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ARTICLE TYPE

Lanthano-phosphotungstates: A water soluble and reusable catalyst for oxidation of alcohols using H₂O₂ as an oxidantMukesh Kumar Saini,^a Rakesh Gupta,^a Swati Parbhakar,^a Surendra Singh^{*a} and Firasat Hussain^{*a}

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A series of water soluble lanthano-phosphotungstate K₁₁[Ln(PW₁₁O₃₉)₂]·xH₂O [Ln = Pr(III), Nd(III), Eu(III), Gd(III), Tb(III), Dy(III), Ho(III), Er(III), Tm(III) and Yb(III)] catalysts were synthesized. These catalysts (0.24 mol %)

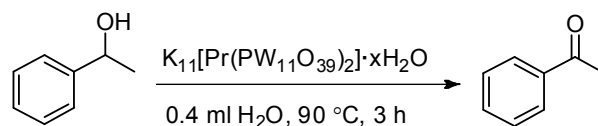
Polyoxyometalates (POMs) inorganic metal-oxo nanocluster has gained much importance in research due to their versatile properties. These are basically formed by transition metal oxides in their high oxidation states (mainly Mo, W, V, Nb and Ta). The growing interest in POMs undoubtedly reflects their discrete, molecular nature isolated from a solution-based approach, either from aqueous or non-aqueous media combined with highly flexible and tunable molecular composition, size, shape, charge density, redox potentials, acidity, solubility characteristics and high thermal stability. As a result, these nanoclusters can be used over a wide range of applications including homogeneous and heterogeneous oxidation catalysis, photocatalysis, biomedicine, materials science, data storage, sensors, and nano-biotechnology.¹

Alcohol oxidation to carbonyl compounds is one of the most important transformations in organic chemistry. Hydrogen peroxide and molecular oxygen as most preferable eco-friendly oxidants used in these oxidation processes. For the last three decades, varieties of POMs were used as effective catalysts for the oxidation of various alcohols. Most of the reports till date on alcohol oxidation with POM catalysts have used non-ecofriendly organic solvents² while some have utilized under solvent free conditions.³ To overcome the use of organic solvents and catalyst recovery problems, many researchers explored the use of green synthetic oxidation processes using water as a solvent. In addition water soluble POM catalysts were also explored by many researchers for the effective oxidation of various alcohol compounds e.g. monolacunary K₈[β-SiW₁₁O₃₉]·14H₂O, K₈[BW₁₁O₃₉H]·13H₂O dilacunary K₈[γ-SiW₁₀O₃₆]·13H₂O and trilacunary [SiW₉O₃₄]¹⁰⁻ in conjugation with dioctadecyl dimethyl ammonium anion, Zinc and vanadium substituted POMs.⁴

Lanthanoid containing POM catalysts have been less explored for the oxidation processes. Kera and co-workers studied the oxidation of cyclohexanol in homogeneous medium using [Ce^{IV}W₁₀O₃₆]⁸⁻, [Nd^{III}W₁₀O₃₆]⁹⁻ and [Sm^{III}W₁₀O₃₆]⁹⁻ heteropolytungsto-lanthanate⁵ anions as a catalyst, in the presence

of H₂O₂ oxidant. Later, they also reported the catalytic behaviour of a series of lanthanide decatungstates (Ln^{III}W₁₀O₃₆)⁹⁻ (Ln = La – Yb)⁶ and {C₅H₅N(CH₂)₁₅CH₃}₇H₂Ho^{III}W₁₀O₃₆ POM catalyst for the oxidation of alcohols and olefins, using a biphasic (CHCl₃ – aqueous H₂O₂) solvent system.⁷ Griffith et al. also studied the use of lanthano-polyoxotungstates [Ln{PW₁₁O₃₉}₂]¹¹⁻ (Ln = Y, La, Ce, Pr, Sm, Tb, Yb)⁸ and [M^{IV}{PW₁₁O₃₉}₂]¹⁰⁻ POM catalysts for oxidation of benzyl alcohol and 2-octanol using biphasic systems (*t*-butanol/aqueous and benzene/aqueous) with [N(C₆H₁₃)₄]Cl as a phase transfer agent.⁹ They concluded that lanthano-polyoxotungstates did not retain their identity after the catalysis, and transformed to the [(PO₄){WO(O₂)₂}₄]³⁻, [(PO₄){WO(O₂)₂{WO(O₂)₂(H₂O)}]³⁻ and [(PO₃(OH)){WO(O₂)₂}₂]²⁻ type active species. These active species were previously reported as catalyst for the alcohol oxidation processes.¹¹ Recently, Zhao et al. studied the selective oxidation of various substrates (alkenes, alkenols, sulphides, silane and alcohols) using DA₁₁[La(PW₁₁O₃₉)₂] (DA = Decyltrimethylammonium cation) POM catalyst, and H₂O₂ oxidant in acetonitrile.¹²

Herein, we report the synthesis of a series of water-soluble lanthano-phosphotungstates (POMs) as an oxidation catalyst for various alcohols in the presence of H₂O₂ oxidant. All the POMs K₁₁[Ln(PW₁₁O₃₉)₂]·xH₂O [Ln = Pr(III), Nd(III), Eu(III), Gd(III), Tb(III), Dy(III), Ho(III), Er(III), Tm(III) and Yb(III)] were synthesized by a single step reaction of lanthanoid cations with [PW₁₁O₃₉]¹¹⁻ anion in KOAc buffer at pH 4.8 (see SI for detailed experimental section). All isolated compounds were structurally characterized by ³¹P-NMR, TGA analysis and FT-IR spectroscopy.¹³

Table 1 oxidation of 1-phenylethanol in presence of Pr^{III} - POMs

| Entry | Reaction Temperature (°C) | Catalysts loading (mol %) | Conversion (%) ^b | Reaction time (h) |
|-------|---------------------------|---------------------------|-----------------------------|-------------------|
| 1 | 60 | 0.24 | 42 | 3 |
| 2 | 70 | 0.24 | 68 | 3 |
| 3 | 80 | 0.24 | 80 | 3 |
| 4 | 90 | 0.24 | >99 | 3 |

| | | | | |
|---|----|------|------------------|---|
| 5 | 90 | 0.12 | >99 | 6 |
| 6 | 90 | 0.24 | 100 ^c | 2 |
| 7 | 90 | 5.0 | 38 ^d | 6 |
| 8 | 90 | 0.24 | 78 ^e | 3 |
| 9 | 90 | 0.12 | 90 ^f | 3 |

^a Reaction condition: Catalyst (0.12 – 0.24 mol %), 1-phenylethanol (2 mmol), H₂O₂ (4 mmol) were taken in water (0.4 mL) and heated at specified temperature and time

^b Conversion was determined by Gas Chromatography

^c H₂O₂ was used as 5 equivalent

^d Pr(NO₃)₃·6H₂O used as a catalyst

^e K₇[PW₁₁O₃₉]·14H₂O used as a catalyst

^f Reaction carried out for 3h

The oxidation of 1-phenylethanol (2 mmol) was carried out using Pr-POM catalysts (0.24 mol%), in the presence of water (0.4 mL) and 30% aq. H₂O₂ (4.0 mmol) at different temperature 60, 70, 80 and 90 °C. We observed that increase in temperature from 60 - 90 °C, the conversion of 1-phenylethanol to acetophenone was increased from 40 to >99 % (see Table 1). In addition we have also increased the amount of H₂O₂ (5.0 eq) which resulted in excellent conversion >99% of the reactant to the product after 2 h. We have also decreased the loading of the catalysts upto 0.12 mol%, which was sufficient to convert >99% of 1-phenylethanol to acetophenone after 6 h. We also envisaged the praseodymium salt and monolacunary ligand (PW₁₁O₃₉) independently as a catalyst for the oxidation of 1-phenyl ethanol and found to be less active than their complex (Pr-POM) (See Table 1 entries 7 and 8). We have screened different catalysts Pr - Yb POMs (0.24 mol%) for the oxidation of 1-phenylethanol to acetophenone (see Table S1). The conversions of product vs different catalysts are shown in Fig.1.

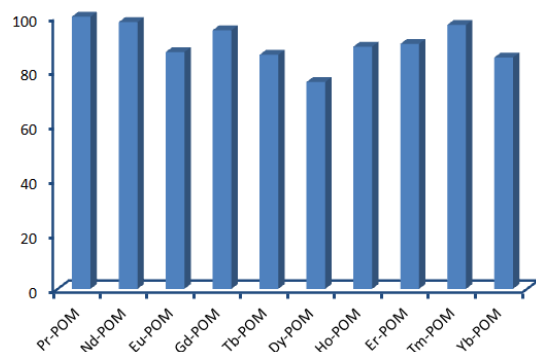


Fig. 1 Plot of product (acetophenone) conversion vs. different catalysts, K₁₁[Ln(PW₁₁O₃₉)₂]_xH₂O [Ln = Pr(III), Nd(III), Eu(III), Gd(III), Tb(III), Dy(III), Ho(III), Er(III), Tm(III) and Yb(III)] for 1-phenylethanol oxidation reaction with H₂O₂ as an oxidant at 90 °C for 3 h.

The conversion of 1-phenylethanol to acetophenone was observed for all the catalysts from 76 to >99 % in 3 h (See SI – Table 1). The Pr-POM catalyst was more active as compared to the other lanthanoid containing POM catalysts.

The turn over frequency (TOF) of the catalyst K₁₁[Pr(PW₁₁O₃₉)₂]₂₂H₂O (0.24 mol%) for the oxidation of 1-phenyl ethanol, was found to be 137.5 h⁻¹. We have also compared the TOF of the reported catalysts in the literature and the catalysts found to be more active than other catalysts and comparable to the zinc substituted POMs (TOF 138.3 – 156.7 h⁻¹) (See SI – Table 2).

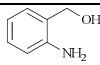


The chemical kinetics for the 1-phenylethanol oxidation reaction has been demonstrated as a function of time for the Pr-POM. The data plotted showed that the oxidation reaction is of first order (R² = 0.99574) with respect to 1-phenylethanol (See SI- Figure 1).

To establish the versatility of our POMs catalyst, we also studied oxidation of various alcohols namely 1-(4-bromophenyl)ethanol, 1-(3-bromophenyl)ethanol, 1-(3-nitrophenyl)ethanol, benzyl alcohol, benzhydrol, cyclopentanol, cyclohexanol and n-butanol at 90 °C using 0.24 - 0.6 mol% catalysts, and 2 - 5 equivalent of H₂O₂ (Table 2).

The oxidation of 1-(4-bromophenyl) ethanol gave 38% conversion of 1-(4-bromophenyl) ethanone (Table 2, entry 1). By increasing the amount of oxidant to 5 equiv. the conversion was

Table 2 Oxidation of various alcohols corresponding to carbonyl compounds catalysed by Pr(III)-POM in water^a

| Entry | Substrate | Product | Conversion (%) | Time (h) |
|-------|-----------|--------------|-----------------|----------|
| 1 | | | 38 | 14 |
| 2 | | | 66 ^b | 14 |
| 3 | | | 95 ^c | 24 |
| 4 | | | 89 ^c | 24 |
| 5 | | | 51 | 14 |
| 6 | | | 93 ^c | 8 |
| 7 | | | 70 | 3 |
| | | | 12 | |
| 8 | | | 42 | 8 |
| 9 | | | 90 ^c | 14 |
| 10 | | | >99 | 3 |
| 11 | | | >99 | 3 |
| 12 | n-Butanol | Butyric acid | >99 | 8 |

| | | | | |
|----|---|--|---|---|
| 13 | n-Butanol | Butyraldehyde | 83 ^d | 3 |
| 14 | n-Butanol | Butyraldehyde Butyric acid | 37 48 | 3 |
| 15 |  |   Impurity | 21 ^b 23 ^b 45 ^b | 6 |

^a Reaction condition: Catalyst (0.24 mol %), alcohols (2 mmol), H₂O₂ (4 mmol) were taken in water (0.4 mL) and heated at 90 °C

^b H₂O₂ was used as (10 mmol),

^c Catalyst (0.6 mol %), and H₂O₂ (10 mmol) was used.

^d Reaction was carried out under inert (N₂) atmosphere.

improved (Table 2, entry 2). Furthermore, on increasing the catalysts loading from 0.24 to 0.6 mol% the conversion increased to 95% after 24 h, whereas 1-(3-bromophenyl) ethanol shows 89% conversion (Table 2, entries 3-4). On oxidation of 1-(3-nitrophenyl) ethanol, 51% conversion was observed after 14 h, which was improved upto 93% by increasing the catalysts loading (0.6 mol%) and H₂O₂ (5 equiv.) (Table 2, entries 5 and 6). The oxidation of benzyl alcohol gave benzaldehyde (70%) and benzoic acid (12%) after 3 h (Table 2, entry 7). The oxidation of benzhydrol converted to benzophenone 42% after 8 h and 90% after 14 h by increasing catalyst loading from 0.24 to 0.6 mol% (Table 2, entry 8-9). The cyclic alcohols cyclohexanol and cyclopentanol show excellent conversion (>99%) to the corresponding ketones after 3 h (Table 2, entries 10 and 11). We have also conducted the oxidation of n-butanol which gave butyric acid >99% after 8 h (Table 2, entry 12). As butyraldehyde is easily oxidized in air, therefore we performed the oxidation of n-butanol under N₂-atmosphere, gave exclusively butyraldehyde as a product in 83% conversion after 3 h (Table 2, entries 13). The identical reaction in absence of N₂-atmosphere gave butyraldehyde (48%) and butyric acid (37%) (Table 2, entry 14). The oxidation of 2-amino-benzylalcohol was carried out to know the chemo-selectivity of catalytic process. We found the process not to be chemo-selective, and gave 2-nitro-benzylalcohol, 2-nitrobenzoic acid, and other impurities as products, which indicates that the amino group is oxidized quickly, and then to the corresponding primary alcohol (Table 2, entry 15).

The product was extracted with diethyl ether and the catalysts present in the aqueous medium were used for next catalytic cycle.⁴¹ The Pr-POM shows consistent activity for oxidation of 1-phenylethanol to acetophenone (see Table 3). After five catalytic cycles, Pr-POM was recovered on addition of ethanol to the aqueous medium and FTIR spectra was recorded on KBr pellets, which shows no change in the POM structure (see SI for detailed procedure of catalyst recovery, figure S3).

Table 3 Recyclability of Pr-POM catalyst for oxidation of 1-phenylethanol^a

| Entry | Catalyst Cycle | Conversion (%) |
|-------|----------------|----------------|
| 1 | 1 | >99 |
| 2 | 2 | >99 |
| 3 | 3 | 95 |
| 4 | 4 | 98 |
| 5 | 5 | 90 |

^a Reaction conditions: Pr-POM (0.24 mol %), 1-phenylethanol (2 mmol), H₂O₂ (4 mmol) were taken in water (0.4 mL) and heated at 90 °C for 3h.

In conclusion, we have reported the synthesis of a series of water-soluble lanthano-phosphotungstates in a single step reaction and also investigated the catalysis for the oxidation of alcohols using environmental friendly oxidant (H₂O₂). 1-Phenylethanol was oxidized to acetophenone with >99% conversion and the non-aromatic cyclic alcohols shows excellent conversion to corresponding ketones for Pr(III)-POM. The Pr(III)-POM catalyst was also envisaged for the oxidation of substituted 1-phenyl ethanol. The primary alcohols were also oxidized to corresponding aldehydes in good yields in presence of inert atmosphere. The catalysts could be recovered and reused up to five catalytic cycles without the loss of its activity.

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Notes and references

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† Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/b000000x/

‡ Footnotes should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

- (a) M. T. Pope, *Heteropoly and Isopoly Oxometalates*, Springer-Verlag, Berlin, 1983; (b) C. L. Hill, and C. M. Prosser-McCartha, *Coord. Chem. Rev.*, 1995, **143**, 407; (c) M. T. Pope, and A. Müller, *Angew. Chem. Int. Ed. Engl.*, 1991, **30**, 34; (d) *Chem. Rev.*, 1998, **98**, (Special Issue on Polyoxometalates; Ed.: C. L. Hill); (e) A. Müller, and S. Roy, *Coord. Chem. Rev.*, 2003, **245**, 153; (f) E. Coronado, and P. Day, *Chem. Rev.*, 2004, **104**, 5419; (g) L. Cronin, in *Compr. Coord. Chem. II*, vol. 7 (Eds.: J. A. McCleverty, and T. J. Meyer), Elsevier, Amsterdam, 2004, p. 1-57; (h) C. L. Hill, *J. Mol. Catal. A*, 2007, **262**, 2-6; (i) U. Kortz, A. Müller, J. van Slageren, J. Schnack, N. S. Dalal, and M. Dressel, *Coord. Chem. Rev.*, 2009, **253**, 2315; (j) B. Hasenknopf, in *Front. Biosci.*, 2005, **10**, 275; (k) L. Zhongfeng, L. Weisheng, L. Xiaojing, P. Fengkui, L. Yingxia, and L. Hao, *Magn. Reson. Imaging.*, 2007, **25**, 412; (l) *Eur. J. Inorg. Chem.*, 2009, **34** (Issue dedicated to Polyoxometalates; Guest Ed.: U. Kortz)

- 2 (a) M. V. Vasylyev and R. Neumann, *J. Am. Chem. Soc.*, 2004, **126**, 884; (b) M. Carraro, L. Sandei, A. Sartorel, G. Scorrano and M. Bonchio, *Org. Lett.*, 2006, **8**, 3671; (c) F. F. Bamoharram, M. Roshani, M. M. Heravi and S. Safaie, *Phosphorus, Sulfur Silicon Relat. Elem.*, 2006, **181**, 2833; (d) Z. H. Weng, J. Y. Wang and X. G. Jian, *Catal. Commun.*, 2008, **9**, 1688; (e) X. Lang, Z. Li and C. Xia, *Synth. Commun.*, 2008, **38**, 1610; (f) B. G. Donoeva, T. A. Trubitsina, G. M. Maksimov, R. I. Maksimovskaya and O. A. Kholdeeva, *Eur. J. Inorg. Chem.*, 2009, 5142; (g) O. A. Kholdeeva, B. G. Donoeva, T. A. Trubitsina, G. Al-Kadamany and U. Kortz, *Eur. J. Inorg. Chem.*, 2009, 5134; (h) B. G. Donoeva, T. A. Trubitsyna, G. Al-Kadamany, U. Kortz and O. A. Kholdeeva, *Kinet. Catal.*, 2010, **51**, 816; (i) Y. Kikukawa, K. Yamaguchi and N. Mizuno, *Inorg. Chem.*, 2010, **49**, 8194; *Angew. Chem. Int. Ed.*, 2010, **49**, 6096 (j) P. Tundo, G. P. Romanelli, P. G. Vazquez and F. Arico, *Catal. Commun.*, 2010, **11**, 1181; (k) Y. Ding, W. Zhao, *J. Mol. Catal. A: Chem.*, 2011, **337**, 45; (l) Z. Nadealian, V. Mirkhani, B. Yadollahi, M. Moghadam, S. Tangestaninejad and I. Mohammadpoor-Baltork, *J. Coord. Chem.*, 2012, **65**, 1071.
- 3 (a) R. H. Ingle, N. K. K. Raj and P. Manikandan, *J. Mol. Catal. A: Chem.*, 2007, **262**, 52; (b) S. J. Zhang, G. D. Zhao, S. Gao, Z. W. Xi and J. Xu, *J. Mol. Catal. A: Chem.*, 2008, **289**, 22; (d) W. Tian, Y. Hou, X. G. Wang, B. Lu, J. X. Zhao and Q. H. Cai, *Chin. J. Chem.*, 2012, **30**, 433.
- 4 (a) D. Sloboda-Rozner, P. L. Alsters and R. Neumann, *J. Am. Chem. Soc.*, 2003, **125**, 5280; (b) D. Sloboda-Rozner, P. Witte, P. L. Alsters and R. Neumann, *Adv. Synth. Catal.*, 2004, **346**, 339; (c) J. Wang, L. Yan, G. Li, X. Wang, Y. Ding and J. Suo, *Tetrahedron Lett.*, 2005, **46**, 7023; (d) P. Maity, D. Mukesh, S. Bhaduri and G. K. Lahiri, *J. Chem. Sci.*, 2009, **121**, 377; (e) B. Ma, Y. Zhang, Y. Ding and W. Zhao, *Catal. Commun.*, 2010, **11**, 853; (f) W. Zhao, Y. Zhang, B. Ma, Y. Ding and W. Y. Qiu, *Catal. Commun.*, 2010, **11**, 527; (g) Y. Ding, W. Zhao, B. Ma and W. Y. Qiu, *Can. J. Chem.*, 2011, **89**, 13; (h) Y. Ding, W. Zhao, Y. S. A. Zhang, B. Ma and W. Y. Qiu, *React. Kinet. Mech. Catal.*, 2011, **102**, 85; (i) W. Zhao, Y. Ding, B. Ma and W. Y. Qiu, *Synth. Commun.*, 2012, **42**, 554; (j) Z. Zhang, Q. Zhu and Y. Ding, *Synth. Commun.*, 2013, **43**, 1211.
- 5 R. Shiozaki, H. Goto and Y. Kera, *Bull. Chem. Soc. Jpn.*, 1993, **66**, 2790.
- 6 R. Shiozaki, A. Inagaki, A. Ozaki, H. Kominami, S. Yamaguchi, J. Ichihara and Y. Kera, *J. Alloys Comp.*, 1997, **261**, 132.
- 7 R. Shiozaki, A. Inagaki, H. Kominami, S. Yamaguchi, J. Ichihara and Y. Kera, *J. Mol. Catal. A: Chem.*, 1997, **124**, 29.
- 8 W. P. Griffith, R. G. H. Moreea and H. I. S. Nogueira, *Polyhedron*, 1996, **15**, 3493.
- 9 N. M. Gresley, W. P. Griffith, A. C. Laemmel, H. I. S. Nogueira and B. C. Parkin, *J. Mol. Catal. A: Chem.*, 1997, **117**, 185.
- 10 W. P. Griffith, N. Morley-Smith, H. I. S. Nogueira, A. G. F. Shoair, M. Suriaatmaja, A. J. P. White and D. J. Williams, *J. Organomet. Chem.*, 2000, **607**, 146.
- 11 C. Venturello and M. Gambaro, *J. Org. Chem.*, 1991, **56**, 5924.
- 12 S. Zhao, Y. Q. Jia and Y. F. Song, *Appl. Catal., A*, 2013, **453**, 188.
- 60 13 R. Gupta, M. K. Saini, F. Doungmene, P. de Oliveira, F. Hussain, *Dalton Trans.*, 2014, **43**, 8290.