

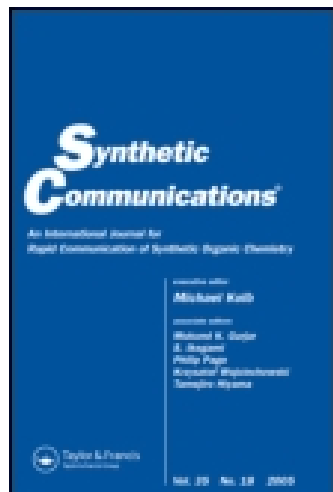
This article was downloaded by: [University of Calgary]

On: 22 October 2014, At: 02:36

Publisher: Taylor & Francis

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office:

Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry

Publication details, including instructions for authors and subscription information:

<http://www.tandfonline.com/loi/lcyc20>

$[\alpha\text{-PW}_{12}\text{O}_{40}]^{3-}$ Immobilized on Ionic Liquid-Modified Polymer as a Heterogeneous Catalyst for Alcohol Oxidation with Hydrogen Peroxide

Xianjun Lang^{a,b}, Zhen Li^a & Chungu Xia^a

^a State Key Laboratory for Oxo Synthesis and Selective Oxidation, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou, China

^b Graduate University of Chinese Academy of Sciences, Beijing, China

Published online: 24 Apr 2008.

To cite this article: Xianjun Lang, Zhen Li & Chungu Xia (2008) $[\alpha\text{-PW}_{12}\text{O}_{40}]^{3-}$ Immobilized on Ionic Liquid-Modified Polymer as a Heterogeneous Catalyst for Alcohol Oxidation with Hydrogen Peroxide, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 38:10, 1610-1616, DOI: [10.1080/00397910801929564](https://doi.org/10.1080/00397910801929564)

To link to this article: <http://dx.doi.org/10.1080/00397910801929564>

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the "Content") contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden. Terms & Conditions of access and use can be found at <http://www.tandfonline.com/page/terms-and-conditions>

[α -PW₁₂O₄₀]³⁻ Immobilized on Ionic Liquid-Modified Polymer as a Heterogeneous Catalyst for Alcohol Oxidation with Hydrogen Peroxide

Xianjun Lang,^{1,2} Zhen Li,¹ and Chungu Xia¹

¹State Key Laboratory for Oxo Synthesis and Selective Oxidation,
Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences,
Lanzhou, China

²Graduate University of Chinese Academy of Sciences, Beijing, China

Abstract: Ionic liquid-modified polystyrene resin beads were demonstrated to be an appropriate support for polyoxometalate. In this heterogeneous catalytic system, alcohols can be efficiently oxidized to corresponding carbonyl groups with H₂O₂ in CH₃CN. The catalyst can be easily recovered by filtration and recycled without apparent loss of catalytic performance.

Keywords: Alcohol oxidation, heterogeneous catalysis, hydrogen peroxide, polyoxometalate

INTRODUCTION

Polyoxometalates (POMs) constitute a versatile class of inorganic, anionic clusters that have applications involving medicine, catalysis, materials science, geochemistry, nuclear waste processing, and photochemical or electrochemical response.^[1] However, the majority of the applications of POMs is in the area of catalysis; about 80–85% of patent and applied literature claims or investigates POMs for their catalytic activity.^[2] POMs have received much

Received in Japan November 5, 2007

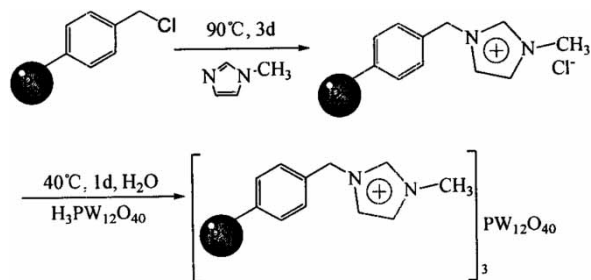
Address correspondence to Chungu Xia, State Key Laboratory for Oxo Synthesis and Selective Oxidation, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou, China. E-mail: cgxia@lzb.ac.cn

attention in catalysis because of their hydrolytic and thermal stability, solubility in various media, tunable acid and redox properties at the molecular or atomic level, and so on.^[3] Molybdenum- and tungsten containing-POMs have been well established as efficient catalysts for oxidation of various organic substrates with aqueous H_2O_2 , such as epoxidation of olefins^[4,5] and allylic alcohols,^[6] oxidation of alcohols,^[7,8] and so on in homogeneous or two-phase systems. Although the efficiency of these systems is rather high, they share common drawbacks such as difficult catalyst/product separation and poor catalyst reusability. To avoid this problem, one of the best choices is to immobilize POMs on an appropriate support without loss of the intrinsic activity and selectivity.^[9]

The unique properties of ionic liquids, including high thermal stability, tunability of their acidities, and excellent retention of polar or charged catalysts, make them appealing media for a broad range of catalytic applications.^[10] Supported ionic liquid catalysis is a concept that combines the advantages of ionic liquids with those of heterogeneous support materials.^[11] Tungsten-containing POMs $[\text{W}_2\text{O}_3(\text{O}_2)_4(\text{H}_2\text{O})]^{2-}$ ^[12] and $[\gamma\text{-}1,2\text{-H}_2\text{SiV}_2\text{W}_{10}\text{O}_{40}]^{4-}$ ^[13] have been successfully immobilized on ionic liquid-modified SiO_2 as efficient heterogeneous oxidation catalysts with H_2O_2 . However, to our knowledge, polymeric materials-based support for polyoxometalate modified by ionic liquid has never been reported before. Herein we present a heterogeneous catalytic system for a range of alcohol oxidations with 30% aqueous H_2O_2 catalyzed by $[\alpha\text{-PW}_{12}\text{O}_{40}]^{3-}$ immobilized on ionic liquid-modified polystyrene resin beads (PS-IL-PW). The catalytically active polyoxometalate anion $[\alpha\text{-PW}_{12}\text{O}_{40}]^{3-}$ was immobilized onto the support by stoichiometric anion exchange via a very simple preparation procedure under relatively benign and easy-to-handle conditions. The activity of the recovered catalyst is almost intact upon recycling by a simple filtration step.

RESULTS AND DISCUSSION

Catalyst preparation process is shown in Scheme 1. In the first step, chlorinated polystyrene resin beads were vigorously stirred in *N*-methylimidazole at 90 °C to anchor a covalently ionic liquid fragment to the beads' surface (PS-IL). IR spectrum shows the characteristic bands of the parent imidazole salt, for example, $\nu(\text{C-H})$ 3150, $\nu(-\text{CH}_3, -\text{CH}_2-)$ 2950, 2850, and $\nu(\text{C}=\text{N})$ 1570, 1460 cm^{-1} . After anion exchange with polyoxometalate anion, the support catalyst was characterized with IR. Apart from the bands assigned for ionic liquid skeleton, the IR spectrum shows $\nu(\text{P-O}_a)$ 1080, $\nu(\text{W-O}_d)$ 982, $\nu(\text{W-O}_b\text{-W})$ 891, and $\nu(\text{W-O}_c\text{-W})$ 801 cm^{-1} , which are the characteristic bands of Keggin-type polyoxometalate, indicating that $[\alpha\text{-PW}_{12}\text{O}_{40}]^{3-}$ had been successfully immobilized on ionic liquid-modified polymer (PS-IL). The potential of this supported catalyst for oxidation of alcohols to



























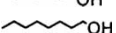
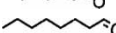
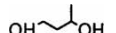
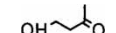




Scheme 1. Catalyst preparation process; PS = polymer support.

corresponding carbonyl compounds with H_2O_2 was examined with cyclohexanol as the probe substrate. The catalytic activity of the *N*-methylimidazole salt of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ ($[\text{Hmim}]_3\text{PW}_{12}\text{O}_{40}$) was also investigated for a comparison between homogeneous and heterogeneous catalysis systems. The results are presented in Table 1 (entries 1–5). At first, we examined the catalytic activity of PS-IL-PW in water (entry 3). The conversion of cyclohexanol was rather low. That may be attributed to the low surface area of polystyrene resin beads, and cyclohexanol is insoluble in water. It is reasonable for low conversion as a result of low contact area between substrate and catalyst. However, when $[\text{Hmim}]_3\text{PW}_{12}\text{O}_{40}$ was used as the catalyst (entry 5), the reaction proceeded by the substrate/water biphasic manner, and the conversion of cyclohexanol was satisfied. To improve the reaction efficiency of the current heterogeneous catalytic system, we used CH_3CN instead of water as the reaction medium, and the yield of cyclohexanone apparently increased (entry 1) to reach 83.75%. Nevertheless, when the catalyst of $[\text{Hmim}]_3\text{PW}_{12}\text{O}_{40}$ was used in this manner (entry 4), the yield of cyclohexanone was much lower than the biphasic system (entry 5), even lower than the heterogeneous catalysis system (entry 1). That may be because CH_3CN was not a suitable solvent for alcohol oxidation when $[\text{Hmim}]_3\text{PW}_{12}\text{O}_{40}$ was used as the catalyst. However, PS-IL-PW catalyzed the reaction through the solid/liquid interface, which can surpass this limitation. The catalyst can be easily recovered and recycled for five rounds without apparent loss of its catalytic activity (entry 2). The IR spectrum of the recovered catalyst showed the absorption in the region 1050 cm^{-1} (peaks at 1111, 1078, and 1018 cm^{-1}), which were assigned to P-O stretching vibrations. A strong peak at 978 cm^{-1} indicated the presence of $\text{W}=\text{O}$, and peaks at 896, 817 (O-O), and 620 cm^{-1} (W-O-O asym), which were the characteristic bands of $[\text{PO}_4\{\text{W}_2\text{O}_2(\mu\text{-O}_2)_2(\text{O}_2)_2\}_2]^{3-}$, indicating the $\text{PW}_{12}\text{O}_{40}^{3-}$ was decomposed to this active intermediate in the presence of H_2O_2 .

The present system could be applied to oxidation various kinds of alcohols. Representative results are summarized in Table 1 (entries 6–16). Several trends should be noted. First, liquid secondary alcohols were all selectively oxidized to the corresponding ketones in high yields (entries 7–12).

Table 1. Oxidation of alcohols with H₂O₂ catalyzed by PS-IL-PW

Entry	Substrate	Substrate/ H ₂ O ₂ ^a	Product	Yield ^b (%)
1		2/3		83.75
2 ^c		2/3		82.96
3 ^d		2/3		31.68
4 ^e		2/3		44.95
5 ^f		2/3		89.30
6		2/3		33.36
7		1/3		81.28
8		1/3		73.16
9		1/3		100
10		1/3		99
11		1/3		99
12		1/3		100 (91.61 ^g)
13		2/3		99
14		1/3		12.30
15		1/3		3.00
16		2/3		99

Note: Reaction conditions: substrate 20 mmol, PW-IL-PS 0.3 g, CH₃CN 10 mL, 80 °C, 12 h.

^aMolar ratio.

^bBased on GC.

^cAfter 5 catalytic recycles.

^dSolvent, 10 mL H₂O.

^eCatalyst, 0.15 g [Hmim]₃PW₁₂O₄₀.

^fCatalyst, 0.15 g [Hmim]₃PW₁₂O₄₀, solvent, 10 mL H₂O.

^gIsolated yield.

Oxidation of 2-pentanol with 1.5 equivalents of H₂O₂ was not so good (entry 6), giving 33.7% of yield of 2-pentanone. However, when the amounts of H₂O₂ increased to 3.0 equivalents, the yield of 2-pentanone could increase to 82.1%. For other short-chain secondary alcohol oxidation, 2-propanol (entry 9) and 2-butanol (entry 10) achieved excellent yields of 100%. 3-Pentanol gave a good yield of 73.9% when 3.0 equivalents of H₂O₂ were used as the oxidant. The benzylic substrates were more reactive (entries 11 and 12). The yields of benzophenone (entry 11) and acetophenone (entry 12) were 99% and 100%, respectively. Primarily alcohol oxidation afforded corresponding aldehydes (entries 13–15). Those results were different from those experiments carried out in substrate/water biphasic manner, which

usually afforded the corresponding carboxylic acids (7). That may be caused by the support effect, which might partially modify the reaction behavior. The oxidation of the benzyl alcohol (entry 13) with 1.5 equivalents of H_2O_2 afforded benzaldehyde with an excellent yield of 99%. For the primary aliphatic alcohol oxidation, 1-hexanol can be oxidized to hexanal with a yield of 12.3%. For 1-octanol oxidation, the efficiency was much lower: only 3.0% of yield was achieved. Note that 1,3-butanediol (entry 16) was oxidized almost exclusively at the secondary position to produce 4-hydroxy-2-butanone with excellent yield of 99%.

In summary, we have designed an alcohol oxidation system with 30% H_2O_2 catalyzed by $[\alpha\text{-PW}_{12}\text{O}_{40}]^{3-}$ immobilized on ionic liquid-modified polystyrene resin beads. The catalytic system was capable of heterogeneously oxidizing a broad range of alcohols with high selectivity to the desired products. In addition, the catalyst can be easily recycled with retention of the catalytic activity. Further investigation into the influence of the imidazole side chain and the anions of the ionic liquid on catalytic activity are currently in progress.

EXPERIMENTAL

Preparation for the Catalyst

Preparation for the Support Ionic Liquid (PS-IL)^[14]

Chlorinated polystyrene resin beads, (0 g) 4.0 mL of *N*-methylimidazole, and 50 mL of toluene were charged in a 100-mL round-bottom flask and refluxed at 90 °C for 3 d. The solid was then filtered off and washed with toluene, 0.1 M HCl, water, and methanol for several times to achieve polymer-supported ionic liquid (PS-IL). The elemental analysis of PS-IL revealed the amount of support ionic liquid was $3.6 \text{ mmol} \cdot \text{g}^{-1}$.

Preparation of $[\alpha\text{-PW}_{12}\text{O}_{40}]^{3-}$ Supported on PS-IL

$\text{H}_3\text{PW}_{12}\text{O}_{40}$ (5 g) was dissolved in distilled water and heated to 40 °C. Then 2 g of PS-IL was added to this solution, and the resulting mixture was vigorously stirred at this temperature for 1 d. The resulting product was washed with a large amount of water and dried in vacuo to afford 5.7 g final product (PS-IL-PW). The loading amount of $[\alpha\text{-PW}_{12}\text{O}_{40}]^{3-}$ was found to be $224 \text{ } \mu\text{mol} \cdot \text{g}^{-1}$.

Preparation of $[\text{Hmim}]_3\text{PW}_{12}\text{O}_{40}$

$[\text{Hmim}]\text{H}_2\text{PO}_4$ (4.8 mmol) was dissolved in 15 mL of distilled water under magnetic stirring. Then a solution containing 1.6 mmol of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ was

added dropwise to this solution, and white precipitation appeared. The resulting solid was then filtered off, washed with water, and dried in vacuo to afford $[\text{Hmim}]_3\text{PW}_{12}\text{O}_{40}$.

General Procedure for Alcohol Oxidation

A 100-mL round-bottom flask equipped with a condenser was charged with 0.3 g of PW-1L-PS, 20 mmol of substrate, and 10 mL of CH_3CN . After vigorous stirring (1000 rpm) for 10 min at 80 °C, the reaction was initiated by adding 30 mmol of H_2O_2 (3.4 mL of 30% aqueous H_2O_2). The mixture was kept at this temperature for 12 h and then cooled to room temperature. After decomposition of the excess amount of H_2O_2 , the products were dried over Na_2SO_4 . The oxidation products were determined by GC/MS (HP 6890/5973), and quantitative analyses were performed on GC (Agilent 6820) with a flame ionization detector, SE-54 capillary column, and N_2 carrier gas, and decane was used as the internal reference.

ACKNOWLEDGMENT

This work is financially supported by the National Natural Science Foundation of China (No. 20373082) and National Science Fund for Distinguished Young Scholars (No. 20625308).

REFERENCES

1. Pope, M. T.; Müller, A. Polyoxometalate chemistry: An old field with new dimensions in several disciplines. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 34–48.
2. Katsoulis, D. E. A survey of applications of polyoxometalates. *Chem. Rev.* **1998**, *98*, 359–388.
3. Kozhevnikov, I. V. Catalysis by heteropoly acids and multicomponent polyoxometalates in liquid-phase reactions. *Chem. Rev.* **1998**, *98*, 171–198.
4. Venturello, C.; D'Aloisio, R.; Bart, J. C. J.; Ricci, M. A new peroxotungsten heteropoly anion with special oxidizing properties: Synthesis and structure of tetrahexylammonium tetra(diperoxotungsto)phosphate(3-). *J. Mol. Catal.* **1985**, *32*, 107–110.
5. Ishii, Y.; Yamawaki, K.; Ura, T.; Yamada, H.; Yoshida, T.; Ogawa, M. Hydrogen peroxide oxidation catalyzed by heteropoly acids combined with cetylpyridinium chloride. *J. Org. Chem.* **1988**, *53*, 3587–3593.
6. Matoba, Y.; Inoue, H.; Akagi, J.-I.; Okabayashi, T.; Ishii, Y.; Ogawa, M. Epoxidation of allylic alcohols with hydrogen peroxide catalyzed by $[\text{PMo}_{12}\text{O}_{40}]^{3-}[\text{C}_5\text{H}_5\text{N}^+(\text{CH}_2)_{15}\text{CH}_3]_3$. *Synth. Commun.* **1984**, 865–873.
7. Venturello, C.; Gambaro, M. Selective oxidation of alcohols and aldehydes with hydrogen peroxide catalyzed by methyltrioctylammonium tetrakis(oxodiperoxotungsto)phosphate(3-) under two-phase conditions. *J. Org. Chem.* **1991**, *56*, 5924–5931.

8. Shiozaki, R.; Kominami, H.; Kera, Y. H₂O₂ oxidation by Ce(IV) contained Weakley-type heteropolyoxometalate for various alcohols. *Synth. Commun.* **1996**, 1663–1688.
9. Mizuno, N.; Yamaguchi, K.; Kamata, K. Epoxidation of olefins with hydrogen peroxide catalyzed by polyoxometalates. *Coordin. Chem. Rev.* **2005**, 249, 1944–1956.
10. Zhang, Z. C. Catalysis in ionic liquids. *Adv. Catal.* **2006**, 49, 153–237.
11. Mehnert, C. P. Supported ionic liquid catalysis. *Chem. Eur. J.* **2005**, 11, 50–56.
12. Yamaguchi, K.; Yoshida, C.; Uchida, S.; Mizuno, N. Peroxotungstate immobilized on ionic liquid–modified silica as a heterogeneous epoxidation catalyst with hydrogen peroxide. *J. Am. Chem. Soc.* **2005**, 127, 530–531.
13. Kasai, J.; Nakagawa, Y.; Uchida, S.; Yamaguchi, K.; Mizuno, N. [γ -1,2-H₂SiV₂W₁₀O₄₀] immobilized on surface modified SiO₂ as a heterogeneous catalyst for liquid-phase oxidation with H₂O₂. *Chem. Eur. J.* **2006**, 12, 4176–4184.
14. Byun, J. W.; Lee, Y. S. Preparation of polymer-supported palladium/N-heterocyclic carbene complex for Suzuki cross-coupling reactions. *Tetrahedron Lett.* **2004**, 45, 1837–1840.