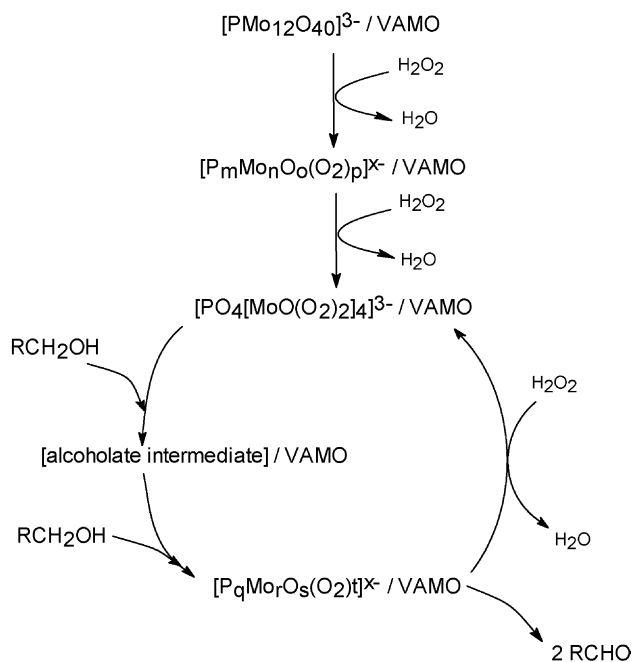

Fig. 8. Schematic representation of PPOM/VAMO.

$[PMo_{12}O_{40}]^{3-}$ / VAMO

H_2O_2 → H_2O

$[P_mMo_nO_o(O_2)_p]^{x-}$ / VAMO

H_2O_2 → H_2O

$[PO_4[MoO(O_2)_2]_4]^{3-}$ / VAMO

RCH_2OH

[alcoholate intermediate] / VAMO

RCH_2OH

$[P_qMo_rO_s(O_2)_t]^{x-}$ / VAMO

H_2O_2 → H_2O

2 RCHO

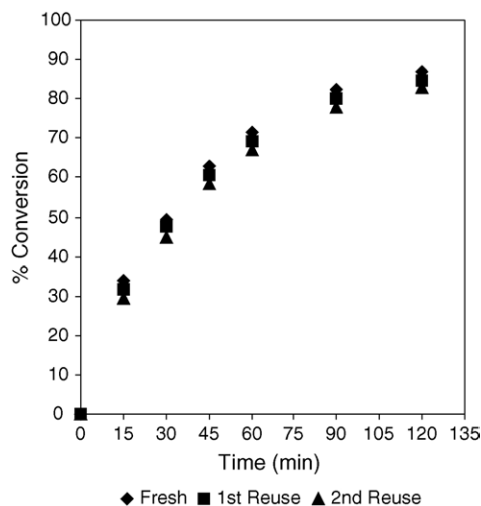Scheme 1. Possible reaction mechanism for the oxidation of alcohols.

Fig. 9. Reusability of PMA/VAMO.

catalyst particles. No make up quantity of catalyst was added during subsequent experiments.

4. Conclusions

Structural characterisations of the newly synthesised catalyst displayed that VO monolayer can stabilize the Keggin anion on the surface of alumina by inhibition of the Al–P interaction. Its application in oxidation of various alcohols to the corresponding aldehydes with high selectivity and yields, further confirm that the immobilisation of PPOM species on VAMO provides a stable and efficient heterogeneous catalyst. Apart from being highly versatile in oxidising wide array of primary and secondary alcohols of benzylic, alicyclic, and aliphatic nature, PMA/VAMO also showed capability of oxidising reactive methylene group,

which is otherwise difficult to achieve. Furthermore, high yields obtained in the oxidation of heterocyclic alcohols make this new catalyst an outstanding example of the heterogeneous catalysis. An extension of this protocol for other oxidations is being actively pursued.

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