

the cell in the absence of a sensitizer. It seems to be charge injection of the cell mainly via excited dye molecules attached to TiO₂ film. The IPCE spectrum of TiO₂|N3|MEH-PPV|I₂|graphite cell is shown in Figure 2. Maximum IPCE of 33% was observed at 550 nm for the cell. The TiO₂|N3|MEH-PPV|I₂|graphite cell gives a moderate performance compared to other dye-sensitized systems under illumination^{9,16}. It has been pointed out that atmospheric oxygen and moisture traps are major concerns in the use of MEH-PPV in similar devices due to fast degradation of the polymer¹⁷. The TiO₂|N3|MEH-PPV|I₂|graphite cell exhibited poor stability under illumination at atmospheric conditions. Performance of the cell could be further improved by increasing the conductivity of the polymer and finding a proper sealant that prevents the entry of moisture and oxygen into the cell.

MEH-PPV has been used as an electron donor for regeneration of dye molecules in titania-based, dye-sensitized solar cells. Maximum short-circuit photocurrent of 2.4 mA cm⁻² and open circuit voltage of 475 mV were observed for the TiO₂|N3|MEH-PPV|I₂|graphite cell under illumination with the light intensity of 100 mW cm⁻² AM at the electrode.

1. Marletta, A., Goncalves, V. C. and Balogh, D. T., *J. Lumin.*, 2006, **116**, 87–93.
2. Burroughes, J. H. *et al.*, *Nature*, 1990, **347**, 539–541.
3. Braun, D. and Heeger, A. J., *Appl. Phys. Lett.*, 1991, **58**, 1982–1984.
4. Qiao, Q., Beck, J. and Mc Leskey, J. T., Proc. 2005 SPIE 5938 59380E.
5. Dittmer, J. J. *et al.*, *Sol. Energy Mater. Sol. Cells*, 2000, **61**, 53–61.
6. Sirimanne, P. M., Senevirathna, M. K. I., Premalal, E. V. A., Pitigala, P. K. D. D. P., Sivakumar, V. and Tennakone, K., *J. Photochem. Photobiol. A: Chem.*, 2006, **2–3**, 324–327.
7. Sirimanne, P. M., Senevirathna, I. and Tennakone, K., *Chem. Lett.*, 2005, **34–11**, 1568–1569.
8. Sirimanne, P. M., Shirata, T., Soga, T. and Jimbo, T., *J. Solid State Chem.*, 2002, **166**, 142–147.
9. Bach, U. *et al.*, *Nature*, 1998, **395**, 583–585.
10. Gebeyehu, D. *et al.*, *Synth. Mater.*, 2001, **125**, 279–287.
11. Miller, E. K., Brabec, C. J., Neugebauer, H., Heeger, A. J. and Sariciftci, N. S., *Chem. Phys. Lett.*, 2001, **335**, 23–26.
12. Macdiarmid, A. G., Huang, F., Hsieh, B. R., Kippelen, B. and Donald, D. C. B., Proceedings of the Polymer Photonic Devices Conference, San Jose, CA, SPIE Proc. Ser., 1998, vol. 3281, pp. 156–163.
13. Kitamura, T., Maitani, M., Matsuda, M., Wada, Y. and Yanagida, S., *Chem. Lett.*, 2001, **30**, 1054.
14. Savenije, T. J., Warman, J. M. and Goossens, A., *Chem. Phys. Lett.*, 1998, **287**, 148–153.
15. Daoud, W. A. and Turner, M. L., *React. Funct. Polym.*, 2006, **66**, 13–20.
16. O'Regan, B. and Gratzel, M., *Nature*, 1991, **353**, 737–739.
17. Killian, R. K., Su, Y. and Varahramyan, K., *Thin Solid Films*, 2005, **483**, 416–419.

Received 21 February 2007; revised accepted 26 June 2007

P. M. SIRIMANNE^{1,*}
E. V. A. PREMALAR¹
T. SOGA²

¹*Institute of Fundamental Studies,
Hantana Road, Kandy,
Sri Lanka*

²*Department of Environmental and
Urban Planning,
Nagoya Institute of Technology,
Gokiso, Showa ku,
Nagoya 466-8555, Japan*

*For correspondence.
e-mail: psirimane@hotmail.com

Environmentally benign oxidation of some alcohols with 34% hydrogen peroxide catalysed by H₃PW₁₂O₄₀

Selective oxidation of alcohols to the corresponding oxygenated products is of significance to the synthetic organic community and has been a challenge for many years^{1–3}. The known chemical protocols for oxidation of hydroxyl groups use either conventional mineral oxidants in stoichiometric amounts⁴ or environmentally benign oxidizing agents such as molecular oxygen and hydrogen peroxide in the presence of several transition metal complexes as catalysts^{5–12}. The former method generates considerable amount of inorganic waste, and is therefore environmentally not attractive.

Over the last few years, several smart catalytic oxidation methodologies using complexes of noble metals like Pt, Pd and Ru have proved to be promising, as exemplified by numerous examples^{13–16}. However, most of the catalytic systems

are expensive and difficult to make. In this context, the polyoxometallates are definitely attractive and challenging while looking for economically viable and easy to manufacture alternatives. These compounds include early transition metal ions with *d*⁰ configuration, e.g. Mo(VI) and W(VI) and have been recognized as potential redox catalysts in many organic transformations^{17–20}.



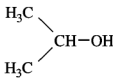
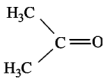
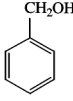
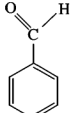
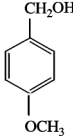
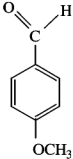
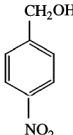
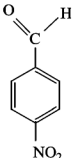
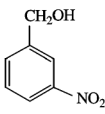
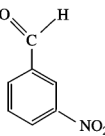
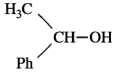
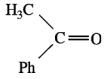
An eco-friendly, simple and efficient method is described here for the oxidation of some alcohols with 34% hydrogen peroxide, catalysed by H₃PW₁₂O₄₀ as the simplest class of heteropolyoxometallates.

Solvents, reagents and other chemicals used in this study were of the highest grade available and were purchased from SD Fine Chemicals (India). The reagents were stored at 5°C and purified just before use. Silica gel 60 (70–230 mesh,

purchased from E-Merck A.G., Germany) was used for column chromatography. Purity of the substances and progress of the reactions were monitored using gas chromatography (GC). GLC analyses were performed on a Shimadzu GC-17A instrument equipped with a flame ionization detector using 25 m × 0.25 mm CPB 5-20 and fused silica WCOT 25 m × 0.23 mm capillary columns. Na₃PW₁₂O₄₀·7H₂O was prepared according to the literature^{21,22}.

Na₂WO₄·2H₂O (30 mmol, 10 g) was slowly added to 20 ml of distilled water and the mixture was warmed to 60°C with complete stirring. Then 85% H₃PO₄ (15 mmol, 1 ml) and HCl (100 mmol, 8 ml) were added and the resulting mixture was stirred for 1 h. The white afforded precipitate was washed with water and was recrystallized twice from hot water.

Table 1. Oxidation of some alcohols with 34% H₂O₂ in normal drinking water catalysed by H₃PW₁₂O₄₀.^a

Substrate	Product	Conversion (%)	Selection (%)	Time (min)	Turnover frequency (h ⁻¹) ^b
		100	100	150	130.5
		67	100	180	105
		78	100	150	101.7
		73	100	120	76.2
		52	100	120	54.3
		69	100	150	90
		85	100	150	110.9
H ₃ C-(CH ₂) ₂ -CH ₂ OH	H ₃ C-(CH ₂) ₂ -COH	30	75	150	39.1
H ₃ C-(CH ₂) ₅ -CH ₂ OH	H ₃ C-(CH ₂) ₅ -COH	9	60	270	21.1

^aTo a solution of catalyst (0.018 mmol) and 34% H₂O₂ (5 mmol) in 5 ml of water: ¹butanol (3 : 1) as solvent, substrate was added (0.94 mmol). The reaction mixture was refluxed and stirred at 65–70°C for the required time. Progress of the reactions was followed by the aliquots withdrawn directly and periodically from the reaction mixture, and analysed by gas chromatography. Products were isolated as described in the text.

^bTurnover frequency was calculated²⁷ by the expression [Product]/[catalyst] × time (h⁻¹).

To a solution of catalyst (0.018 mmol) and 34% H₂O₂ (5 mmol) in 5 ml of water: ¹butanol (3 : 1) as solvent, alcohol was added (0.94 mmol) and the reaction mixture was stirred at 65–70°C for the required time. Progress of the reaction was followed by the aliquots withdrawn directly from the reaction mixture, analysed by GC using internal standard. After completion of the reaction, products were extracted with 20 ml CHCl₃. The extract was dried over anhydrous sodium sulphate, filtered and concentrated under reduced pressure. Finally, the concentrated filtrate was treated with 2,4-dinitrophenylhydrazine in 6% HCl to give 2,4-dinitrophenylhydrazone of the corresponding carbonyl compound.

At the end of the reaction, to regenerate the catalyst the aqueous phase (~7 ml) of the reaction mixture was dried slowly at 50°C under intense light for 2 h and then at 130°C for 3 h. The regenerated solid acid catalyst was washed with dichloromethane, dried at 130°C for 1 h and reused in another reaction. The recycled catalyst could be reused several times without considerable loss of activity. After five runs using the recycled catalyst, efficiency of the oxygenation system decreased by ~10%. Noteworthy, after oxidation of one alcohol, the catalyst could be reused for oxidation of another alcohol. For example, the recovered catalyst from the oxidation of benzyl alcohol, was used for the oxidation of cyclohexanol and no dif-

ference was found regarding the yield and time of the reaction.

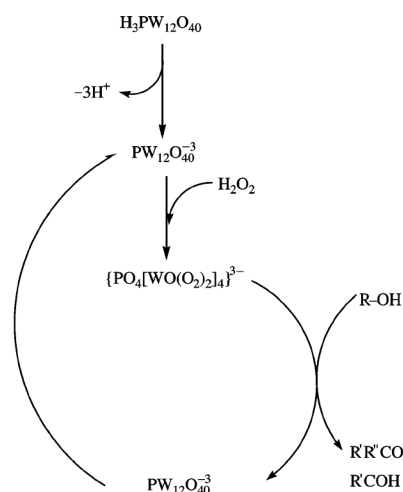
The oxidation of alcohols to carbonyl compounds is an important transformation and several methods have been explored to accomplish such a conversion.

Instead of conventional waste-producing oxidation procedures using stoichiometric reagents, application of environmentally benign protocols has gained preference in the last decade^{23–25}. The present methodology provides an environment-friendly route to the conversion of alcoholic functions to carbonyl groups with good to excellent yields and selectivities.

Table 1 describes the results of an efficient methodology for catalytic oxidation of different alcohols with 34% H₂O₂ in

the presence of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ in a mixture of ¹butanol–normal drinking water (electrical conductivity 550 s, total dissolved solids 350 mg l^{-1} , and pH 8.3) at 65–70°C. Aromatic alcohols were effectively oxidized with this oxygenation system. Benzyl alcohol provided 78% of conversion after 150 min. To test the role of electronic influences of phenyl substituents on the efficiency of oxygenation, 4-OMe-benzyl alcohol and 4-NO₂-benzyl alcohol were exposed to the oxidation system. These two substrates obtained 73 and 52% of conversions respectively, after 120 min. The electron-withdrawing nitro-group reduced the reactivity of benzyl alcohol toward oxidation, whereas the methoxy-group on the para-position of the phenyl ring increased the tendency of benzyl alcohol oxidation. Meanwhile, 3-NO₂-benzyl alcohol was almost less reactive than benzyl alcohol, leading to 69% of 3-NO₂-benzaldehyde after 150 min.

Secondary alcohols were also converted to the corresponding ketones with good to excellent yields and with complete selectivity. Cyclohexanol, 1-phenyl ethanol and isopropanol resulted in 67–100% of conversions during 120–180 min. Linear aliphatic alcohols clearly showed lower reactivity and selectivity than secondary alcohols in the oxygenation system. *n*-Butanol and *n*-heptanol led to 30 and 9% of the corresponding aldehydes with 75 and 60% selectivity after 2.5 and 4.5 h respectively.



Scheme 1. General formulation of catalytic oxidation of alcohols with $\text{H}_3\text{PW}_{12}\text{O}_{40}$.

Reusability of the catalyst was established by carrying out repeated oxidation of cyclohexanol with the recovered catalyst. Cyclohexanol led to complete conversion with fresh catalyst, whereas conversion decreased to 90% during the fifth run. Selectivity towards cyclohexanone remained almost 100% during each run. The decrease in conversion could be attributed to the observed losses due to attrition during filtration of the catalyst, which is otherwise difficult to achieve. An extension of this protocol for other oxidations is being actively pursued.

Venturello *et al.*²⁶, using crystallography techniques characterized polyperoxometallate $\{\text{PO}_4[\text{WO}(\text{O}_2)_2]_4\}^{3-}$ as the active oxygen transfer agent in the oxygenation of organic compounds by hydrogen peroxide catalysed by $\text{H}_3\text{PW}_{12}\text{O}_{40}$. Accordingly, Scheme 1 represents the general formulation of the catalytic system in the oxygenation of alcohols.

In conclusion, the oxidation of a variety of alcohols was studied in the presence of an inexpensive, reusable, non-corrosive and environmentally benign solid acid catalyst. This recyclable catalyst offers several advantages, including simplicity of operation, easy work-up, high yield and high selectivity. The catalyst could be recovered and subjected to another reaction without considerable loss of activity.

1. Dirk, S. M., Mickelson, E. T., Henderson, J. C. and Tour, J. M., *Org. Lett.*, 2000, **2**, 3405.
2. Firouzabadi, H. and Jafari, A. A., *J. Iran Chem. Soc.*, 2005, **2**, 85.
3. Hill, C. L. and Prosser-McCartha, G. M., *Coord. Chem. Rev.*, 1995, **143**, 407.
4. Hudlucky, M., *Oxidations in Organic Chemistry*, ACS Monograph no. 186, ACS, Washington, DC, 1990, p. 127.
5. Mori, K., Hara, T., Mizugaki, T., Ebitani, K. and Kaneda, K., *J. Am. Chem. Soc.*, 2004, **126**, 10657.
6. Venturello, C. and Gambaro, M., *J. Org. Chem.*, 1991, **56**, 5924.
7. Abramovici, S., Neumann, R. and Sasson, Y., *J. Mol. Catal. A: Chem.*, 1985, **29**, 299.
8. Mallat, T. and Baiker, A., *Chem. Rev.*, 2004, **104**, 3037.
9. Rafelt, J. S. and Clark, J. H., *Catal. Today*, 2000, **57**, 33.
10. Munakata, M., Nishibayashi, S. and Sakamoto, H., *J. Chem. Soc., Chem. Commun.*, 1980, 219.

11. Marko, I. E., Giles, P. R., Tsukazaki, M., Brown, S. M. and Urch, C. J., *Science*, 1996, **274**, 2044.
12. Mallat, T. and Baiker, A., *Catal. Today*, 1994, **19**, 247.
13. Brink, G., Arends, I. W. C. E. and Sheldon, R. A., *Science*, 2000, **287**, 1636.
14. Jensen, D. R., Pugsley, J. S. and Signam, M. S., *J. Am. Chem. Soc.*, 2001, **123**, 7475.
15. Makwana, V. D., Son, Y.-C., Howell, A. R. and Suib, S. L., *J. Catal.*, 2002, **210**, 46.
16. Takezawa, E., Sakaguchi, S. and Ishii, Y., *Org. Lett.*, 1999, **1**, 713.
17. Zhao, Z. H., *J. Mol. Catal. A: Chem.*, 2001, **168**, 147.
18. Nishimura, T., Okuhara, T. and Misono, M., *Appl. Catal.*, 1991, **73**, L7–L11.
19. Alizadeh, M. H. and Tayebbe, R., *J. Braz. Chem. Soc.*, 2005, **16**, 108.
20. Alizadeh, M. H., Razavi, H., Bamoharram, F. F., Hassanzadeh, M. K., Khoshnavazi, R. and Zonoz, F. M., *Kinet. Catal. (Engl. Transl.)*, 2003, **44**, 524.
21. Wu, H., *J. Biol. Chem.*, 1920, **43**, 189.
22. Brevard, C., Schimpf, R., Tourne, G. and Tourne, C. M., *J. Am. Chem. Soc.*, 1983, **105**, 7059.
23. Backvall, J. E., *Modern Oxidation Methods*, Wiley-VCH, 2004.
24. Mallat, T. and Baiker, A., *Chem. Rev.*, 2004, **104**, 3037.
25. Zhan, B.-Z. and Thompson, A., *Tetrahedron*, 2004, **60**, 2917.
26. Venturello, C., D'Aloiso, R., Bart, J. C. and Ricci, M., *J. Mol. Catal.*, 1985, **32**, 107.
27. In more chemical fields turnover number (abbreviated TON) is used as the number of moles of substrate that a mole of catalyst can convert before becoming inactivated. An ideal catalyst would have an infinite TON in this sense, because it would not ever be consumed. However, in actual practice, one often sees TON which go from 100 to a million or more. The term turnover frequency (abbreviated TOF) is used to refer to the turnover per unit time.

Received 18 November 2006; revised accepted 11 June 2007

REZA TAYEBEE^{1,*}
MOHAMMAD H. ALIZADEH²

¹Department of Chemistry,
Sabzevar University,
Sabzevar 397, Iran

²Department of Chemistry,
Ferdowsi University,
Mashhad, Iran

*For correspondence.
e-mail: rtayebbe@yahoo.com