

A rugged lead-ruthenate pyrochlore membrane catalyst for highly selective oxidation of alcohols

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Abstract

A rugged lead-ruthenate pyrochlore (Py, $\text{Pb}_2\text{Ru}_2\text{O}_7$) Nafion 417 membrane catalyst ($|\text{NPy}|$) has been demonstrated for highly efficient and fully selective oxidation of primary and secondary alcohols to aldehydes and ketones. Under a triphasic condition of $\text{CH}_2\text{Cl}_2(\text{org})/|\text{NPy}|(\text{s})/\text{NaOCl-pH } 11(\text{aq})$, the $|\text{NPy}|$ can be recycled and reused effectively on oxidations of alcohols. Using a same piece of $|\text{NPy}|$, similar reaction yields were obtained by repeating benzyl alcohol oxidation reaction for 20 times. Electrochemical mechanistic investigation indicated that the perruthenate ion (RuO_4^-) intermediate was responsible for selective mediation of the alcohol oxidation.

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1. Introduction

The catalytic conversion of primary alcohols to aldehydes is essential for the preparation of fragrances, food additives, and many organic intermediates [1,2]. Ruthenium oxide-related reagents were often used as catalytic materials for efficient alcohol oxidation reactions [3–8]. Among these, perruthenate (RuO_4^-)/ruthenate (RuO_4^{2-})-supported materials were particularly active in this purpose [9–16]. Barak et al. [17] reported a Ru catalyst (RuCl_3) coupled with H_2O_2 as a co-oxidant and didecyl-dimethyl-ammonium bromide as a phase transfer catalyst (PTC) for alcohol oxidation reactions in CH_2Cl_2 with 67–99% selectivity. Sheldon and co-workers used a Ru(TPAP)/NaOCl system for the oxidation of secondary alcohols and ethers in a biphasic condition (CH_2Cl_2 or chlorobenzene/water) to improve the selectivity to 89–>99% [18]. The same group also reported a $\text{RuCl}_2(\text{PPh}_3)_3/\text{TEMPO}$ system for >99% selective alcohol oxidation in chlorobenzene medium [7]. However, some of the practical problems [1–24], such as the requirement of stoichiometric or high concentration of ruthenium catalyst, the difficulty

in product separation, the need to eliminate trace water in reaction mixture, and the choice of non-aqueous co-oxidants, are still waited to be overcome to achieve selective alcohol oxidations.

There is an increasing trend, for heterogeneously catalyzed liquid-phase oxidation, toward replacement of stoichiometric quantities of inorganic oxidants. Previously, ruthenium pyrochlore oxides were reported as aerobic oxidation catalysts by Felthouse et al. [25,26]. Our group first reported a lead-ruthenate pyrochlore (Py, $\text{Pb}_2\text{Ru}_2\text{O}_7$)/Nafion catalytic system by chemically modifying the catalyst on an electrode surface (designated as NPyCME) for the application in electrocatalysis and chemical sensors [27–30]. Later it was prepared as a rugged lead-ruthenate pyrochlore (Py, $\text{Pb}_2\text{Ru}_2\text{O}_7$) Nafion membrane catalyst (designated as $|\text{NPy}|$) and used for selective sulfoxidation application coupled with a $\text{Ru}(\text{bpy})_3^{2+}$ photosensitizer [31]. Recently the $|\text{NPy}|$ catalyst was characterized by physicochemical techniques of X-ray diffraction (XRD), thermogravimetry (TGA), scanning electron microscopy (SEM), and atomic force microscopy (AFM) with a main conclusion that the Nafion membrane can assist for the nucleation of nano-sized Py crystalline units inside the ionic cluster with a net Py loading of ~6 wt.% [32]. The catalytic activity of the $|\text{NPy}|$ was further evaluated using a model reaction of benzyl alcohol oxidation coupled with an H_2O_2 co-oxidant at 80 °C. The heterogeneous pseudo first order constant (k_h) and turnover frequency

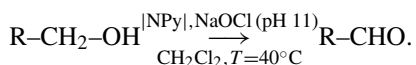
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(TOF) were measured as $2.03 \times 10^{-5} \text{ s}^{-1}$ and 16 h^{-1} , respectively.

In this study, the [NPy] coupled with NaOCl co-oxidant was demonstrated for >99% selective oxidation of both primary and secondary alcohols in a triphasic condition of $\text{CH}_2\text{Cl}_2(\text{org})//[\text{NPy}]_{(\text{s})}/\text{NaOCl-pH } 11(\text{aq})$. In pH 10–11, the OCl^- species can partially soluble in organic solvent (especially CH_2Cl_2) and hence can also act as a PTC to help the oxidation [33,34],



The use of NaOCl can considerably improve the catalytic performance of the [NPy] membrane catalyst. This is not surprised as ruthenium can easily convert into a higher oxidation state of Ru^{VIII} tetraoxide in the presence of NaOCl [33,35]. This high oxidation state, however, cannot be attained in either H_2O_2 or molecular oxygen systems. Unfortunately even though the Ru^{VIII} oxidation state can afford high oxidation rate, the strong oxidation power always guides to unselective products, especially for primary alcohols. This is not the case in the [NPy] system, presumably because of a lower oxidation state of Ru^{VII} (as RuO_4^-) is generated. Probable heterogeneous mechanism was further interpreted based on electrochemical studies. Even though the usage of CH_2Cl_2 in this work is not environmental friendly; the solvent medium can help to first assess the catalytic ability and its performance of the [NPy] in comparison with classical reports. Nowadays, the solid and recyclable catalysts that use molecular oxygen is an attractive alternative, as the oxidant is converted to water and the oxidations are in general more selective [23,24]. Future green-chemistry design related to molecular oxygen-based solvent-free alcohol oxidation using the [NPy] is also discussed in this study. To the best of our knowledge, this is the first report for the >99% selective oxidation of alcohols to aldehydes using a Ru-membrane based triphasic catalytic system coupled with NaOCl co-oxidant.

2. Experimental

2.1. Chemicals

$\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ (99%), $\text{RuO}_2 \cdot x\text{H}_2\text{O}$ (99.9%), $\text{Pb}(\text{NO}_3)_2$ (99%), Nafion solution in lower aliphatic alcohols (5 wt.%), and Nafion 417 membrane (perfluorinated membrane reinforced with Teflon and Dacron, 0.017 inch in thickness) were purchased from Aldrich. All other compounds: KOH (99.5%), H_2O_2 (30%), NaOCl (12%), NaH_2PO_4 (99%), CH_2Cl_2 (99.9%), phenyl methanol (99%) (benzyl alcohol), (4-chlorophenyl)methanol (99%), (4-methoxyphenyl)methanol (98%), (4-methylphenyl)methanol (98%), (4-nitrophenyl)methanol, (99%), (2-bromophenyl)methanol (98%), 3-phenylpropan-1-ol (98%), (pyridine-2-yl)methanol (98%), (thiophen-2-yl)methanol (99%), heptan-1-ol (99%), octan-1-ol (99%), decan-1-ol (98%), undecan-1-ol (99%), cyclohexanol (99%), 5-methyl-2-propan-2-yl-cyclohexan-1-ol (99%), and norbornan-2-ol (92%), were used as received.

2.2. Apparatus and measurements

Gas liquid chromatography (GLC, China chromatography 9800, Taiwan) was used for all quantitative and qualitative analysis. The GLC measurements were all carried out using a homemade stainless steel column consisting of 10% SP-2100 on a chromosorb W HP (80/100 mesh) support or fax map 250 on a chromosorb W HP of 80/100 mesh support with a flame-ionization detector (FID). The optimized GLC temperature conditions were (for benzyl alcohol): injection = 200°C , FID = 200°C and the oven was programmed at 150°C for 4 min then increased at a rate of $10^\circ\text{C}/\text{min}$ to 250°C as a final temperature for 5 min. The GLC conditions were optimized for each alcohol separately prior to the routine catalytic oxidation reactions. A $5 \mu\text{l}$ sample injection volume was used without any loop. Relative GLC peak areas with respect to their standards were uniformly taken as quantitative parameter for the % conversion calculation.

Product analyses were all carried in parallel with 400 MHz H^1 NMR (in CDCl_3) to confirm the selectivity of the reaction. Some representative oxidation reactions (benzyl alcohol, (2-bromophenyl) methanol, heptan-1-ol, octan-1-ol, 5-methyl-2-propan-2-yl-cyclohexan-1-ol, (pyridine-2-yl)methanol, (thiophen-2-yl)methanol) and were also subjected to GLC-MS measurements (Varian Saturn 2200). Cyclic voltammetric measurements were carried out using a CHI 406 electrochemical workstation with a conventional 10 ml working cell. The three-electrode system consisted of the NPyCME working electrode, an Ag/AgCl (3M KCl) reference electrode (Model RE-5, BAS), and a platinum wire auxiliary electrode. Either $\text{CH}_2\text{Cl}_2/0.1 \text{ M}$ tetrabutylammonium bromide (TBAB) or 12% NaOCl/pH 11 phosphate buffer solution (PBS, $\text{Na}_2\text{HPO}_4 + \text{NaOH}$) were used as supporting electrolyte in electrochemical studies.

2.3. Catalyst preparation and oxidation procedure

The [NPy] catalyst was prepared by in-situ precipitation directly inside the Nafion 417 membrane (after ion-exchanged with Ru^{3+} and Pb^{2+} ions) in alkaline medium under constant O_2 purging as per our previous reported procedure and the net Py loading was measured as 6 wt.% (76 $\mu\text{mol}/\text{g}$ Py units) by TGA [32]. Fig. 1 shows the difference in the appearance of the [NPy] and Nafion 417 membrane. The catalytic activity was regenerated by washing in sequence with copious amount of $\text{CH}_2\text{Cl}_2 \rightarrow \text{CH}_3\text{-CO-CH}_3 \rightarrow \text{H}_2\text{O} \rightarrow 1.1 \text{ M KOH}$ (with stirring at least for 1 h) $\rightarrow \text{H}_2\text{O}$ and then dried at 50°C for 3 h.

Organic oxidation reactions were performed under a triphasic condition of 15 ml $\text{CH}_2\text{Cl}_2 + 32 \text{ mM}$ alcohol, 9 ml 30% H_2O_2 (with/without 1 mM TBAB as PTC) or 3–6 ml NaOCl (2.5–4.1 mol) in pH 11 PBS, and a small piece of $\sim 1 \text{ g}$ [NPy] membrane catalyst (or 60 mg RuO_2 or 60 mg $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$) at $T = 40^\circ\text{C}$ under constant stirring of the reaction mixture in a 100 ml four neck RB flask sealed with gasket-septum. After completion of the NaOCl-assisted reaction, NaHSO_3 was used to quench the hypochlorite and then for separation steps. The reaction kinetics was continuously monitored by GLC by ana-

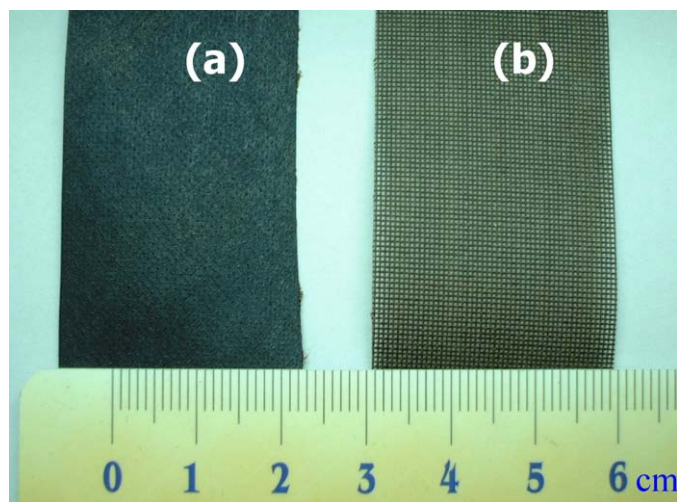


Fig. 1. Typical photographs for Nafion 417 membrane after (a) and before (b) Py modification.

lyzing the organic fraction under a pre-selected timing. Relative GLC peak areas with respect to their standards were uniformly taken as a quantitative parameter for the % of conversion calculation. After a prescribed reaction time, the catalyst was removed using a tong and then the product was simply separated via evaporation of the nonaqueous layer using a rotatory evaporator.

2.4. Preparation of the NPyCME

The NPyCME was prepared by first spin-coating 5 μ l of Nafion (5 wt.%) solution on a clean glassy carbon electrode (GCE) at 3600 rpm. The procedure can allow the coating of a thin film of Nafion on GCE surface and it is further subjected to in situ precipitation of Py units as described by our previous reports [27,28]. The NPyCME is stored in 1.1 M KOH and the film can be stable for more than 3 months. Prior to the electrochemical measurements, the NPyCME was pretreated for five continuous cycles in base electrolyte solution at a scan rate of 50 mV/s. Formation of the fine Py crystalline units was confirmed by X-ray diffraction technique for both [NPy] and NPyCME systems [27,28,32].

3. Results and discussion

3.1. Catalytic performance

Selective oxidation of benzyl alcohol to benzaldehyde was used as a synthetic model to evaluate the catalytic activity of the [NPy] and the role of co-oxidants (i.e., 30% H_2O_2 and 12% NaOCl). As can be seen in Table 1, the addition of H_2O_2 co-oxidant can yield 84% of conversion and >99% of selectivity to benzaldehyde in 24 h at $T=80^\circ\text{C}$ with a turnover number (TON) and TOF of 381 and 16 h^{-1} , respectively (Table 1, entry 2) [32]. Interestingly, the benzyl alcohol oxidation reaction can be completed within 3 h with >99% conversion and selectivity when the co-oxidant was changed from H_2O_2 into NaOCl at a lower reaction temperature of $T=40^\circ\text{C}$ (entry 4). The calculated TON and TOF were 465 and 155 h^{-1} , respectively, with the TOF improved by ~ 10 times over the H_2O_2 -assisted reaction.

Based on the above results, the role of ClO^- is believed to be bi-functional, i.e., to act as an efficient co-oxidant to push up the Ru species in the Py network to perruthenate ion (RuO_4^-) as well as a PTC to enhance the TOF. Control experiments under similar experimental conditions using both $\text{RuO}_2/\text{NaOCl}$ (pH 11) and $\text{RuCl}_3/\text{NaOCl}$ (pH 11) systems failed to give such catalytic responses (entries 6 and 7). Both RuO_2 (pale yellow at 40°C) and RuCl_3 (black at room temperature) were found to dissolve in NaOCl. Presumably ruthenium tetraoxide was formed as an intermediate in the RuO_2 and RuCl_3 systems leading to overoxidation and/or decomposition of benzyl alcohol. The exact detail for the absence of catalysis is unknown for us till now. But using the RuCl_3 catalyst in the presence of H_2O_2 and PTC yielded >99% of benzoic acid within 1.5 h at 80°C . This is also true for other metal salts, such as $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$, PdCl_2 , $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, and $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ [36]. The RuCl_3 -based catalytic system, however, can not be recycled due to irreversible formation of RuO_2 and/or ruthenium oxy-hydroxyl compounds. Conventional TPAP catalyst during the course of the catalytic reaction was also troublesome to recycle the catalyst [37]. The [NPy], on the other hand, is >99% selective and >99% recoverable with perfectly separated products. A simple use of a laboratory tong can fully recover the [NPy]. The easy recovery process is an obvious advantage for mass scale production.

Table 1
Benzyl alcohol oxidation reaction with different catalytic systems ($T=40^\circ\text{C}$)

Entry/catalyst	Co-oxidant	Time (h)	Conversion (%)	TOF (h^{-1})	S_{CHO} (%)	Recycle
1. –	H_2O_2 (80°C)	24	6.3	–	70	–
2. [NPy]	H_2O_2 (80°C)	24	84	16	>99	1 ^a (fresh)
3. –	NaOCl	24	20	–	80	–
4. [NPy]	NaOCl/pH 11	3	>99	155	>99	1 ^b (fresh)
5. –	NaOCl/pH 11	3	–	–	–	–
6. RuO_2	NaOCl/pH 11	3	>99	–	<1	–
7. RuCl_3	NaOCl/pH 11	3	>99	–	<1	–

Entries 1 and 2 by Ref. [32]. [Benzyl alcohol] = 32 mM (0.051 ml in 15 ml CH_2Cl_2); NaOCl = 6 ml of 12% solution (4.1 mol); 60 mg of RuO_2 , RuCl_3 , samples and ~ 1 g of [NPy] used in the reaction. $\text{TOF} = [\text{product}]_{\text{Mol}} / ([\text{catalyst}]_{\text{Mol}} \times t_{\text{h}})$; [catalyst, Py] = $70.56\ \mu\text{M/g}$ of [NPy]; S_{CHO} = percentage of aldehyde selectivity by GLC. The values 1^a and 1^b correspond to the [NPy] catalyst “a” and “b”, respectively, used for 1st time.

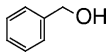
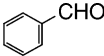
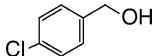
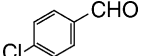
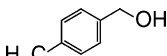
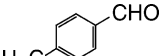
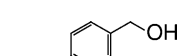
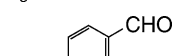
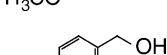
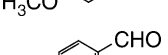
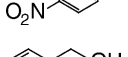
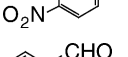
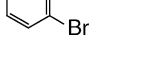
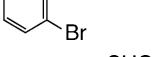
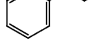
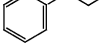
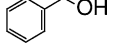
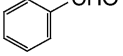
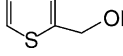
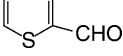
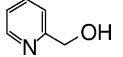
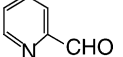
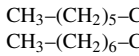
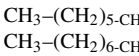
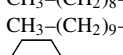
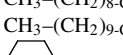
3.2. [NPy]-catalyzed alcohol oxidation reactions

A variety of primary and secondary alcohols were selectively oxidized to aldehyde or carbonyl compounds in moderate to excellent yields as summarized in Table 2. As can be seen, *p*-substituted benzyl alcohols (e.g., –Cl, –CH₃, –OCH₃, and –NO₂) yielded >90% of product conversion in ~3–4 h of reaction time with TOF in the range of 84–155 h⁻¹ (entries 2–5, Table 2), which is ~50 times higher over that of Ru/hydroxyapatite system [24]. Heterocyclic alcohols with sulfur- and nitrogen-containing compounds were found to show the best catalytic effect with TOF of 1517 and 902 h⁻¹ for (pyridin-2-yl)methanol and (thiophene-2-yl)methanol, respectively (entries 9 and 10, Table 2). In contrast to the observation on conventional Ru-based catalysts (Ru/Al₂O₃/O₂ and Ru-HAP/O₂) with TOF = 0.6 h⁻¹ for (pyridin-2-yl)methanol [23,24], the high conversion rate

might have something to do with the synergetic effect of both aromatic electrons and lone pair electrons on nitrogen and sulfur atoms to help for the adsorption to the [NPy] catalytic surface to improve the catalysis.

Some of aliphatic primary alcohols (long chain alcohols) and secondary alcohols (cyclohexanol, its methyl substituted derivatives and norbornan-2-ol) were also selectively oxidized by the membrane catalyst (entries 11–14 and 15–17, Table 2) with TOF values in the window of 8–41 h⁻¹. Even though the TOF is relatively lower than those of the aromatic and heterocyclic compounds; there is still no overoxidation to carboxylic acid in any of the aliphatic systems. Note that, for the case of octan-1-ol and its derivatives, it is highly difficult to control the reaction to octanal. For example, the Ru-HAP/O₂ catalyst with octan-1-ol was found to yield 82% of octanoic acid conversion (TOF = 1 h⁻¹) without any corresponding aldehyde [24]. The Ru/Al₂O₃/O₂ catalyst

Table 2
[NPy] catalyst for various alcohol oxidation reactions

Entry	Substrate	Product	Time (h)	Yield (%)	TOF (h ⁻¹)	S _{CHO} (%)	Recycle (#)
1			3	>99	155	>99	6 ^b
2			4	92	107	>99	8 ^b
3			5	91	84	>99	9 ^b
4			3	93	131	>99	12 ^b
5			3.5	99	144	>99	13 ^b
6			10	83	38	>99	15 ^b
7			10	18	8	>99	17 ^b
8			3	>99	155	>99	20 ^b
9			0.5	97	902	>99	1 ^c (fresh)
10			0.2	98	1517	>99	3 ^c
11	CH ₃ –(CH ₂) ₅ –CH ₂ OH	CH ₃ –(CH ₂) ₅ –CHO	13	>99	36	>99	1 ^d (fresh)
12	CH ₃ –(CH ₂) ₆ –CH ₂ OH	CH ₃ –(CH ₂) ₆ –CHO	11	97	41	>99	1 ^e (fresh)
13	CH ₃ –(CH ₂) ₈ –CH ₂ OH	CH ₃ –(CH ₂) ₈ –CHO	15	50	15	>99	1 ^f (fresh)
14	CH ₃ –(CH ₂) ₉ –CH ₂ OH	CH ₃ –(CH ₂) ₉ –CHO	15	59	18	>99	1 ^g (fresh)
15			7.5	43	27	>99	11 ^b
16			15	31	10	>99	4 ^c
17			10	98	45	>99	18 ^b

[Alcohol] = 32 mM in 15 ml CH₂Cl₂; NaOCl = 3–6 ml of 12% solution; [NPy] catalyst = 1 g; conversion results by GLC or NMR (entry 5); S_{CHO} = percentage of aldehyde selectivity by GLC and NMR. The “a–g” were different [NPy] catalysts used under various recyclable conditions.

required 1 equivalent (based on Ru) hydroquinone in the reaction mixture to control the reaction selectively to its octanal [23]. The classical TPAP/O₂/molecular sieves also resulted in considerable carboxylic acid product [21]. No such complication was noticed in the present case with the [NPy]/NaOCl system. The [NPy]/NaOCl (at 40 °C) catalyzed secondary alcohols (cyclohexanol) are close to the reported TPAP/NaOCl (0.7 mol) system at room temperature (selectivity 89%) [18]. Note that, for most of the alcohol oxidation systems, the co-oxidants were slowly fed into the reaction mixture in order to control the reaction selectivity [17,18,23,24,36,38]; whereas the NaOCl was added only once in the reaction mixture at the beginning in the present case. Nevertheless it is interesting to investigate the performance with the addition of promoters like pyridine oxide and bromide salts (HOCl/HOBr is known to be a more efficient oxidant) in the future continuous study [38].

3.3. Catalytic mechanism

To reaction mechanism of the [NPy] catalytic system was studied by cyclic voltammetry using the NPyCME under the working condition similar to that of the synthetic alcohol oxidation. Our previous comparative electrochemical and electrocatalytic studies with various redox probe molecules (glucose, ethanol, and aldehyde) revealed that, the ruthenate ion (i.e., Ru^{VII}O₄²⁻) in the octahedral sites of the Py crystal structure can be electrogenerated as perruthenate ion, RuO₄²⁻, at ~0.6 V vs. Ag/AgCl (i.e., 1.5 V versus RHE) selectively in alkaline solution for efficient oxidation of organic molecules [29]. Prior to the experiments, synthetic aqueous and organic phase model solutions were prepared by separating the aqueous and organic phases of 15 ml CH₂Cl₂ + 6 ml 12% NaOCl + 10 ml pH 11 PBS after reacted at 40 °C for 1 h. Fig. 2 shows typical cyclic voltammetric responses in both organic and aqueous phases

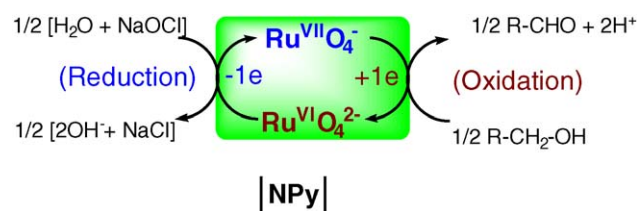


Fig. 3. Mechanism for the [NPy] membrane catalyzed selective alcohol oxidation reaction in the presence of NaOCl co-oxidant (primary alcohol is given here as an example).

without/with the addition of benzyl alcohol at the NPyCME. In aqueous solution, two cathodic peaks at 0.15 and -0.5 V versus Ag/AgCl correspond to the OCl⁻ reduction steps and an anodic shoulder due to the electrogenerated perruthenate species were observed (Fig. 2A). Upon the addition of benzyl alcohol, a profound increase in the anodic side with a decrease in the cathodic response on the potential where the perruthenate species exist started to occur (inset of Fig. 2A). This is the typical example of a mediated oxidation mechanism [39]. Parallel electrochemical experiment with organic phase solution was quite different with a sharp increase in the current response starting from 0.7 V versus Ag/AgCl in the anodic side with/without benzyl alcohol. Net catalytic current in the anodic side, however, is not very noticeable indicating relatively less catalytic behavior in the organic phase.

Although the precise nature of the catalytic reaction is not exactly defined, the available electrochemical behavior is enough to propose that NaOCl can act as electron acceptor to regenerate the catalyst to the Ru^{VII}O₄²⁻ species to mediate the alcohol oxidation reaction effectively (Fig. 3). It is also proposed that the catalyst can interchange between organic and aqueous phase during the course of stirring. The OCl⁻ presents at the interface can then help the medium exchange of alcohol species

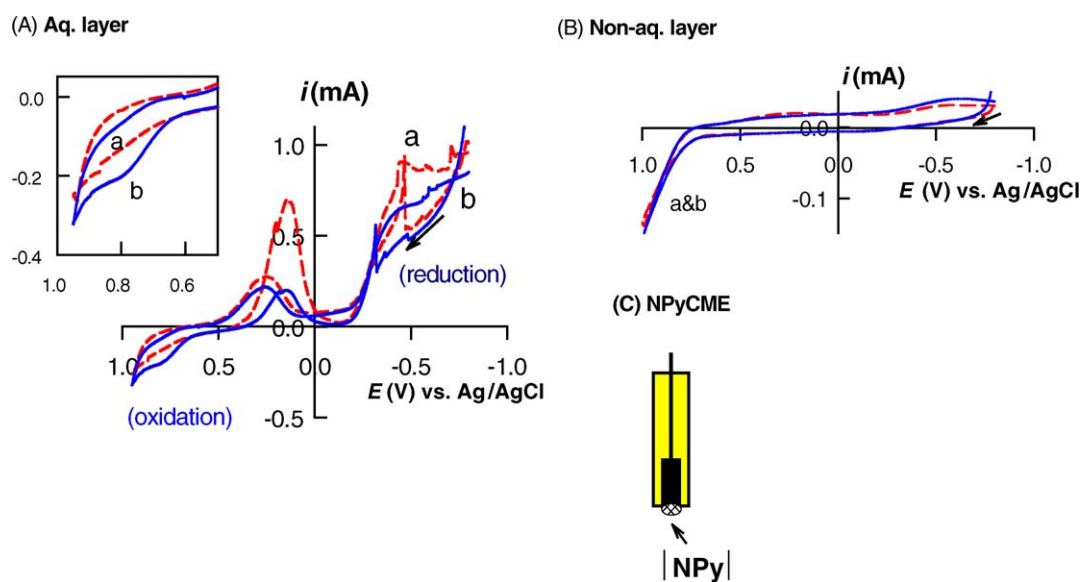


Fig. 2. Cyclic voltammetric response at the NPyCME for the oxidation/reduction reaction of benzyl alcohol (32 mM)/ClO⁻ in aqueous 4.1 mol NaOCl (A) and nonaqueous CH₂Cl₂ (B) solutions at a scan rate of 50 mV/s. (C) Cartoon for the NPyCME. Inset (A) corresponds to an enlarged version of the oxidation part without (a) and with (b) benzyl alcohol. In order to maintain the electrical conductivity, 0.1 M tetrabutylammonium bromide (TBAB) is added into the CH₂Cl₂ solution.

(probably some intermediate) from organic to aqueous phase to assist the mediated oxidation. Apart from this, the hydrophobic site of the Nafion matrix in [NPy] can also help the mediated oxidation. The exact detail for the role is yet to be explored.

3.4. [NPy] stability

Reactions were also carried out at different temperatures (40–80 °C) with excess NaOCl under non-stoichiometric conditions to test the selectivity and stability of the catalyst. Unlike other Ru-based catalyst that aldehyde selectivity depends on mild temperature, all reactions in this study were ended with aldehyde products even under stringent conditions [24]. As confirmed by NMR, GLC, and GLC–MS, none of the primary alcohols were found to over-oxidize to carboxylic acids.

Separation of reaction products is another advantage of the [NPy] system. Benzyl alcohol oxidation reaction under the four systems of RuO₂, RuCl₃, Py, and [NPy] was used for comparison. As can be seen in Fig. 4, both the Ru³⁺ and RuO₄[−] ions were soluble in alcohols and hence it is difficult to separate the catalyst from the reaction mixture. Only the [NPy] system yielded clear reaction products after the filtration. The recoverability and stability of the membrane catalyst was also excellent as the [NPy] catalyst can be reused without any loss in the catalytic activity after used for more than 20 reactions. Similar reaction kinetics (data not enclosed) and yields in 1st run (entry 2, Table 1) and 20th run (entry 8, Table 2) indicates good recyclability of the [NPy] system. Note that ~30% loss of activity after three recycles for RuO₄[−] anchored sol–gel and amberlyst anion exchange resin (IR 27) containing quaternary ammonium

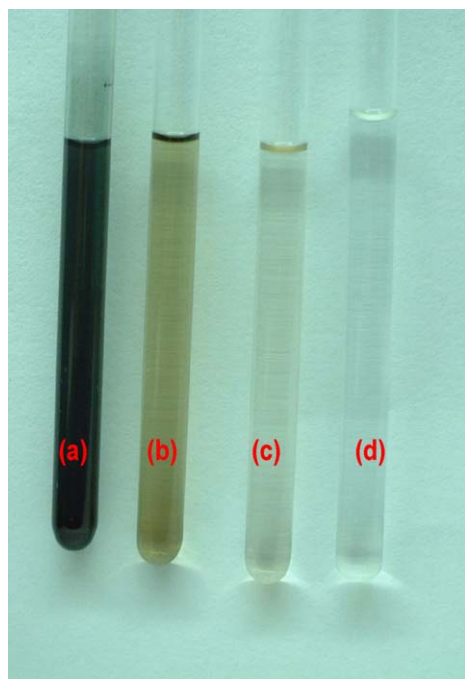


Fig. 4. Photographs of the filtered organic phase for the product of benzyl alcohol oxidation reaction catalyzed by (a) RuCl₃, (b) RuO₂, (c) Py powders, and (d) [NPy] membrane catalyst with 15 ml CH₂Cl₂ + 6 ml NaOCl (4.1 mol)/pH 11 PBS.

systems were reported [6,19–22]. Other Ru catalyst, such as Ru–HAP, Ru/Al₂O₃, RuMnMn and zeolite confined nano-RuO₂, etc., can only be recycled for 3–9 times [23,24,36,40]. Meanwhile elemental analysis also showed no metal leaching behavior for an [NPy]-assisted benzyl alcohol oxidation reaction as no trace of Ru and Pb ions in solution was detected. Actually the [NPy] catalyst is still active after stored in 1.1 M KOH for ~6 month.

Finally a preliminary study with the [NPy] catalyst using molecular O₂ under solvent-free condition was also evaluated here. Aliquot of 20 μl of benzyl alcohol is mixed with 0.2 gram (14 μmol) of [NPy] catalyst under O₂ atmosphere and a yield of 98% benzaldehyde conversion within 24 h was observed (data not included). The appreciable alcohol oxidation reaction may not be that surprised as the NPyCME was reported to be efficient for oxygen reduction reaction [27–29]. From economic and environmental viewpoints, there is an urgent demand for greener and more atom efficient methods that employ clean oxidants with a recyclable catalyst. The [NPy] membrane catalyst can be a judicious choice for solvent free and green catalytic approach. Further work is progress in our laboratory.

4. Conclusions

A rugged lead ruthenate pyrochlore (Py) Nafion 417 membrane catalyst ([NPy]) with NaOCl co-oxidant was found to be highly efficient, recoverable, reusable, and fully selective for the oxidation of alcohols, especially primary alcohol to corresponding aldehyde reaction. Model electrochemical studies reveal a perruthenate (RuO₄[−])-mediated alcohol oxidation mechanism on the [NPy]. There is no leaching of Pb and Ru metals during the course of the alcohol oxidation reactions. Turnover frequency values were either comparable or even superior to other classical Ru-based catalysts. The selectivity is independent of the stoichiometric of the catalyst, oxidant, and temperature. Extendibility to a perfect greener approach with molecular oxygen under solvent free condition is appreciable with the [NPy] membrane catalyst.

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References

- [1] R.A. Sheldon, I.W.C.E. Arends, A. Dijkman, *Catal. Today* 57 (2000) 157.
- [2] T. Mallat, A. Baiker, *Chem. Rev.* 104 (2004) 3037.
- [3] S.-I. Murahashi (Ed.), *Ruthenium in Organic Synthesis*, Wiley-VCH, 2004.
- [4] J.-E. Bäckvall (Ed.), *Modern Oxidations Methods*, Wiley-VCH, 2004.
- [5] M. Hudlický, *Oxidations in Organic Chemistry*, ACS Monograph 186, American Chemical Society, Washington, DC, 1980.
- [6] J. Muzart, *Chem. Rev.* 92 (1992) 113.
- [7] R.A. Sheldon, I.W.C.E. Arends, G.-J. ten Brink, A. Dijkman, *Acc. Chem. Res.* 35 (2002) 774.
- [8] S. Murahashi, T. Naota, *Adv. Met. Org. Chem.* 3 (1994) 225.
- [9] S.V. Ley, J. Norman, W.P. Griffith, S.P. Marsden, *Synthesis* (1994) 639.

- [10] H.B. Friedrich, *Platinum Metals Rev.* 43 (1999) 94.
- [11] R.M. Moriarty, H. Gopal, T. Adams, *Tetrahedron Lett.* 46 (1970) 4003.
- [12] J.L. Courtney, K.F. Swansborough, *Rev. Pure Appl. Chem.* 22 (1972) 47.
- [13] J.H. Cornely, M.S. Leyda, D.E. Meade, V. Dragojlovic, *Green Chem.* 5 (2003) 34.
- [14] D.C. Dengel, R.A. Hudson, W.P. Griffith, *Transition Metal Chem.* 10 (1985) 98.
- [15] W.P. Griffith, J.M. Jolliffe, S.V. Ley, D.J.J. Williams, *Chem. Soc. Chem. Commun.* (1990) 1219.
- [16] D.G. Lee, Z. Wang, W.D. Chandler, *J. Org. Chem.* 57 (1992) 3276.
- [17] G. Barak, J. Dakka, Y. Sasson, *J. Org. Chem.* 53 (1988) 3553.
- [18] L. Gonsalvi, I.W.C.E. Arends, P. Moilanen, R.A. Sheldon, *Adv. Synth. Catal.* 345 (2003) 1321.
- [19] S. Campestrini, M. Carraro, R. Ciriminna, M. Pagliaro, U. Tonello, *Tetrahedron Lett.* 45 (2004) 7283.
- [20] B. Hinzen, S.V. Ley, *J. Chem. Soc. Perkin Trans. I* (1997) 1907.
- [21] R. Lenz, S.V. Ley, *J. Chem. Soc. Perkin Trans. I* (1997) 3291.
- [22] D.G. Lee, L.N. Congson, *Can. J. Chem.* B 68 (1990) 1774.
- [23] K. Yamaguchi, N. Mizuno, *Angew. Chem.* 41 (2002) 4538.
- [24] K. Yamaguchi, K. Mori, T. Mizugaki, K. Ebitani, K. Kaneda, *J. Am. Chem. Soc.* 122 (2000) 7144.
- [25] T.R. Felthouse, *J. Am. Chem. Soc.* 109 (1987) 7566.
- [26] T.R. Felthouse, P.B. Fraundorf, R.M. Friedman, C.L. Schosser, *J. Catal.* 127 (1991) 393.
- [27] J.-M. Zen, C.-W. Wang, *J. Electroanal. Chem.* 368 (1994) 251.
- [28] J.-M. Zen, A.S. Kumar, *Acc. Chem. Res.* 34 (2001) 772.
- [29] J.-M. Zen, A.S. Kumar, C.-C. Chen, *J. Mol. Catal. A* 165 (2001) 177.
- [30] J.-M. Zen, A.S. Kumar, C.-C. Chen, *Anal. Chem.* 73 (2001) 1169.
- [31] J.-M. Zen, S.-L. Liou, A.S. Kumar, M.-S. Hsia, *Angew. Chem.* 43 (2003) 577, 1328.
- [32] J.-H. Ke, A.S. Kumar, J.-W. Sue, S. Venkatesan, J.-M. Zen, *J. Mol. Catal. A* 233 (2005) 111.
- [33] L.A. Paquette (Ed.), *Encyclopedia of Reagents for Organic Synthesis*, Vol. 7, John Wiley & Sons, New York, 1995, p. 4580.
- [34] S. Bani, F. Montanari, S. Quici, *J. Org. Chem.* 54 (1989) 1850.
- [35] L.A. Paquette (Ed.), *Encyclopedia of Reagents for Organic Synthesis*, vol. 7, John Wiley & Sons, New York, 1995, p. 4410.
- [36] B.-Z. Zhan, M.A. White, T.-K. Sham, J.A. Pincock, R.J. Doucet, K.V.R. Rao, K.N. Robertson, T.S. Cameron, *J. Am. Chem. Soc.* 125 (2003) 2195.
- [37] D.G. Lee, Z. Wang, W.D. Chandler, *J. Org. Chem.* 57 (1992) 3276.
- [38] W. Qian, E. Jin, W. Bao, Y. Zhang, *Angew. Chem.* 44 (2005) 952.
- [39] J.-M. Zen, A.S. Kumar, D.-M. Tsai, *Electroanalysis* 15 (2003) 1703.
- [40] K. Ebitani, K. Motokura, T. Mizugaki, K. Kaneda, *Angew. Chem.* 44 (2005) 3423.