Tetrahedron Letters 49 (2008) 4339–4341

Contents lists available at ScienceDirect

Tetrahedron Letters

journal homepage: www.elsevier.com/locate/tetlet

Oxidation of alcohols with molecular oxygen promoted by Nafion ionomer anchored pyrochlore composite at room temperature

S. Venkatesan [a], A. Senthil Kumar [b], J.-M. Zen [a,*]

[a] Department of Chemistry, National Chung Hsing University, Taichung 402, Taiwan
[b] Department of Chemistry, Vellore Institute of Technology University, Vellore 632 014, India

ARTICLE INFO

Article history:
Received 28 February 2008
Revised 2 May 2008
Accepted 9 May 2008
Available online 13 May 2008

Keywords:
Nafion
Catalyst
Lead ruthenate pyrochlore
Alcohols
Oxidation

ABSTRACT

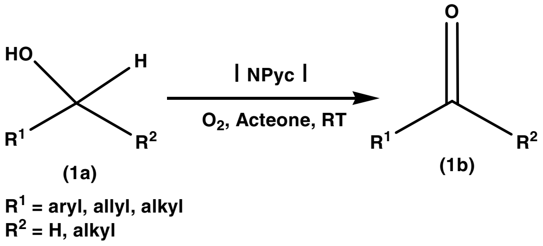
Nafion ionomer anchored ruthenium oxide pyrochlore composite has been demonstrated for selective oxidation of alcohols to aldehydes and ketones in good yields. In the absence of any additives, the reaction was achieved by atmospheric air or molecular oxygen at room temperature.

Selective oxidation of alcohols to aldehydes and ketones is a key reaction in organic synthesis. These transformations are of significant importance, both for fundamental research and industrial manufacturing.[1] The development of new procedures that can use air or molecular oxygen as oxidant is certainly more attractive than other traditional methods which are environmentally undesirable.[2] In this point of view, much of research recently described the use of solid supported heterogeneous catalyst notably ruthenium-based catalysts for the aerobic oxidation of alcohols.[3] Among these, tetra-*n*-propyl ammonium perruthenate (TPAP)–O_2 catalyzed systems were highly active for the preparation of wide range of carbonyl compounds under mild conditions.[4] However, it requires high temperature to regenerate the active site (i.e., RuO_2 to TPAP) and suffers from catalytic deactivation as well as oxidative degradation of polymers. Meanwhile, slow addition of H_2O_2 on organically modified silica gels doped TPAP has been successfully worked out for the selective oxidation reactions at room temperature with good yields.[5] Herein, first time we report ruthenium oxide pyrochlore (Pyc) modified Nafion membrane catalytic system (|NPyc|), which has chemically generated perruthenate/ruthenate active site similar to the TPAP active site for aerobic alcohol oxidation at room temperature (rt).

Nafion, a perfluorinated sulfonate ionomeric membrane has many practical applications in catalysis. For instance, it is used as a solid-acid catalyst for alkylation, esterification, acylation, olefin oligomerization, and isomerization,[6] whereas catalytic active site modified membrane is rarely developed for synthetic applications.

Recently, we developed the Pyc active site-modified Nafion membrane, |NPyc| catalyst for some organic oxidations at elevated temperature with conventional co-oxidants.[7] For instance, the membrane catalyst was effective for selective benzyl alcohol oxidation to benzaldehyde with H_2O_2 or NaOCl co-oxidant at ~80 °C in a biphasic medium (CH_2Cl_2//pH 11).[7b,c] In this Letter, we successfully demonstrate the |NPyc| catalyst for selective aerobic alcohol oxidations at rt using CH_3COCH_3 as a solvent system.

Initially, oxidation of benzyl alcohol was monitored (Scheme 1) by using an in situ attenuated total reflection infrared (ATR-IR) spectroscopy as described elsewhere.[8] The reaction was checked at rt during contact of the benzyl alcohol adsorbed Nafion composite membrane on ZnSe crystal under oxygen atmosphere.[9] The time dependence of the intensity of the C=O signal at 1747 cm^{-1}



Scheme 1.

---

* Corresponding author. Tel.: +886 4 22850864; fax: +886 4 22854007.
E-mail address: jmzen@dragon.nchu.edu.tw (J.-M. Zen).

0040-4039/$ - see front matter © 2008 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tetlet.2008.05.046

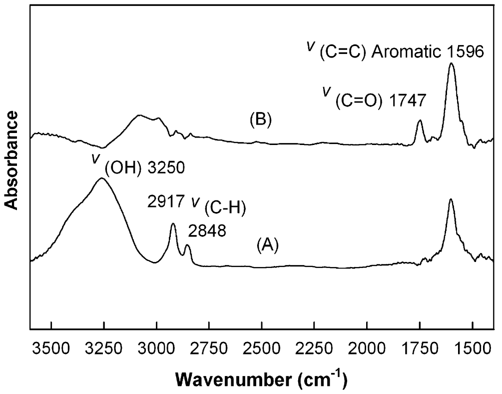


Figure 1. ATR-IR spectra of benzyl alcohol oxidation at two different intervals of (A) 1 h and (B) 9 h.

observed (Fig. 1) together with those signals at 3250 cm^{-1} (OH) and 2917–2848 cm^{-1} (C–H), was all measured to ensure |NPyc| reactive template/air interphase assisted alcohol oxidation reaction. In addition, the reaction mixture was isolated from catalyst and analyzed by GC and GC–MS to confirm its selectivity. The system showed only two-peak responses in GC with retention timings of 5 and 10 min, respectively, corresponding to **1a** and **1b** (Scheme 1), where **1a** $\ll$ **1b** due to the |NPyc|/air interphase assisted catalytic conversion. These results indicate that ionic cluster network of Nafion is a convenient template for both stable pyrochlore formation and oxygen adsorption. Nafion pyrochlore composite catalyst can incorporate higher concentration of alcohols in the active hydrophilic site followed by oxidation of alcohols in the presence of air at room temperature. Figure 2 shows variation in run time, reactant and catalyst amount against yield for alcohol **1a**-adsorbed oxidation reaction at room temperature. As can be seen, the increase of run time and catalyst amount leads to the increase of the reaction up to 99% yield of **1b** (Fig. 2A and B). On the other hand, the increase of the concentration (**1a**) on a fixed surface leads to a decrease in reaction yield (Fig. 2C). This may reflect that some kinetic restriction for the alcohol adsorption on the composite surface and hence less catalyst/air interface area available for the alcohol oxidation. Accordingly, batch reactions were carried out in acetone in the presence of molecular oxygen or argon. It was found that molecular oxygen-assisted reaction was more efficient than air oxidation reaction (50% conversion), and no marked yield was observed in an argon atmosphere which clearly indicates the specific role of oxygen in catalytic reaction. Recycled catalyst is stable and can be reused for a series of alcohols oxidation regardless of the substrate.[10] The results are summarized in Table 1. Alcohols studied in this work were all selectively oxidized to aldehydes (i.e., primary alcohols) or ketones (i.e., secondary alcohols) in good yields. Aromatic alcohols were converted into corresponding aldehydes or ketones in high yields since they have electron-donating groups (entries 2–7, 17, 18 and 21).

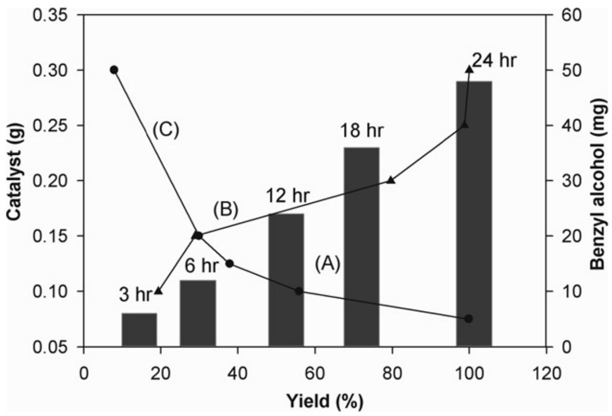


Figure 2. The influence of various parameters: (A) reaction time, (B) catalyst amount, (C) alcohol concentration versus yield on the membrane catalyzed alcohol oxidation reaction at rt.

Similarly, allylic alcohols were oxidized to their respective aldehydes without any cleavage of carbon–carbon double bond (entries 8 and 9). This system was also applicable to heterocyclic alcohols having sulfur and nitrogen atom (entries 10 and 11). Aliphatic and cyclic alcohols (cyclohexanol and menthol) were oxidized in moderate yields without any over-oxidation to carboxylic acids (entries 12–15). The |NPyc| catalyst also shows appreciable chemioselectivity. For example, catalysis of equimolar concentration of benzyl alcohol and 1-phenyl ethanol mixture resulted corresponding benzaldehyde and acetophenone yields of 85% and 15%, respectively, at room temperature (5 h run). The catalytic results of benzylalcohol oxidation between the first run and last run as in the entries 1 and 22 (Table 1) clearly indicate that there is no difference in either reactivity and selectivity of the system. The catalytic performance of the |NPyc| in rt is reasonably closer to the TPAP encapsulated ORMOSIL systems at elevated temperature. Nevertheless, reusable ability of the membrane catalyst is remarkable over the existing catalysts. Regardless of run time and substrate, single piece of |NPyc| could be recycled for 22 times (Table 1) without loss in the active site, while the TPAP-ORMOSIL catalyst lost ~40% of its active sites within five times of recyclic runs evidence enhanced performance of the new membrane catalyst.[5]

Possible mechanism for the selective catalytic alcohol oxidation is due to high-valent oxo-ruthenium active site within the |NPyc| (Pyc–RuO_4^-, perruthenate active site).[7b,c] In the recycling process

Table 1
Oxidation of alcohols to aldehydes and ketones with the membrane catalyst[a]

Entry	Substrate	Time (h)	Yield[b] (%)	Sel.[c] (%)	Membrane recycle number[d]
1	Benzyl alcohol	5	99	>99	1
2	*p*-Cl Benzyl alcohol	4	98	>99	2
3	2-Br Benzyl alcohol	13.5	95	>99	3
4	*p*-Methyl benzyl alcohol	2.5	91	>99	4
5	*p*-Methoxybenzyl alcohol	3.5	98	>99	5
6	2-Methoxybenzyl alcohol	4.5	96	>99	6
7	2,3,4-Trimethoxbenzyl alcohol	7.5	95	>99	7
8	*trans*-Cinnamyl alcohol	6	88	>99	8
9	Geraniol	8.5	96	>99	9
10	2-Thiophenemethanol	3	90	>99	10
11	2-Pyridinemethanol	6	98	>99	11
12	*n*-Octyl alcohol	15	38	>99	12
13	*n*-Decyl alcohol	15	36	>99	13
14	Cyclohexanol	16	40	>99	14
15	Norborneol	12	98	>99	15
16	Benzyl alcohol	5	99	>99	16
17	1-Phenyl ethanol	13	90	>99	17
18	1-(4-Methoxyphenyl) ethanol	9.5	95	>99	18
19	1-(4-Nitrophenyl) ethanol	16	58	>99	19
20	1-(4-*tert*-Butyl phenyl) ethanol	15	40	>99	20
21	Diphenyl methanol	15	88	>99	21
22	Benzyl alcohol	5	99	>99	22

[a] Reaction conditions: 0.05 mmol alcohol, small pieces of membrane composite catalyst (250 mg, 0.007 mmol ruthenium species) in acetone (1.5 mL) was stirred under oxygen atmosphere at room temperature.

[b] Determined by GC analysis.

[c] Selectivity (Sel.) calculated by GC and NMR.

[d] Single run reaction regardless of substrate. Other working conditions are the same as in this table.

the molecular oxygen helps to regenerate the Pyc–RuO_4^- from its reduced form, Pyc–RuO_4^{2-} (ruthenate active site).

In conclusion, a Nafion polymer anchored ruthenium oxide pyrochlore composite has been utilized as a reactive template for selective alcohol oxidation with molecular oxygen at room temperature. A series of alcohols were cleanly oxidized to corresponding aldehydes and ketones in good yields without additives. The catalyst can be recovered and reused several times without any loss of activity.

Acknowledgments

The authors gratefully acknowledge financial support from National Science Council of Taiwan. This work was supported in part by the Ministry of Education, Taiwan under the ATU plan.

References and notes

1. (a) Sheldon, R. A.; Kochi, J. K. *Metal-Catalyzed Oxidations of Organic Compounds*; Academic: New York, 1981; (b) Cainelli, G.; Cardillo, G. *Chromium Oxidations in Organic Chemistry*; Springer: Berlin, 1984.
2. (a) Sheldon, R. A.; Arends, I. W. C. E.; Dijksman, A. *Catal. Today* **2000**, *57*, 157; (b) Punniyamurthy, T.; Velusamy, S.; Javed, I. *Chem. Rev.* **2005**, *105*, 2329; (c) Ishii, Y.; Sakaguchi, S.; Iwahama, T. *Adv. Synth. Catal.* **2001**, *343*, 393.
3. (a) Mallat, T.; Baiker, A. *Chem. Rev.* **2004**, *104*, 3037; (b) Pagliaro, M.; Campestrinian, S.; Ciriminna, R. *Chem. Soc. Rev.* **2005**, *34*, 837.
4. (a) Hinzen, B.; Ley, S. V. *J. Chem. Soc., Perkin Trans. 1* **1997**, 1907; (b) Hinzen, B.; Lenz, R.; Ley, S. V. *Synthesis* **1998**, 977; (c) Ciriminna, R.; Pagliaro, M. *Chem. Eur. J.* **2003**, *9*, 5067; (d) Ciriminna, R.; Campestrini, S.; Pagliaro, M. *Adv. Synth. Catal.* **2003**, *345*, 1261; (e) Wu, D. L.; Wight, A. P.; Davis, M. E. *Chem. Commun.* **2003**, *6*, 758; (f) Campestrini, S.; Carraro, M.; Ciriminna, R.; Pagliaro, M. *Tetrahedron Lett.* **2008**, *49*, 419; (g) Pagliaro, M.; Ciriminna, R. *Tetrahedron Lett.* **2001**, *42*, 4511.
5. Campestrini, S.; Carraro, M.; Tonellato, U. *Tetrahedron Lett.* **2004**, *45*, 7283.
6. (a) Kenneth, M.; Moore, R. B. *Chem. Rev.* **2004**, *104*, 4535; (b) Paquette, L. A. In *Encyclopedia of Reagents for Organic Synthesis*; John Wiley & Sons: New York, 1995; Vol. 6; (c) Jain, S. L.; Sain, B. *Appl. Catal. A* **2006**, *301*, 9117; (d) Schneider, M.; Aquino, F.; Bonrath, W. *Appl. Catal. A* **2001**, *220*, 51; (e) Laufer, W.; Hoelderich, W. F. *Chem. Commun.* **2002**, *16*, 1684.
7. (a) Zen, J.-M.; Liou, S.-L.; Kumar, A. S.; Hsia, M.-S. *Angew. Chem., Int. Ed.* **2003**, *42*, 577; (b) Ke, J.-H.; Kumar, A. S.; Sue, J.-W.; Venkatesan, S.; Zen, J.-M. *J. Mol. Catal. A* **2005**, *233*, 111; (c) Venkatesan, S.; Kumar, A. S.; Zen, J.-M. *J. Mol. Catal. A* **2006**, *250*, 87.
8. Hallinan, D. T.; Elabd, Y. A. *J. Phys. Chem. B* **2007**, *111*, 13221.
9. IR spectroscopy measurements for alcohol oxidation on pyrochlore composite were performed by using FTIR spectrometer (Jasco FT/IR–460 PLUS) equipped with ATR cell. The composite membrane was cut into rectangle (5 cm × 1.5 cm) and immersed in the solution of alcohol in acetone (0.03 mM) for 5–10 min. Then, the alcohol adsorbed membrane was placed on the (ZnSe) ATR crystal and kept into the cell at room temperature. The spectrum was collected using mercury–cadmium–telluride detector with 32 scans per spectrum at a resolution of 4 cm^{-1}.
10. Alcohol oxidation reaction was typically carried out as follows: A mixture of benzyl alcohol (5 mg, 0.05 mmol) and several pieces of the membrane catalyst (250 mg, 0.007 mmol Ru species) in acetone (1.5 mL) was stirred under oxygen atmosphere (1 atm, O_2 ballone) at room temperature. After 5 h, the yield of benzaldehyde (99%) was determined by GC (China chromatography 9800, Taiwan, stainless steel column consists of 10% SP-2100 on a Chromosorb W HP (80/100 mesh) support) using commercially available authentic samples. After separation, the composite catalyst was sequentially washed with an aqueous solution of NaOH (1.0 M), deionized water, acetone, and dried in vacuum prior to recycling.