APPENDIX

I. Identification of styrene oxidation products:

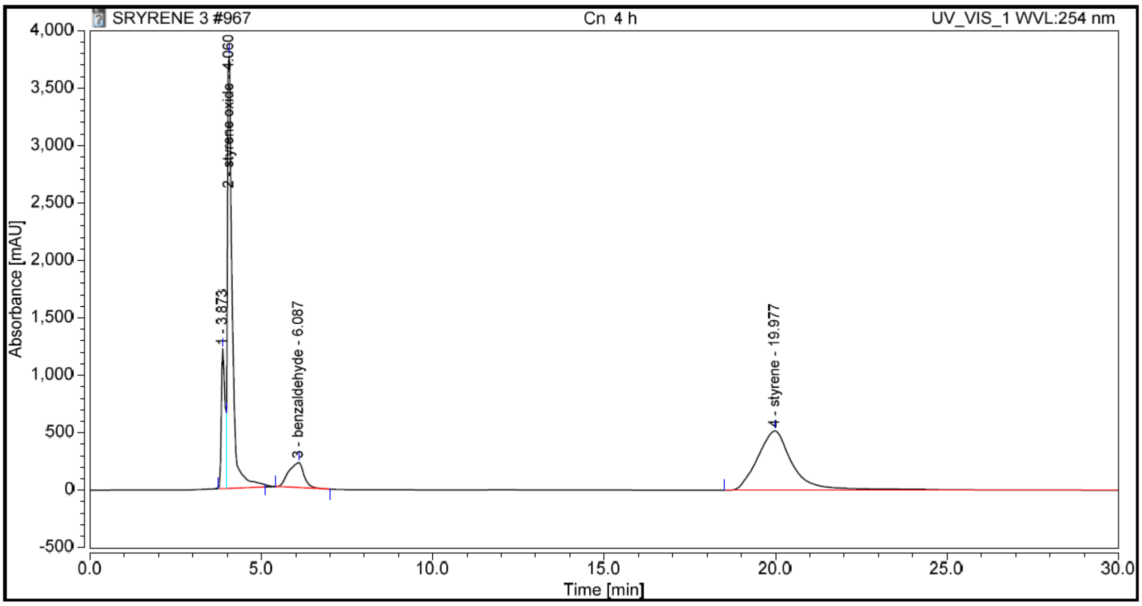

Fig. IA A typical chromatogram of styrene oxidation highlighting resolution of all the components.

II. Characterization of Sulfones:

Sulfone	Characterization
Methylphenylsulfone	Isolated as white solid. mp 85-86 °C; ν (KBr)/cm^{-1} 1322, 1166; ^{1}H NMR (400 MHz; $CDCl_3$, δ): 3.01 (s, 3H), 7.53-7.59 (m, 1H), 7.62-7.71 (m, 2H), 7.79-7.95 (m, 2H); ^{13}C NMR (100.5 MHz; $CDCl_3$, δ): 44.73, 126.33, 128.57, 132.91, 137.54.
Dimethylsulfone	Isolated as white solid. mp 236-237 °C; ν (KBr)/cm^{-1} 1312, 1135; ^{1}H NMR (400 MHz; $CDCl_3$, δ): 3.25 (s, 6H); ^{13}C NMR (100.5 MHz; $CDCl_3$, δ): 44.53.
Dibutylsulfone	Isolated as white solid; mp 42-43°C; ν (KBr)/cm^{-1} 1341, 1134; ^{1}H NMR (400 MHz; $CDCl_3$, δ): 0.97 (t, 6H, J=7.39 Hz); 1.39-1.52 (m, 4H), 1.79-1.87 (m, 4H), 2.87-2.92 (m, 4H);

Continued…

Sulfone	Characterization
Dibutylsulfone	^{13}C NMR (100.5 MHz; $CDCl_3$, δ): 13.51, 21.69, 23.97, 52.51.
Dihexylsulfone	Isolated as pale-yellow liquid; ν (KBr)/cm^{-1} 1323, 1161; ^{1}H NMR (400 MHz; $CDCl_3$, δ): 0.95 (t, 6H, J=7.66 Hz), 1.24-1.40 (m, 12H), 1.92 (m, 4H), 3.36 (t, 4H, J=6.71 Hz); ^{13}C NMR (100.5 MHz; $CDCl_3$, δ): 13.46, 21.75, 32.62, 27.91, 26.44, 53.72.
Methyl-*p*-tolylsulfone	Isolated as white solid; mp 86-87 °C; ν (KBr)/cm^{-1} 1294, 1145 ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.83 (d, 2H), 7.36 (d, 2H), 3.03 (s, 3H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 144.70, 137.63, 129.56, 127.38, 44.33, 22.44.
4-Chlorophenyl-methyl sulfone	Isolated as white solid, mp 95-97 °C; ν(KBr)/cm^{-1} 3058, 2933, 1156, 1315; ^{1}H NMR (400 MHz; $CDCl_3$, δ): 3.03 (s, 3H), 7.52 (d, 2H, J=8.5 Hz), 7.64 (d, 2H, J=8.5 Hz); ^{13}C NMR (100.5 MHz; $CDCl_3$, δ): 44.52, 128.89, 129.76, 139.01, 140.46.
4-Bromophenyl-methyl sulfone	Isolated as solid; mp 103-106 °C; ν(KBr)/cm^{-1} 1303, 1145 cm^{-1}; ^{1}H NMR (400 MHz; $CDCl_3$, δ): 3.03 (s, 3H), 7.80-7.81 (m, 2H), 7.79 (d, 2H, J=8.2 Hz); ^{13}C NMR (100.5 MHz; $CDCl_3$, δ): 44.47, 128.85, 132.66, 139.49.
Allylphenylsulfone	Isolated as pale-yellow liquid; ν (KBr)/cm^{-1} 1317, 1142; ^{1}H NMR (400 MHz; $CDCl_3$, δ): 3.91 (dt, 2H, J=7.19, 1.22 Hz), 5.05 (dq, 1H, J=1.49, 17.21 Hz), 5.18 (dq,1H, J=1.22, 10.32 Hz), 5.63 (ddt, 1H, J= 7.19, 10.31, 17.21 Hz), 7.37-7.44 (m, 1H), 7.62-7.69 (m, 2H), 7.91-7.94 (m, 2H); ^{13}C NMR (100.5 MHz; $CDCl_3$, δ): 60.53, 117.41, 124.44, 128.88, 129.13, 133.72, 137.26.

Continued…

Sulfone	Characterization
Phenylvinylsulfone	Isolated as white solid; mp 63-64 ºC; ν (KBr)/cm^{-1} 1364, 1162; ^{1}H NMR (400 MHz; $CDCl_3$, δ): 6.13 (d, 1H, J=9.60 Hz), 6.45 (d, 1H, J=16.42 Hz), 6.63-6.77 (m, 1H), 7.43-7.49 (m, 1H), 7.58-7.67 (m, 2H), 7.88-7.95 (m, 2H); ^{13}C NMR (100.5 MHz; $CDCl_3$, δ): 127.89, 129.30, 133.75, 138.55, 139.71.
2-(Phenylsulfonyl) ethanol	Isolated as white solid; mp 96-97 ºC; ν (KBr)/cm-1 1335, 1152; 1H NMR (400 MHz; CDCl3, δ): 2.48 (s, 1H), 3.23 (t, 2H, J=5.46 Hz), 3.95 (t, 2H, J=5.26 Hz), 7.44-7.53 (m, 1H), 7.57-7.67 (m, 2H); 7.86-7.95 (m, 2H); ^{13}C NMR (100.5 MHz; $CDCl_3$, δ): 57.35, 61.56, 128.92, 129.58, 134.06, 140.71.
Diphenyl sulfone	Isolated as pale-yellow solid; mp 128ºC; ν (KBr)/cm^{-1} 1313, 1154; ^{1}H NMR (400 MHz; $CDCl_3$, δ): 7.91-7.95 (m, 4H), 7.44-7.54 (m, 6H); ^{13}C NMR (100.5 MHz; $CDCl_3$, δ): 141.68, 133.12, 129.21, 127.64

III. Identification of 5-hydroxymethyl-2-furfural (HMF) oxidation product:

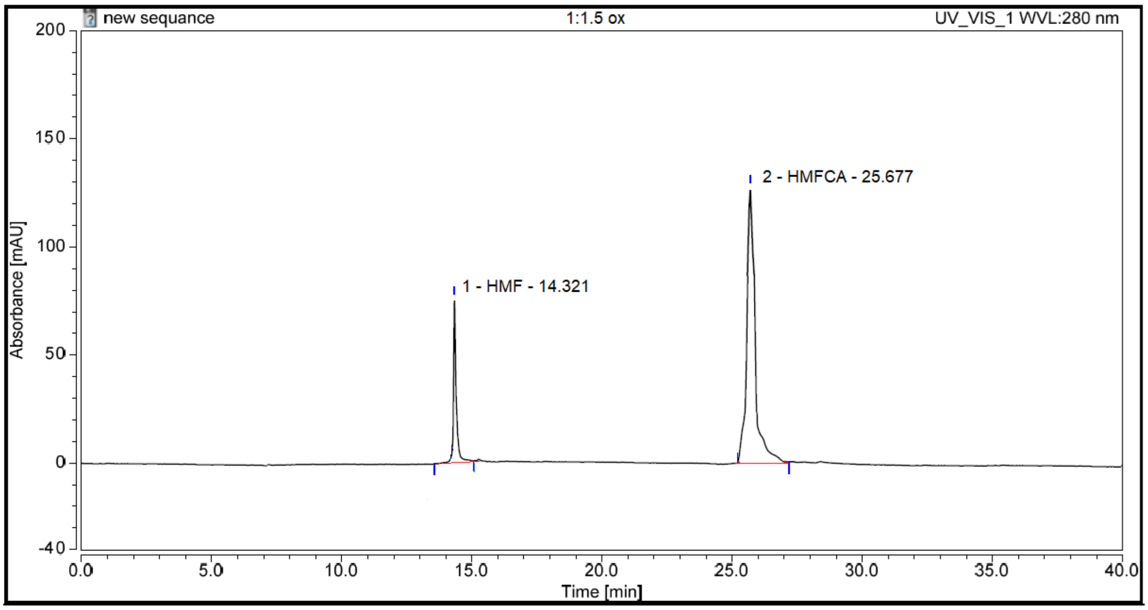

Fig. IIA HPLC chromatogram illustrating the oxidation of 5-hydroxymethyl-2-furfural (HMF) to 5-hydroxymethyl-2-furancarboxylic acid (HMFCA).

IV. Characterization of Sulfoxides:

Sulfoxide	Characterization
Methylphenylsulfoxide	light yellow solid; mp 28-29^{o}C; ν (KBr)/cm^{-1} 1044; ^{1}H NMR: (400 MHz; CDCl$_3$, δ): 2.74 (s, 3H), 7.30-7.35 (m, 1H), 7.42-7.50 (m, 2H), 7.62-7.69 (m, 2H); ^{13}C NMR: (100.5 MHz; CDCl$_3$, δ): 43.83, 121.54, 128.43, 130.75, 145.32.
Dimethylsulfoxide	Isolated as liquid; ν (KBr)/cm^{-1} 1054; ^{1}H NMR: (400 MHz; CDCl$_3$, δ): 2.53(s, 6H); ^{13}C NMR: (100.5 MHz; CDCl$_3$, δ): 40.39.
Dibutylsulfoxide	Isolated as white solid; mp 32-33^{o}C; ν (KBr)/cm^{-1} 1060; ^{1}H NMR: (400 MHz; CDCl$_3$, δ): 0.95(t, 6H, J=7.42 Hz), 1.37-1.47 (m, 4H), 1.67-1.72 (m, 4H), 2.62-2.69 (m, 4H); ^{13}C NMR:(100.5 MHz; CDCl$_3$, δ): 13.64, 22.15, 24.51, 51.81.
Dihexylsulfoxide	Isolated as pale-yellow liquid; ν (KBr)/cm^{-1} 1043; ^{1}H NMR: (400 MHz; CDCl$_3$, δ): 0.96 (t, 6H, J= 7.65 Hz), 1.22-1.40 (m, 12H), 1.67 (m, 4H), 2.70 (t, 4H, J=6.71 Hz); ^{13}C NMR: (100.5 MHz; CDCl$_3$, δ): 13.53, 21.93, 32.84, 27.64, 28.43, 52.64.
Methyl-*p*-tolylsulfoxide	Isolated as pale-yellow liquid; ν (KBr)/cm^{-1} 1035 ^{1}H NMR: (400 MHz; CDCl$_3$, δ): 7.45 (d, 2H), 7.35 (d, 2H), 2.72 (s, 3H), 2.41 (s, 3H); ^{13}C NMR: (100.5 MHz; CDCl$_3$, δ): 142.59, 141.56, 129.93, 123.59, 44.21, 21.42.
4-Chlorophenyl-methyl sulfoxide	Isolated as liquid; ν(KBr)/cm^{-1} 2983, 1054; ^{1}H NMR: (400 MHz; CDCl$_3$, δ): 2.73 (s, 3H), 7.53 (d, 2H, J=8.4 Hz), 7.62 (d, 2H, J=8.4 Hz); ^{13}C NMR: (100.5 MHz; CDCl$_3$, δ): 43.96, 124.94, 129.63, 137.10, 144.08.
Allylphenylsulfoxide	Pale-yellow liquid; ν (KBr)/cm^{-1} 1041; ^{1}H NMR: (400 MHz; CDCl$_3$, δ): 3.42 (dt, 2H, J=7.12, 1.12 Hz); 5.01(dq, 1H, J=1.44, 17.11 Hz); 5.16 (dq, 1H, J=1.12,

Continued…

Sulfoxide	Characterization
Allylphenyl-sulfoxide	10.23 Hz); 5.43 (ddt, 1H, J=7.11, 10.23, 17.11 Hz), 7.26-7.31 (m, 1H); 7.36-7.40 (m, 2H), 7.61-7.64 (m, 2H); ^{13}C NMR: (100.5 MHz; $CDCl_3$, δ): 60.36, 117.93, 124.72, 125.09, 129.07, 131.34, 142.15.
Phenylvinyl-sulfoxide	Pale-yellow liquid; ν (KBr)/cm^{-1} 1053; ^{1}H NMR: (400 MHz; $CDCl_3$, δ): 5.93 (d, 1H, J=10.13 Hz), 6.25 (d, 1H, J=15.89 Hz), 6.56-6.70 (m, 1H), 7.27-7.37 (m, 1H), 7.44-7.54 (m, 2H), 7.62-7.69 (m, 2H); ^{13}C NMR: (100.5 MHz; $CDCl_3$, δ), 120.49; 124.51, 129.36, 131.14, 142.98, 143.41.
2-(Phenylsulfoxyl) ethanol	Light brown solid; mp 42-43^{o}C; ν (KBr)/cm^{-1} 1039; ^{1}H NMR: (400 MHz; $CDCl_3$, δ): 2.44 (s, 1H); 3.11 (t, 2H, J=5.21 Hz); 3.77 (t, 2H, J=5.24 Hz); 7.26-7.89 (m, 1H); 7.48-7.47 (m, 2H); 7.61-7.88 (m, 2H); ^{13}C NMR: (100.5 MHz; $CDCl_3$, δ): 56.18, 60.92, 125.47, 130.04, 131.23, 144.57.
Diphenyl sulfoxide	Isolated as white solid; mp 70 ^{o}C; ν (KBr)/cm^{-1} 1041; ^{1}H NMR: (400 MHz; $CDCl_3$, δ): 7.63-7.68 (m, 4H), 7.43-7.50 (m, 6H); ^{13}C NMR: (100.5 MHz; $CDCl_3$, δ): 144.68, 129.57, 128.03, 123.70.

mp = melting point.

Splitting patterns are designated as s (singlet), d (doublet), t (triplet), dt (double triplet), ddt (double-double triplet), q (quartet), dq (double quartet), m (multiplet).

V. Identification of phenol hydroxylation products:

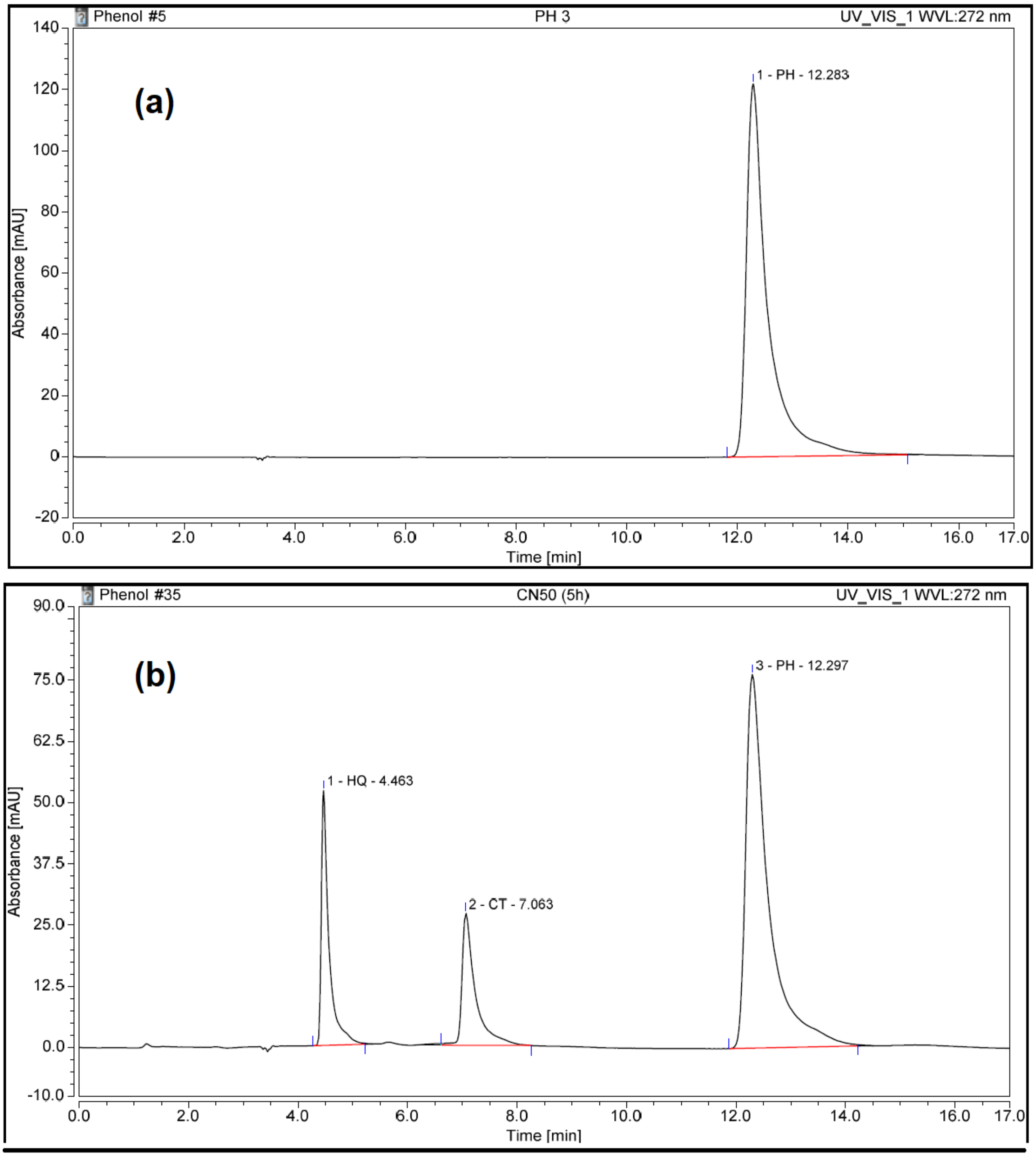

Fig IIIA HPLC chromatogram illustrating (a) phenol at 0 h of the hydroxylation reaction and (b) conversion of phenol to hydroquinone and catechol under the optimized condition. Reaction condition: Phenol (5 mmol), catalyst= **ChpNb (5.1)** (0.1 mmol of Nb), H_2O_2 (20 mmol) without solvent at room temperature and t = 5 h.

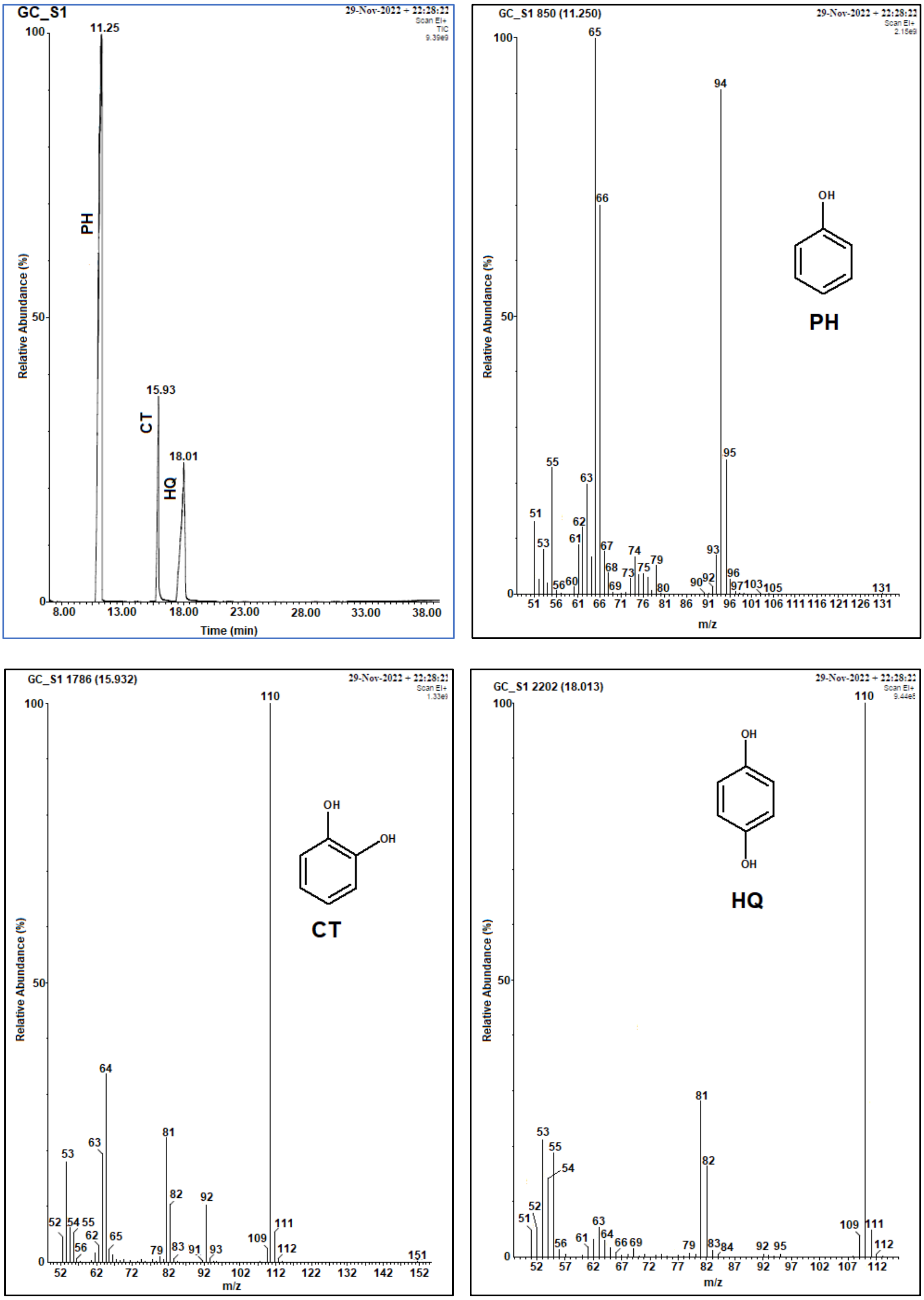

Fig. IVA GC-MS spectra of the reaction mixture of phenol hydroxylation under the optimized condition. Reaction condition: Phenol (5 mmol), catalyst = **ChpNb (5.1)** (0.1 mmol of Nb), H_2O_2 (20 mmol) without solvent at room temperature and t = 5 h.

LIST OF PUBLICATIONS

Publications based on work included in the thesis:

1. **Talukdar, H.**, Gogoi, S. R., Sultana, S. Y., Begum, R., Dowerah, D., Sarma, B., and Islam, N. S. Oxido-and mixed-ligand peroxido complexes of niobium(V) as potent phosphatase inhibitors and efficient catalysts for eco-friendly styrene epoxidation. ***Dalton Transactions***, 52:10165-10182, 2023.
2. **Talukdar, H.**, Saikia, G., Das, A., Sultana, S. Y., and Islam, N. S. Organic-solvent-free oxidation of styrene, phenol and sulfides with H_2O_2 over eco-friendly niobium and tantalum based heterogeneous catalysts. ***Journal of Industrial and Engineering Chemistry***, 121:249-263, 2023.
3. **Talukdar, H**., Sultana, S. Y., Kalita, A., and Islam, N. S. Selective and mild oxidation of 5-hydroxymethylfurfural to 5-hydroxymethyl-2-furancarboxylic acid over organic polymer-Supported peroxidoniobium(V) catalysts. ***ChemistrySelect***, 7(38):202202374, 2022.
4. **Talukdar, H**., Gogoi, S. R., Saikia, G., Sultana, S. Y., Ahmed, K., and Islam, N. S. A sustainable approach towards solventless organic oxidations catalyzed by polymer immobilized Nb(V)-peroxido compounds with H_2O_2 as oxidant. ***Molecular Catalysis***, 516:111988, 2021.

Other Publications:

1. Sultana, S. Y., **Talukdar, H**., Borah, B. J., Sharma, M., and Islam, N. S. Synthesis, structure and catalytic activity of new oxovanadium (V) complexes with deferiprone and N, N-donor ligands. ***Inorganica Chimica Acta***, 534:120813, 2022.
2. Saikia, G., **Talukdar, H.**, Ahmed, K., Gour, N. K., and Islam, N. S. Tantalum(v) peroxido complexes as phosphatase inhibitors: a comparative study vis-a-vis peroxidovanadates. ***New Journal of Chemistry***, 45(29):12848-12862, 2021.
3. Saikia, G., Ahmed, K., Rajkhowa, C., Sharma, M., **Talukdar, H.**, and Islam, N. S. Polymer immobilized tantalum(V)-amino acid complexes as selective and recyclable heterogeneous catalysts for oxidation of olefins and sulfides with aqueous H_2O_2. ***New Journal of Chemistry***, 43:17251-17266, 2019.

4. Saikia, G**.**, Ahmed, K., Gogoi, S. R., Sharma, M., **Talukdar, H.**, and Islam, N. S. A chitosan supported peroxidovanadium(V) complex: Synthesis, characterization and application as an eco-compatible heterogeneous catalyst for selective sulfoxidation in water. ***Polyhedron***, 159:192-205, 2019.
5. Ahmed, K., Saikia, G**.**, Paul, S., Baruah, S. D., **Talukdar, H.**, Sharma, M., and Islam, N. S. Water-soluble polymer anchored peroxotitanates as environmentally clean and recyclable catalysts for mild and selective oxidation of sulfides with H_2O_2 in water. ***Tetrahedron***, 75(44):130605, 2019.
6. Ahmed, K., Saikia, G., Begum, P., Gogoi, S. R., Sharma, M., **Talukdar, H.**, and Islam, N. S. Selective and green sulfoxidation in water using a new chitosan supported Mo(VI) complex as heterogeneous catalyst. ***ChemistrySelect***, 3(44):12563-12575, 2018.

LIST OF CONFERENCES ATTENDED

- National conference on Sustainability, Medicine, and Clean Energy (SMCE), organized by Department of Chemical Sciences, Tezpur University, 1st March 2022 (**Oral presentation)**.
- International conference on Emerging Trends in Chemical Sciences (ETCS), organized by Department of Chemistry, Gauhati University, 13-15th February, 2020 (**Poster presentation**).
- International conference on Modern Trends in Inorganic Chemistry (MTIC XVIII), organized by IIT Guwahati in association with Gauhati University and Tezpur University, 11-14th December, 2019 (**Poster presentation**).

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Oxido- and mixed-ligand peroxido complexes of niobium(V) as potent phosphatase inhibitors and efficient catalysts for eco-friendly styrene epoxidation†

Hiya Talukdar, Sandhya Rani Gogoi, Sazida Yasmin Sultana, Reshma Begum, Dikshita Dowerah, Bipul Sarma and Nashreen S. Islam *

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The present study describes the facile synthesis and comprehensive characterization of new oxido and peroxidoniobium(V) complexes with biogenic ligands, maltol (malt) and deferiprone (def) in their co-ordination sphere, *viz.*, $[NbO(malt)_3]_2 \cdot 9H_2O$ (**1**), $Na_2[Nb(O_2)_3(malt)] \cdot H_2O$ (**2**) and $Na_2[Nb(O_2)_3(def)] \cdot 2H_2O$ (**3**). The complexes were characterized using various analytical and spectroscopic techniques (FTIR, Raman, NMR, UV-visible, TGA, ICP-OES and elemental analysis). The charge neutral complex **1** was further characterized by single crystal XRD analysis, and the proposed structures of the peroxidoniobium (pNb) complexes **2** and **3** were validated by density functional theory (DFT) studies. A comparative investigation on the *in vitro* effect of the title compounds and a set of previously reported polymer-anchored peroxidoniobium complexes, $[Nb(O_2)_3(sulfonate)_2]^{3-}$-PSS [PSS = poly(sodium 4-styrene sulfonate)] (**5**), $[Nb_2(O_2)_6(carboxylate)_2]^{4-}$-PA [PA = poly(sodium acrylate)] (**6**) and $[Nb(O_2)_3(carboxylate)]^{2-}$-PMA [PMA = poly(sodium methacrylate)] (**7**), on the activity of the model enzyme wheat thylakoid acid phosphatase has revealed that each of the compounds is an effective inhibitor of the enzyme (IC_{50} values varying within the range 1–64 μM). The results of the detailed enzyme kinetic study demonstrated that the compounds induce their inhibitory effect *via* distinct pathways. The oxidoniobium complex **1** as well as polymer-anchored pNb complexes acted as classical non-competitive inhibitors of ACP, whereas the monomeric pNb complexes emerged as mixed inhibitors of the enzyme ($K_{ii} > K_i$). Notably, the complexes serve as excellent recyclable catalysts for selective styrene epoxidation with H_2O_2, affording 99% styrene conversion, ≥98% epoxide selectivity and a high turnover number of 1740 under eco-friendly solventless conditions.

Introduction

Niobium being a bioinert and non-toxic metal with a very high LD_{50} value,[1,2] utility of Nb-based materials in the field of medicinal and biological chemistry is not new. Oxides of niobium have been documented to be chemically and thermally stable, biocompatible, and hypoallergenic materials with great biological features.[1] Markedly, vanadate and niobate have been reported as strong inhibitors of the sarcoplasmic reticulum (SR) Ca^{2+}-ATPase that can influence a variety of cellular processes, including calcium homeostasis.[3] Compounds of Nb have also been investigated for antibacterial, antioxidant and anti-cancer activities.[4,5] Heteropolytungstate substituted with niobium was documented to be an effective anti-hepatitis B agent.[6] Moreover, Nb–oxide materials have been gaining a great deal of importance due to their versatility as water-tolerant catalysts in a variety of organic oxidations with H_2O_2, such as oxidation of thioethers,[7] alcohols,[8,9] amines,[10] and furfural,[11] as well as olefin epoxidation.[12–15] Design and synthesis of water-soluble Nb(V)-based compounds still remains a notable challenge and a matter of great demand mainly due to their potential use as precursors for obtaining Nb-based oxide materials for advanced technology implementations.[16,17] In fact, peroxidoniobates have been recognised as water-soluble valued precursors for developing Nb-based oxide materials.[16,17] However, in spite of Nb being a member of the

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† Electronic supplementary information (ESI) available: Characterization of the synthesized complexes, optimization of reaction conditions for styrene epoxidation, details of materials and methods and cartesian coordinates of optimized structures of **2** and **3**. CCDC 2149737 and 1426204. For ESI and crystallographic data in CIF or other electronic format see DOI: **https://doi.org/10.1039/d3dt01177a**

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Organic-solvent-free oxidation of styrene, phenol and sulfides with H_2O_2 over eco-friendly niobium and tantalum based heterogeneous catalysts

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Phenol hydroxylation
Sulfoxidation

ABSTRACT

Immobilization of triperoxido derivatives of Nb(V) and Ta(V) on chitosan, an abundant and renewable support material, afforded a pair of stable heterogeneous catalysts, which could be successfully implemented in a variety of organic oxidations under ecologically sustainable organic-solvent-free conditions. The catalysts were extensively characterized by elemental analysis, SEM-EDX, powder XRD, XPS, BET, TG-DTG, FT-IR, Raman and NMR analysis. The supported catalysts showed excellent activity in the non-solvent epoxidation of styrene with H_2O_2 to provide 96% conversion with nearly 100% selectivity of the desired epoxide and a high TON value of 260 at room temperature. Moreover, phenol was selectively converted into 100% dihydroxybenzene (HQ:CT = 2:1) at ambient temperature, in absence of organic solvent, with a TON value of 80. In addition, both the catalysts were highly active towards the oxidation of a diverse range of sulfides such as aromatic, aliphatic, vinylic, allylic, and alcoholic sulfides to chemoselectively produce the desired sulfoxides in an aqueous medium with a TON value as high as 1900. The heterogeneous nature of the insoluble catalysts was confirmed by a hot filtration test. The catalysts are stable, water tolerant and easily recyclable at least up to five successive cycles of epoxidation and sulfoxidation with undiminished activity and selectivity.

Introduction

Selective oxidative transformations of organic substrates such as epoxidation of olefins, hydroxylation of phenol (PH) into hydroquinone (HQ) and catechol (CT), as well as oxidation of thioethers into sulfoxide/sulfone, represent some of the most essential and industrially important processes in organic synthesis [1–5]. The resulting oxygenated products, *viz.*, epoxy compounds, sulfoxides/sulfones, as well as CT and HQ serve as key intermediates or precursors to a vast range of bio-active molecules [3–6], fine and commodity chemicals [1,2,7]. In addition, phenol being toxic, carcinogenic, and less biodegradable industrial waste [8,9], from the environmental standpoint, there has been tremendous emphasis on the transformation of phenol to value-added products. The phenomenal progress witnessed during the past decades in the field of catalytic organic oxidations resulted in the emergence of a plethora of effective and high performing transition metal-based catalyst systems for accomplishing the aforementioned types of organic oxidations [1,10–18]. Nevertheless, methods which can satisfy all the requirements suitable for industrial goals (e.g., high productivity and selectivity along with cost efficiency and environmental acceptability) remain mostly elusive [1,12,14,15,18]. Thus, the uninterrupted quest for selective, sustainable and energy-efficient oxidation strategies which are compatible with benign solvent and green reagents, still continues [13,18,19].

In this regard, solvent-free organic oxidations facilitated by recyclable transition metal-based catalysts have emerged as excellent cost-effective strategies which can contribute significantly toward waste minimization and environmental protection [20–25]. Lately, a considerable number of innovative and active heterogeneous catalysts, mostly based on metals such as Mn, Ni, Ti, V, Mo and W, have been reported, especially for the solvent-less epoxidation of olefins [20–26]. However, majority of the reported non-solvent processes utilized toxic and volatile organic hydroperoxides like cumene hydroperoxide (CHP) and *tert*-butyl hydroperoxide (TBHP) as oxidizing agents under anhydrous condition and required elevated temperature for attaining high activity [21–23,25,26]. These factors significantly compromise the sustainability standard of such otherwise effective procedures.

Aqueous H_2O_2, with its high oxygen content, has been recognized as the greener and more desirable choice among the variety of available terminal oxidants as it's economical, non-polluting and

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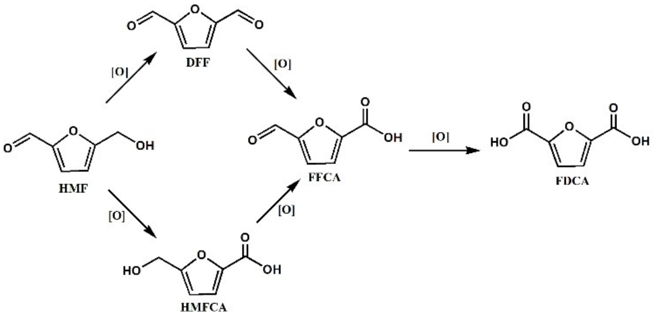
Selective and Mild Oxidation of 5-Hydroxymethylfurfural to 5-Hydroxymethyl-2-furancarboxylic Acid over Organic Polymer-Supported Peroxidoniobium(V) Catalysts

Hiya Talukdar, Sazida Yasmin Sultana, Arnab Kalita, and Nashreen S. Islam*[a]

Niobium-based homogeneous and heterogeneous catalysts were prepared by immobilizing triperoxidoniobium, $[Nb(O_2)_3]^-$ species on poly(sodium methacrylate), a linear water-soluble polymer, and glycine functionalized poly(styrene-divinylbenzene), a cross-linked polymer resin, respectively. The compounds were characterized by elemental analysis, NMR (^{1}H, ^{13}C, and ^{93}Nb), FTIR, Raman, XRD, XPS, SEM, EDX, UV-Visible, BET, and TGA analysis. The catalysts were successfully applied in the targeted synthesis of 5-hydroxymethyl-2-furancarboxylic acid (HMFCA) *via* 5-hydroxymethylfurfural (HMF) oxidation with H_2O_2 as oxidant, under eco-compatible reaction condition. Both the catalysts displayed excellent activity with 100% conversion of HMF to yield HMFCA with 100% selectivity. The oxidation protocol provided the highest TON and TOF values of 50 and of 78 h^{-1}, respectively. The heterogeneity of the insoluble catalyst was confirmed by a hot filtration test. The heterogeneous catalyst showed impressive recyclability at least up to five consecutive cycles without any significant alteration in its activity or HMFCA selectivity. Overall, the use of water as a solvent, environmentally benign H_2O_2 as oxidant, reasonably low catalyst: substrate ratio, workable reaction temperature (60 °C), and acceptable reaction time (1.5 h), are the distinct green attributes of the developed catalytic procedure.

Introduction

Over the past decade, enormous efforts have been dedicated to exploiting the abundant and renewable biomass resources for the production of sustainable biofuels and generating bulk and fine chemicals to overcome the growing scarcity of non-renewable fossil resources such as oil and natural gas.[1] 5-Hydroxymethyl-2-furfural (HMF), the key platform molecule acting as a link between biomass and chemicals, has been considered as the most suitable bio-derived building block to reduce the dependence on non-renewable petrochemical resources, owing to its ready availability from biorefinery carbohydrates.[2] Myriads of reports are available pertaining to the oxidation of HMF to a large variety of value-added compounds such as 5-hydroxymethyl-2-furancarboxylic acid (HMFCA), 2,5-diformylfuran (DFF), 5-formyl-2-furancarboxylic acid (FFCA), levulinic acid (LA) and 2,5-furandicarboxylic acid (FDCA) (Scheme 1) by using various biological[3] and chemical catalysts.[4] All of these HMF derivatives are valuable precursors for bioplastics,[5] functional polymers,[4b,c,6] pharmaceuticals,[4b,c,7] biofuel additives, etc.[4b,c,8] Recently, Kucherov and the group comprehensively reviewed the advancements in the field of biomass-derived C6-furanic platform chemicals, mainly by focusing on the significant chemical reactions for the sustainable processing of biomass.[8a]



Scheme 1. Schematic representation of biomass conversion into value-added chemicals.

Hydroxymethyl-2-furancarboxylic acid (HMFCA) is a relatively less explored product formed by the selective oxidation of the aldehydic group of HMF (Scheme 1).[3a,8a,9] The partially oxidized HMFCA, in addition to being an intermediate in FDCA synthesis and a useful monomer for a variety of polyesters,[6] is also known to exhibit antitumor and antimicrobial activities.[3a,7] However, in contrast to substantial research on the synthesis of FDCA and DFF from HMF,[2b,4b,c,8a,c] there are much fewer reports dealing with the targeted synthesis of HMFCA.[9,10] This is likely to be due to the difficulty encountered in the selective oxidation of the formyl group of HMF into carboxylic acid without affecting its alcohol functional group.[10c] Nevertheless, apart from the classic Cannizzaro reaction,[11] a number of promising catalytic methodologies have been developed lately for the oxidation of HMF to HMFCA.[9,10,12] Aerobic oxidation of HMF to HMFCA with 87% selectivity was reported by Zhang *et al.* using a montmorillonite K-10 clay-supported molybdenum catalyst in toluene.[10c] The majority of the available

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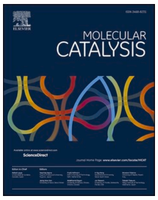

A sustainable approach towards solventless organic oxidations catalyzed by polymer immobilized Nb(V)-peroxido compounds with H_2O_2 as oxidant

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A B S T R A C T

New heterogeneous catalysts comprising of peroxidoniobium(V) complexes immobilized on amino acid grafted cross-linked poly(styrene-divinylbenzene) resin has been developed. Results of FTIR, Raman, NMR, XPS, XRD, EDX, SEM, BET, TGA, and elemental analysis confirmed the successful anchoring of triperoxidoniobium(V), $[Nb(O_2)_3]^-$ species to the host polymer *via* the pendant amino acid groups. The supported catalysts exhibited excellent performance in epoxidation of styrene and a range of cyclic and terpenic compounds under environmentally acceptable solvent-free condition, with aqueous H_2O_2 as oxidant. The catalytic protocols provided excellent conversion to the desired epoxide (up to 100%) with selectivity > 99%, TON as high as 1000, and high H_2O_2 utilization efficiency (92–97%). Moreover, the catalysts efficiently facilitated chemoselective solvent-free oxidation of a variety of thioethers to sulfones at room temperature. Simple operational strategy, easy recyclability for multiple reaction cycles with the consistent activity-selectivity profile are the additional significant attributes of the developed catalytic processes.

1. Introduction

Among the vast range of organic oxidations, epoxidation of olefins, as well as oxidation of organosulfur compounds to sulfoxide or sulfone, are outstanding industrial transformations representing the basis of a variety of chemical processes for the production of commodity and fine chemicals [1–7]. Moreover, the sulfide-oxidation based procedure of oxidative desulfurization has been recognized as a greener alternative method for the removal of sulfur from fuel feedstock [8,9]. The mounting environmental concerns in recent times have triggered a dramatic upsurge in interest in the development of safer and sustainable alternative synthetic routes to target compounds [10–13]. The use of heterogeneous catalysts that support clean and energy-efficient transformations and can perform optimally in absence of hazardous organic solvents, are emerging as issues of paramount importance in green synthetic strategy.

Solvent-free organic synthesis in addition to being cost-effective, contributes significantly towards waste minimization and environmental protection and thus displays tremendous application potential for larger-scale chemical processes [14–19]. Scores of innovative and promising supported transition metal heterogeneous catalysts have been reported over the recent years for olefin epoxidation under solvent less condition [14–19]. However, in order to attain high activity, the majority of these protocols required to employ organic hydroperoxides e.g., *tert*-butyl hydroperoxide (TBHP) and cumene hydroperoxide (CHP) as oxidants under anhydrous condition [14–17]. It is intriguing to note that, niobium-based solid catalysts so far have rarely been tested in solvent free organic oxidations, although such systems were often reported to display superior activity when aqueous hydrogen peroxide was used as a terminal oxidant [3,20-26]. This feature offers a significant advantage as catalytic epoxidation of olefins with aqueous H_2O_2, an ideal non-polluting, and cost-effective oxidant, is the focus of much contemporary research [10–13].

Work from several laboratories has demonstrated that silica supported Nb(V) catalysts are highly stable towards hydrolysis and metal leaching and such systems were observed to provide faster rates of oxidation compared to the more standard Ti-SiO_2 catalysts [20–26]. The advancement in liquid phase olefin epoxidation over niobium and tungsten-based catalysts has been comprehensively reviewed by Yan *et al.* recently [3]. It has been noted that notwithstanding the considerable progress in improving the activity of nanostructured Nb and W catalysts, poor selectivity and stability of such systems are still major issues to

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