Closure Report

File Number : EMR/2016/003158

Project Title : Development of Polymer Supported Niobium and Tantalum Based catalysts for Organic Oxidations under Ecologically Sustainable Reaction Conditions

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Total Sanctioned 43,40,506 (INR)

Total Released Amount 43,86,565 (INR)

Start Date of the 18 Aug, 2017

Date of completion: 17 Aug, 2020 (36 months)

Approved Objectives :

- Major objectives of the proposed research programme are outlined below: (i) To immobilize pNb or pTaspecieson insoluble cross-linked polymer resins in order to generate safer, efficient and recoverable heterogeneous catalysts for oxidative organic transformations. (ii) To anchor pNb or pTa species to water soluble linear polymers in order to gain an access to water soluble and water tolerant oxidation catalysts compatible with aqueous reaction medium. (iii) To comprehensively characterize the synthesized immobilized compounds and to determine their stability in solid state as well as in solution (iv) To establish eco-compatible catalytic protocols using the synthesized supported complexes for the following organic oxidative transformation: a) Selective oxidation of 5-hydroxymethylfurfural (HMF) to diformylfuran (DFF) or furandicarboxylic acid (FDCA). b) Selective epoxidation of alkenes. c) Selective oxidation of thioethers and dibenzothiophene to the corresponding sulfoxide or sulfone. (v) To undertake a comparative studyon the efficacy of the developed homogeneous as well as heterogeneous polymer supported catalysts with respect to the targeted reactions.

Deviation made from original objectives (If Any) :

None

Ph.D. Produced/ Likely to be : 1

Technical Personnel Trained : 0

Total Expenditure : 43,40,506 (INR)

Concise Research Accomplishment :

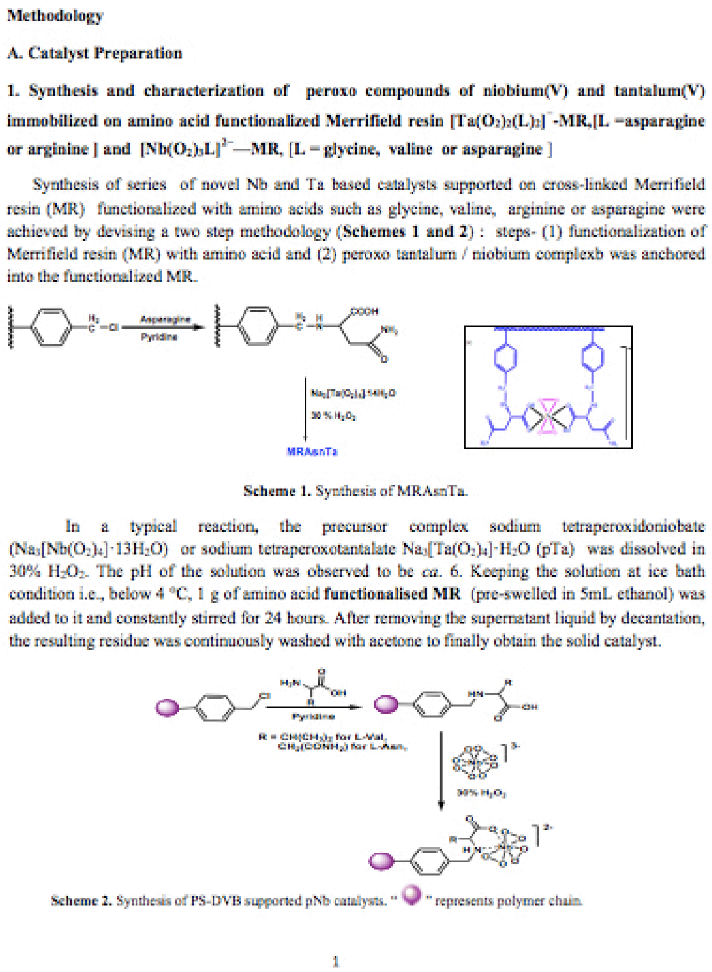
Series of novel homogeneous and heterogeneous catalyst systems have been developed by grafting peroxometal species viz., Nb(V) or Ta(V) on polymer supports. Variety of organic polymersupports ranging from natural biopolymer, linear soluble polymers to insoluble cross-linked polymer resins have been exploited for the first time to generate the immobilised catalysts. The efficacy of the newly developed catalysts have been explored with respect to the following orgainc oxidative transformations. • selective epoxidation of alkene with green oxidant H_2O_2 under solvent-free condition. • selective oxidation of biomass derived 5-hydroxy methyl-2-furfural (HMF) to 5-hydroxy methyl-2-furan carboxylic acid (HMFCA) with H_2O_2. • clean conversion of sulfides to high purity sulfoxide or sulfone by H_2O_2, in water or under solvent free eco-sustainable reaction conditions In addition to their remarkable efficiency, the catalytic strategies are characterized by simplicity, versatility and sustainability.

Closure Details

Experimental/ Theoretical Investigation carried out

* Full details of experimental methods etc., along with tables and figures, are being provided in the attached file: OTHER INFORMATION (ANNEXURE I) Methodology A. Catalyst Preparation 1. Synthesis and characterization of peroxo compounds of niobium(V) and tantalum(V) immobilized on amino acid functionalized Merrifield resin [Ta(O2)2(L)2]-MR,[L =asparagine or arginine] and [Nb(O2)3L]2—MR, [L = glycine, valine or asparagine] Synthesis of series of novel Nb and Ta based catalysts supported on cross-linked Merrifield resin (MR) functionalized with amino acids such as glycine, valine, arginine or asparagine were achieved by devising a two step methodology (Schemes 1 and 2) : steps- (1) functionalization of Merrifield resin (MR) with amino acid and (2) peroxo tantalum / niobium complexb was anchored into the functionalized MR. Scheme 1. Synthesis of MRAsnTa. In a typical reaction, the precursor complex sodium tetraperoxidoniobate (Na3[Nb(O2)4]·13H2O) or sodium tetraperoxotantalate Na3[Ta(O2)4]·H2O (pTa) was dissolved in 30% H2O2. The pH of the solution was observed to be ca. 6. Keeping the solution at ice bath condition i.e., below 4 °C, 1 g of amino acid functionalised MR (pre-swelled in 5mL ethanol) was added to it and constantly stirred for 24 hours. After removing the supernatant liquid by decantation, the resulting residue was continuously washed with acetone to finally obtain the solid catalyst. 2. Synthesis and characterization of Chitosan supported niobium(V), tantalum(V) and molybdenum(VI) complexes The peroxo compounds of d0 metal ions of the type [M(O2)3(NH2)(OH)]-chitosan [M= Nb(V), Ta (V) and Mo(VI)] supported on a natural chelating polymer, chitosan were synthesised and comprehensively characterized by elemental analysis (CHN, ICP-OES, energy dispersive X-ray spectroscopy), spectral studies (FT-IR, Raman, 13C NMR, diffuse reflectance UV–Vis and XPS), SEM, XRD, Brunauer–Emmett–Teller (BET) and thermogravimetric analysis (TGA). Apart from being thermally stable, the compoundis water-tolerant, non-hygroscopic. and stable for several weeks. The typical procedure to obtain Ta(O2)3(NH2)(OH)]-chitosan comprises of addition of chitosan to the reaction solution containing tetraperoxotantalate and 30% H2O2. The pH of the reaction mixture was recorded to be ca. 7.3. Dilute HNO3 (2 N) was added dropwise to reach pH of ca. 7. The reaction mixture was kept under ice-cool condition for 24 h with occasional stirring. After the specified reaction time, the supernatant liquid was decanted out from the reaction solution and the remained residue was treated with acetone repeatedly to obtain the solid catalysts. Fig. 1 Proposed structure of ChpTa. (* represents polymer chain) 3. Synthesis and characterization of a new Nb (V) and Ta(V) macromolecular complex immobilized on watersoluble polymer A new peroxoniobium(V) species immobilized on water soluble non-crosslinked polymer (WSP) formulated as, [Nb(O2)3(sulfonate)2]-PSS [PSS = poly(sodium styrene sulfonate)] (PSSNb) has been synthesized from the reaction of sodium tetraperoxoniobate (NaNb) with 30% H2O2 and the macromolecular ligand poly(sodium styrene sulfonate) in an aqueous medium (Fig. 2) Facile Synthesis of a pair of peroxotantalate incorporated water soluble macro complexes of the type, [Ta(O2)3(carboxylate)]-PA, [PA= poly(sodium acrylate)] (PATa) (5.2), [Ta(O2)3(sulfonate)2]-PSS, PSS= poly(sodium 4-styrene sulfonate) (PSSTa) (5.3) has been achieved by reacting Na3[Ta(O2)4]·H2O (pTa) with the respective WSP in presence of 30% H2O2 in water. Fig. 2. Proposed structure of PSSNb. 4. Soluble Polymer Anchored Peroxotitanium(IV) compounds : synthesis and characterization We have introduced a set of peroxotitanium(pTi) compounds anchored to water soluble polymer (WSP) matrices viz., poly(sodium acrylate) (PA) poly(sodium methacrylate) (PMA) or poly(sodium 4-styrene sulfonate) (PSS). The macrocomplexes of thetype, [Ti2(O2)2O2(OH)2(carboxylate)]-PA(PATi) (3.1),[Ti2(O2)2O2(OH)2(carboxylate)]-PMA (PMATi) (3.2) and [Ti2(O2)2O2(OH)2(sulfonate)]-PSS (PSSTi) (3.3) were synthesized by reacting freshly prepared titanic acid, with 30 % H2O2 in presence of the respective WSP, The pH was maintained atca. 4 which was found to be crucial for the formation of the μ-oxo peroxotitanium(IV) complexes and their co-ordination to the pendant functional groups such as carboxylate or sulfonate, of the polymer chain (Fig 3) . B. Catalyst Characterization The catalysts were characterized by a combination of analytical and spectroscopic techniques viz. FT-IR, Raman, 13C NMR, powder XRD, ICP-OES, SEM-EDX, XPS, BET, and TG-DTG analysis. C. Catalytic activity of the supported catalysts : Performance of the catalysts in the following organic oxidations were examined : a) Selective oxidation of 5-hydroxymethylfurfural (HMF) to 5-hydroxy methyl-2-furan carboxylic acid (HMFCA). b) Selective epoxidation of alkenes. c) Selective oxidation of thioethers and dibenzothiophene to the corresponding sulfoxide or sulfone. C.1 Optimization of reaction conditions: The reaction conditions were optimized in each case by investigating the effect of each of the reaction parameters viz., nature of solvent, reaction temperature, reaction time, ratios of amounts of catalyst : substrate as well as substrate : oxidant on the product selectivity, yield and rate

of conversions. C.2 The products obtained will be analyzed and characterized by GC, GC-MS and HPLC techniques, IR, UV-Vis, NMR spectroscopy and melting point / boiling determination,. C.3 Catalytic efficiency in terms of turn over number (TON) and turn over frequency (TOF) were determined. C.4 Test for stability of the catalyst – catalyst recyclability: Stability of the catalysts in terms of their regeneration and reusability were assessed. For practical utility of a catalytic process the longevity of the catalyst and its potential for regeneration and reusability are of fundamental importance. Scalability: Suitability of the developed protocols for larger scale application were explored by conducting the reactions under optimized conditions.



Methodology

A. Catalyst Preparation

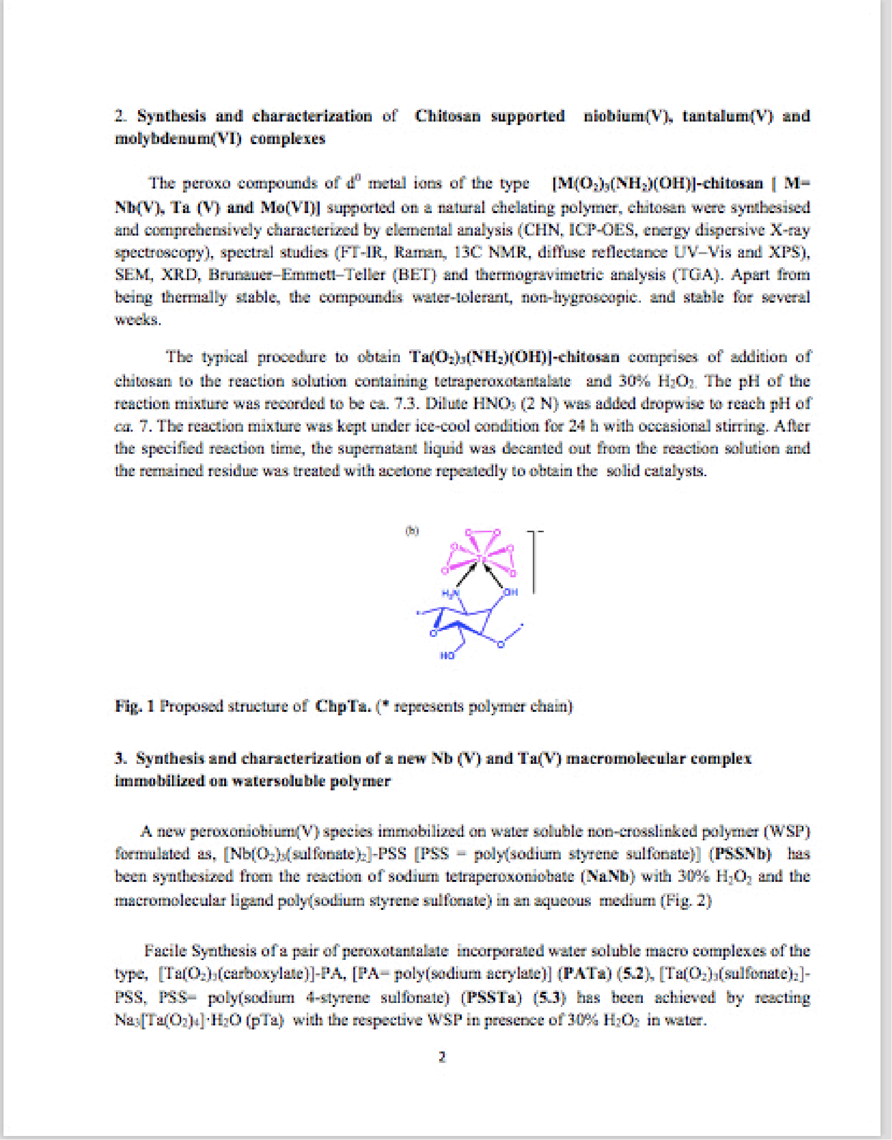
1. Synthesis and characterization of peroxo compounds of niobium(V) and tantalum(V) immobilized on amino acid functionalized Merrifield resin $[Ta(O_2)_2(L)_2]^-$-MR,[L =asparagine or arginine] and $[Nb(O_2)_3L]^{2-}$—MR, [L = glycine, valine or asparagine]

Synthesis of series of novel Nb and Ta based catalysts supported on cross-linked Merrifield resin (MR) functionalized with amino acids such as glycine, valine, arginine or asparagine were achieved by devising a two step methodology (**Schemes 1 and 2**) : steps- (1) functionalization of Merrifield resin (MR) with amino acid and (2) peroxo tantalum / niobium complexb was anchored into the functionalized MR.

Scheme 1. Synthesis of MRAsnTa.

In a typical reaction, the precursor complex sodium tetraperoxidoniobate ($Na_3[Nb(O_2)_4]\cdot 13H_2O$) or sodium tetraperoxotantalate $Na_3[Ta(O_2)_4]\cdot H_2O$ (pTa) was dissolved in 30% H_2O_2. The pH of the solution was observed to be *ca.* 6. Keeping the solution at ice bath condition i.e., below 4 °C, 1 g of amino acid **functionalised MR** (pre-swelled in 5mL ethanol) was added to it and constantly stirred for 24 hours. After removing the supernatant liquid by decantation, the resulting residue was continuously washed with acetone to finally obtain the solid catalyst.

Scheme 2. Synthesis of PS-DVB supported pNb catalysts. " ● " represents polymer chain.



2. Synthesis and characterization of Chitosan supported niobium(V), tantalum(V) and molybdenum(VI) complexes

The peroxo compounds of d^0 metal ions of the type **$[M(O_2)_3(NH_2)(OH)]$-chitosan [M= Nb(V), Ta (V) and Mo(VI)]** supported on a natural chelating polymer, chitosan were synthesised and comprehensively characterized by elemental analysis (CHN, ICP-OES, energy dispersive X-ray spectroscopy), spectral studies (FT-IR, Raman, 13C NMR, diffuse reflectance UV–Vis and XPS), SEM, XRD, Brunauer–Emmett–Teller (BET) and thermogravimetric analysis (TGA). Apart from being thermally stable, the compoundis water-tolerant, non-hygroscopic. and stable for several weeks.

The typical procedure to obtain **$Ta(O_2)_3(NH_2)(OH)]$-chitosan** comprises of addition of chitosan to the reaction solution containing tetraperoxotantalate and 30% H_2O_2. The pH of the reaction mixture was recorded to be ca. 7.3. Dilute HNO_3 (2 N) was added dropwise to reach pH of *ca.* 7. The reaction mixture was kept under ice-cool condition for 24 h with occasional stirring. After the specified reaction time, the supernatant liquid was decanted out from the reaction solution and the remained residue was treated with acetone repeatedly to obtain the solid catalysts.

Fig. 1 Proposed structure of **ChpTa.** (* represents polymer chain)

3. Synthesis and characterization of a new Nb (V) and Ta(V) macromolecular complex immobilized on watersoluble polymer

A new peroxoniobium(V) species immobilized on water soluble non-crosslinked polymer (WSP) formulated as, $[Nb(O_2)_3(sulfonate)_2]$-PSS [PSS = poly(sodium styrene sulfonate)] (**PSSNb**) has been synthesized from the reaction of sodium tetraperoxoniobate (**NaNb**) with 30% H_2O_2 and the macromolecular ligand poly(sodium styrene sulfonate) in an aqueous medium (Fig. 2)

Facile Synthesis of a pair of peroxotantalate incorporated water soluble macro complexes of the type, $[Ta(O_2)_3(carboxylate)]$-PA, [PA= poly(sodium acrylate)] (**PATa**) (**5.2**), $[Ta(O_2)_3(sulfonate)_2]$-PSS, PSS= poly(sodium 4-styrene sulfonate) (**PSSTa**) (**5.3**) has been achieved by reacting $Na_3[Ta(O_2)_4]\cdot H_2O$ (pTa) with the respective WSP in presence of 30% H_2O_2 in water.

Detailed Analysis of result

* Detailed Analysis of results are provided in the attached file: OTHER INFORMATION (ANNEXURE II) Detailed analysis of Results : (contributions made towards increasing the state of knowledge of the subject) 1. Niobium(V)-amino acid complexes supported on organic polymers as sustainable catalysts for solventless olefin epoxidation and sulfide oxidation 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 confirm the successful anchoring of triperoxidoniobium(V), [Nb(O2)3]- to the host polymer via the pendant amino acid groups. Our findings are summarized in the following Figure. Figure 1 : Solventless olefin epoxidation and sulfide oxidation catalyzed by Niobium(V)-amino acid complexes supported on organic polymers. 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 H2O2 as oxidant. The catalytic protocols provided high conversion to the desired epoxide (up to 100%) with selectivity > 99%, TOF as high as 1330 h-1 and high H2O2 utilisation efficiency (92-97%). The results are depicted in Table 1. Moreover, the catalysts efficiently facilitated chemoseltcive solvent-free oxidation of variety of thioethers to sulfones with H2O2 at room temperature. Simple operational strategy, easy recyclability for multiple reaction cycles with consistent activity-selectivity profile are the additionl significant attributes of the developed catalytic processes 2. Tantalum(V) peroxides immobilized on asparagine or arginine grafted polymer resin as highly selective heterogeneous catalysts for organic oxidations under eco-compatible reaction conditions Polymer supported heterogeneous peroxotantalum(V) catalysts were developed by anchoring Ta(V)-diperoxo species to chloromethylated poly(styrene-divinylbenzene) resin functionalized with amino acids, asparagine and arginine. The structurally well-defined catalysts, [Ta(O2)2(L)2]¯-MR, [L =asparagine (Catalyst 1) or arginine

(Catalyst 2) and MR=Merrifield resin] (Figure 1) displayed excellent activity and selectivity in alkene epoxidation as asparagines as well as sulfoxidation with aqueous 30% H2O2 under mild condition. Fig . 2. Tantalum(V) peroxides immobilized on asparagine or arginine grafted polymer resin as highly selective heterogeneous catalysts for organic oxidations with H2O2 Solvent-free epoxidation of olefines with aqueous H2O2 : The catalysts mediated epoxidation of olefins under solvent –free condition with high TOF and TON. We examined the performances of the catalysts with respect to their selectivity, reusability, TON and TOF and environmental compatibility. The oxidation of olefins viz, styrene, cyclohexene and norbornene has been achieved under solvent-free condition. No report appears to exist pertaining to alkene epoxidation catalyzed by Ta-based heterogeneous catalysts under solvent-less condition. Selective oxidation of sulphides to sulfoxides: The heterogeneous catalysts 1 and 2 also facilitated chemoselective oxidation of a broad range of organic sulphides to the desired sulfoxides in methnol, a relatively safer organic solvent, at ambient temperature. (Table 2) . Recyclability of the supported peroxotantalum catalysts: The immobilized catalysts are remarkably robust affording easy recyclability for epoxidation as well as sulfoxidation up to a minimum of five reaction cycles in each case with stable selectivity/activity profile. (Figure 1) 3. Merrifield resin supported Nb(V) and Ta(V) complexes as efficient heterogeneous catalysts for selective oxidation of biomass derived HMF to HMFCA Highly selective oxidation of biomass derived 5-hydroxy methyl-2-furfural (HMF) to 5-hydroxy methyl-2-furan carboxylic acid (HMFCA) using a set of peroxido complexes of Nb and Ta supported on amino acid functionalized Merrifield resin (MR) as catalysts. Results obtained after investigating a number of important reaction parameters demonstrated that under optimized condition it was possible to attain nearly 99% HMF conversion with 100% HMFCA selectivity within 30 min of reaction, using 12% H2O2 as oxidant at 60 0C, in water. The maximum TOF was observed to be of 198 h-1 . Thus compared to several reported methods on metal catalyzed HMFCA synthesis from HMF, our catalytic protocols offered a number of advantages with respect to conversion, selectivity and reaction conditions employed, as shown in the following Scheme 1. Scheme 1 : Oxidation of HMF to HMFCA by H2O2 using catalyst [Nb(O2)3(valine)]- MR. Fig 3. % HMF conversion vs. amount of H2O2 (eq.) for catalyst [Nb(O2)3(valine)]- MR. Reaction condition: 0.4 mmol of HMF (50 mg), catalyst(0.004 mmol of Nb, 13.3 mg), 1.6 mmol of NaOH (dissolved in 3 mL H2O), 60 0C in 3 mL water. 4. Macromolecular Nb(V) and Ta(V) anchored to water soluble polymer supports and their application as homogeneous catalysts in organic oxidations In this work, we have synthesised new water soluble polymer supported niobium and tantalum derivatives, [Nb(O2)3(sulfonate)2]-PSS [PSS = poly(sodium styrene sulfonate)] (catalyst 1), [Ta(O2)3(carboxylate)]-PA, [PA= poly(sodium acrylate)] (PATa) and [Ta(O2)3(sulfonate)2]-PSS, PSS= poly(sodium 4-styrene sulfonate) (PSSTa). The catalytic activities of the compounds were studied on two different organic oxidations- alkene epoxidation and sulfide oxidation under eco-compatible conditions. Apart from being high-yielding (maximum TOF OF 9600 h-1 obtained for dimethyl sulfide oxidation) and operationally simple, the additional environmentally significant characteristics which enhance the sustainability of the water-based oxidation protocol include: chemoselectivity of the catalysts towards oxidation for sulfides and easy recyclability of the catalyst with consistent activity and selectivity for several cycles of oxidation (Figure 4). Fig. 4. Macromolecular Nb(V) and Ta(V) anchored WSP supports as homogeneous catalysts in organic oxidations The macromolecular complexes efficiently catalyzed selective epoxidation of three different alkene substrates, viz. styrene, cyclohexene and norbornene with 30% H2O2 under solvent-less condition. Moreover, All the catalysts afforded oxidation of a number of structurally different sulfides substrates with impressive yield and turn over frequency under mild condition. Another salient feature of the catalysts is its chemoselectivity towards sulfur group in presence of other oxidation prone functionalities such as –C=C- and –OH group. The methodologies developed for both the oxidation reactions were devoid of organic co-solvent, co-catalysts or any other toxic auxiliaries to adhere to the green concept. The catalysts were recyclable with respect to sulfide oxidation with undiminished activity and selectivity, while in case of styrene oxidation, the activity of the catalysts were observed to decline after each run. 5. Peroxo compounds of Nb (V), Ta(V) and Mo(VI) anchored to biopolymer chitosan. Synthesis characterization and activity as heterogeneous catalyst for selective sulfoxidation in water Heterogeneous water-compatible and recyclable catalysts has been developed by immobilizing peroxometalates on natural biopolymer, chitosan for chemoselective and ecologically sustainable oxidation of sulphides to high purity sulfoxide in aqueous medium at room temperature (Scheme) . The oxidation protocol is high yielding, straightforward and halogen-free. Fig. 5 Chitosan supported Mo(VI) complex catalyzes selective sulfoxidation of thioethers 6. Water-soluble polymer anchored peroxotitanates as environmentally clean and recyclable catalysts for mild and selective oxidation of sulfides in water with H2O2 Anchoring of peroxotitanium species to non-cross linked linear polymers, poly(sodium acrylate) (PA) and poly(sodium methacrylate) (PMA) led to the successful synthesis of a pair of new, water-tolerant and recyclable catalysts of the type [Ti2(O2)2O2(OH)2]-L (L=PA or PMA), highly active in chemoselective sulfoxidation of organic sulfides with 30% H2O2 in aqueous medium at ambient temperature. The catalytic protocol, in addition to being high yielding (TOFs up to 11538 h-1) and operationally simple, is free from halogenated solvent and is environmentally clean and safe. The catalysts are sufficiently stable to afford easy recyclability for at least 10 consecutive reaction cycles of sulfoxidation with consistent activity selectivity profile. Oxidation of thioethers and dibenzothiophene (DBT) to respective high purity sulfoxide or sulfone could also be accomplished using the same catalysts by variation of reaction conditions. Considering the mild reaction conditions the TOF values obtained in the present study, reaching up to a highest value of 11,280 h-1, are indeed remarkable in comparison to most of the water-based catalytic sulfoxidations reported so far. Both the catalysts displayed high functional group tolerance towards sensitive groups such C=C and OH. Thus allylic and alcoholic sulfides were chemoselectively oxidized to yield targeted sulfoxide without affecting any other functional group transformation under the optimized condition. 7. Synthesis, structure and catalytic activity of new oxovanadium(V) complexes with deferiprone and N,N-donor ligands A pair of new water-soluble oxovanadium(V) complexes comprising of deferiprone (def) and N,N-donor ligands, 2,2-bipyridine (bpy) or 1,10-phenanthroline (phen), [VO2(def)(bpy)]H2O (1) and [VO2(def)(phen)]4H2O (2) were synthesized. The complexes were characterized by elemental analysis, spectral studies and single crystal X-ray diffraction analysis. The X-ray crystal structures of 1 and 2 reveal that both the complexes possess distorted octahedral coordination geometries with O4N2 coordination sphere around the vanadium center, and the deprotonated deferiprone occupying the equatorial plane. The complexes 1 and 2 efficiently catalyzed selective epoxidation of styrene with 30% H2O2 under ecologically sustainable organic solvent-free conditions, at ambient temperature. The catalysts afforded good styrene conversion and high TON value along with excellent epoxide selectivity (>99%). Recyclability of the catalysts at least up to three consecutive cycles without significant alteration in activity or selectivity, is an additional remarkable feature of the developed catalytic protocol.

Conclusions

The results of our investigation demonstrate for the first time that, • it is possible to generate highly efficient, recyclable and environmentally benign catalysts for organic oxidations, by immobilising peroxo complexes of Nb and Ta on macromolecular supports. • biopolymers and water soluble linear polymers can also serve as viable alternatives to insoluble cross-linked polymer supports for designing water-tolerant Nb and Ta based catalysts for organic oxidations. • polymer immobilised Nb and Ta based systems can effctively mediate epoxidation of alkenes and sulfide oxidation under organic solvent free condition. • The immobilised Nb and Ta systems catalyse selective oxidation of HMF to HMFCA with H2O2 in aqueous medium, with remarkable efficiency and selectivity. Simplicity in the method of synthesis of the catalysts using commercially available a starting materials, their recyclability for several catalytic cycles and excellent chemoselectivity are some of the environmentally significant characteristics of the catalysts.

Scope of future work

The developed catalysts are expected to be useful additions to the range of safer and environmentally suitable catalysts with the potential for accomplishing a broad range of oxidative organic transformations.

List of Publications (only from SCI indexed journals) :

Title of the Paper	List of Authors	Journal Details	Month & Year	Volume	Status	DOI No	Impact Factor
Selective and green sulfoxidation in water using a new chitosan supported Mo (VI) complex as heterogeneous catalyst	K.Ahmad, G. Saikia, P. Begum, S.R. Gogoi, M. Sharma, H. Talukdar and N.S.Islam	ChemistrySelect (International)	Nov-2018	3 (12563)	Published	10.1002/slct.201803000	
Synthesis, structure and catalytic activity of new oxovanadium(V) complexes with deferiprone and N, Ndonor ligands	S.Y.Sultana, H.talukdar, B.J.Borah, M.Sharma and N.S.Islam	INORGANICA CHIMICA ACTA (International)	Jan-2022		Accepted	doi.org/10.1016/j.ica, 2022.120813	2.545
Macromolecular metal complexes of Nb as catalysts for selective and eco-compatible oxidation of organic sulfides in water	S.R.Gogoi, K.Ahmad, G. Saikia and N.S.Islam	, J.Indian Chem.Soc., (Invited paper, Special issue on Organometallics and Catalysis) (Others)	Jul-2018	95 (801-812)	Published		
A sustainable approach towards solventless organic oxidations catalyzed by polymer immobilized Nb(V) peroxido compounds with HO as oxidant	Hiya Talukdar, S. R.Gogoi, G. Saikia, S.Y. Sultana, K. Ahmed, N.S. Islam	Molecular Catalysis (International)	Nov-2021	516 (111988)	Published	doi.org/10.1016/j.mcat.2021.111988	5.062
Polymer immobilized tantalum-aminoacid complexes as selective and recyclable heterogeneous catalysts for oxidation of lefines and sulfides with aqueous H2O2.	Saikia G., Ahmed K., Gogoi S. R., Sharma M., Talukdar H. and Islam N. S.,	NEW JOURNAL OF CHEMISTRY (International)	Nov-2019	43 (17251)	Published	DOI: 10.1039/C9NJO41806	3.069
Water-soluble polymer anchored peroxotitanates as environmentally clean and recyclable catalysts for mild and selective oxidation of sulfides with H2O2 in water	Ahmed K., Saikia G., Paul S., Baruah S. D., Talukdar H., Sharma M., Islam N. S	TETRAHEDRON (International)	Aug-2019	75 (130650)	Published	DOI: 10.1039/C8DT02433B	2.645

List of Papers Published in Conference Proceedings, Popular

Title of the Paper	List of Authors	Journal Details	Month & Year	Volume	Status	DOI No	Impact Factor
Not Available							

List of Patents filed/ to be filed :

Patent Title	Authors	Patent Type	Country/Agency Name	Patent Status	Application/ Grant No.
Not Available					

Equipment Details :

Equipment Name	Cost (INR)	Procured	Make & Model	Utilization %	Amount Spent	Date of Procurement
Minor Equipment	3,00,000	No		100	0	
Laptop/Computer	1,12,000	No		100	0	
Laser Printer	15,000	No		100	0	
High-Performance Liquid Chromatography (HPLC) System with UV detector	15,00,000	No		100	0	

Plans for utilizing the equipment facilities in

The equipment will be effectively utilised by the researchers of the Department including Ph.D students.

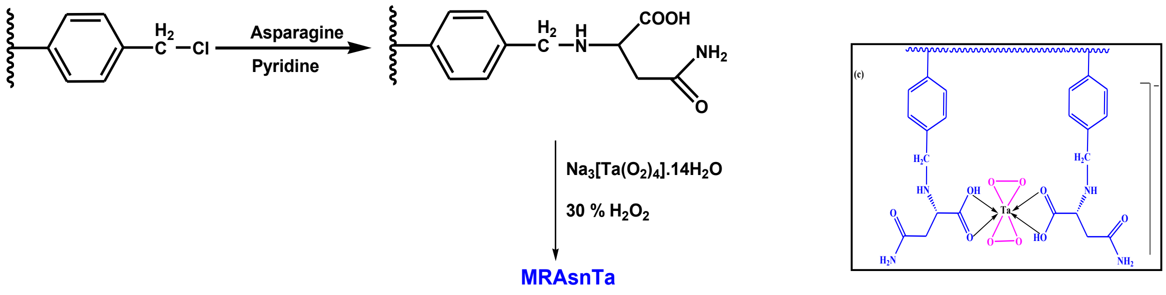
ANNEXURE I

Experimental Methods

A. Catalyst Preparation

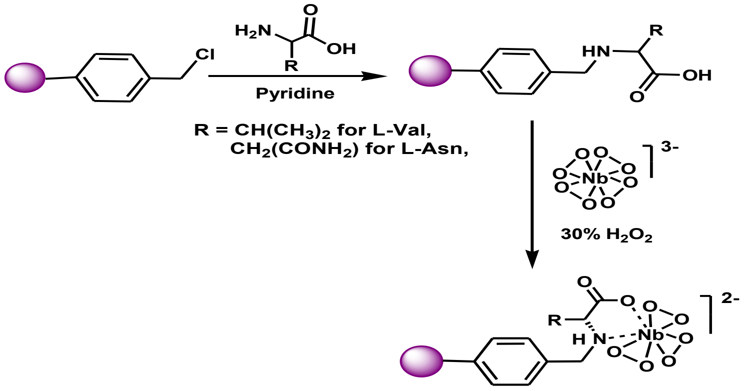
1. Synthesis and characterization of peroxo compounds of niobium(V) and tantalum(V) immobilized on amino acid functionalized Merrifield resin $[Ta(O_2)_2(L)_2]^{-}$-MR,[L =asparagine or arginine] and $[Nb(O_2)_3L]^{2-}$—MR, [L = glycine, valine or asparagine]

Synthesis of series of novel Nb and Ta based catalysts supported on cross-linked Merrifield resin (MR) functionalized with amino acids such as glycine, valine, arginine or asparagine were achieved by devising a two step methodology (**Schemes 1 and 2**) : steps- (1) functionalization of Merrifield resin (MR) with amino acid and (2) peroxo tantalum / niobium complexb was anchored into the functionalized MR.



Scheme 1. Synthesis of MRAsnTa.

In a typical reaction**,** the precursor complex sodium tetraperoxidoniobate $(Na_3[Nb(O_2)_4]\cdot 13H_2O)$ or sodium tetraperoxotantalate $Na_3[Ta(O_2)_4]\cdot H_2O$ (pTa) was dissolved in 30% H_2O_2. The pH of the solution was observed to be *ca.* 6. Keeping the solution at ice bath condition i.e., below 4 °C, 1 g of amino acid **functionalised MR** (pre-swelled in 5mL ethanol) was added to it and constantly stirred for 24 hours. After removing the supernatant liquid by decantation, the resulting residue was continuously washed with acetone to finally obtain the solid catalyst.



Scheme 2. Synthesis of PS-DVB supported pNb catalysts. “ ● ” represents polymer chain.

2. **Synthesis and characterization** of **Chitosan supported niobium(V), tantalum(V) and molybdenum(VI) complexes**

The peroxo compounds of d^0 metal ions of the type **$[M(O_2)_3(NH_2)(OH)]$-chitosan [M= Nb(V), Ta (V) and Mo(VI)]** supported on a natural chelating polymer, chitosan were synthesised and comprehensively characterized by elemental analysis (CHN, ICP-OES, energy dispersive X-ray spectroscopy), spectral studies (FT-IR, Raman, 13C NMR, diffuse reflectance UV–Vis and XPS), SEM, XRD, Brunauer–Emmett–Teller (BET) and thermogravimetric analysis (TGA). Apart from being thermally stable, the compoundis water-tolerant, non-hygroscopic. and stable for several weeks.

The typical procedure to obtain **$Ta(O_2)_3(NH_2)(OH)]$-chitosan** comprises of addition of chitosan to the reaction solution containing tetraperoxotantalate and 30% H_2O_2. The pH of the reaction mixture was recorded to be ca. 7.3. Dilute HNO_3 (2 N) was added dropwise to reach pH of *ca.* 7. The reaction mixture was kept under ice-cool condition for 24 h with occasional stirring. After the specified reaction time, the supernatant liquid was decanted out from the reaction solution and the remained residue was treated with acetone repeatedly to obtain the solid catalysts.

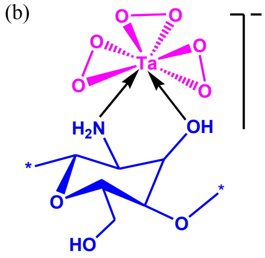


Fig. 1 Proposed structure of **ChpTa.** (* represents polymer chain)

3. Synthesis and characterization of a new Nb (V) and Ta(V) macromolecular complex immobilized on watersoluble polymer

A new peroxoniobium(V) species immobilized on water soluble non-crosslinked polymer (WSP) formulated as, $[Nb(O_2)_3(sulfonate)_2]$-PSS [PSS = poly(sodium styrene sulfonate)] (**PSSNb**) has been synthesized from the reaction of sodium tetraperoxoniobate (**NaNb**) with 30% H_2O_2 and the macromolecular ligand poly(sodium styrene sulfonate) in an aqueous medium (Fig. 2)

Facile Synthesis of a pair of peroxotantalate incorporated water soluble macro complexes of the type, $[Ta(O_2)_3(carboxylate)]$-PA, [PA= poly(sodium acrylate)] (**PATa**) (**5.2**), $[Ta(O_2)_3(sulfonate)_2]$-PSS, PSS= poly(sodium 4-styrene sulfonate) (**PSSTa**) (**5.3**) has been achieved by reacting $Na_3[Ta(O_2)_4]\cdot H_2O$ (pTa) with the respective WSP in presence of 30% H_2O_2 in water.

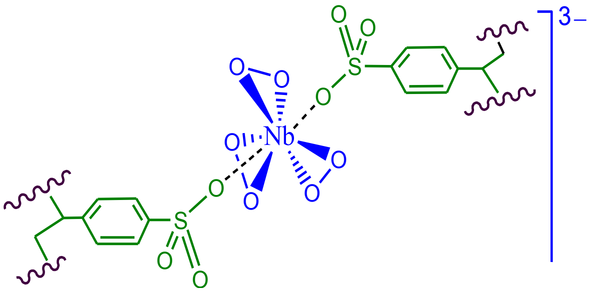


Fig. 2. Proposed structure of **PSSNb.**

4. Soluble Polymer Anchored Peroxotitanium(IV) compounds : synthesis and characterization

We have introduced a set of peroxotitanium(**pTi**) compounds anchored to water soluble polymer (**WSP**) matrices viz., poly(sodium acrylate) (**PA**) poly(sodium methacrylate) (**PMA**) or poly(sodium 4-styrene sulfonate) (**PSS**). The macrocomplexes of thetype, $[Ti_2(O_2)_2O_2(OH)_2(carboxylate)]$-PA**(PATi) (3.1),**$[Ti_2(O_2)_2O_2(OH)_2(carboxylate)]$-PMA **(PMATi) (3.2)** and $[Ti_2(O_2)_2O_2(OH)_2(sulfonate)]$-PSS **(PSSTi) (3.3)** were synthesized by reacting freshly prepared titanic acid, with 30 % H_2O_2 in presence of the respective **WSP**, The pH was maintained at*ca.* 4 which was found to be crucial for the formation of the μ-oxo peroxotitanium(IV) complexes and their co-ordination to the pendant functional groups such as carboxylate or sulfonate, of the polymer chain (Fig 3) .

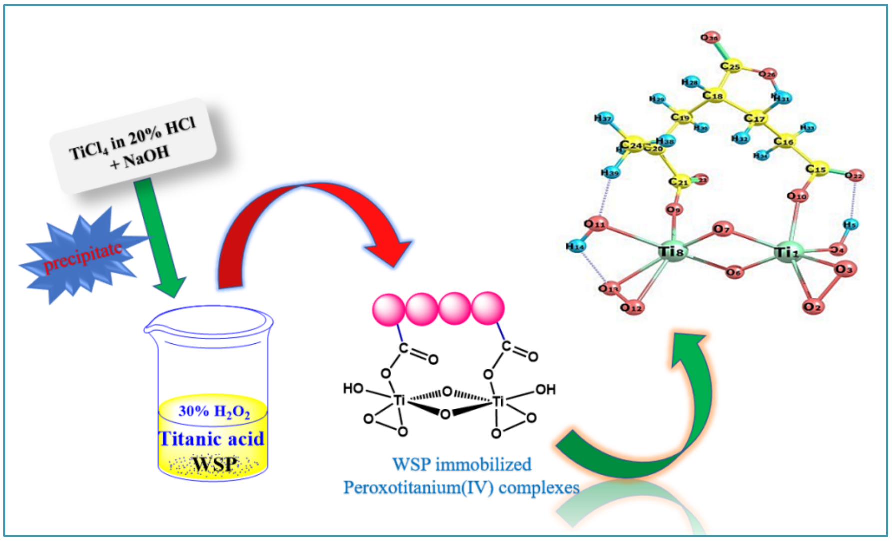


Fig. 3 Synthesis of WSP anchored peroxotitanate catalysts

B. Catalyst Characterization

The catalysts were characterized by a combination of analytical and spectroscopic techniques *viz.* FT-IR, Raman, ^{13}C NMR, powder XRD, ICP-OES, SEM-EDX, XPS, BET, and TG-DTG analysis.

C. Catalytic activity of the supported catalysts :

Performance of the catalysts in the following organic oxidations were examined :

a) Selective oxidation of 5-hydroxymethylfurfural (**HMF**) to 5-hydroxy methyl-2-furan carboxylic acid (HMFCA).
b) Selective epoxidation of alkenes.
c) Selective oxidation of thioethers and dibenzothiophene to the corresponding sulfoxide or sulfone.

C.1 Optimization of reaction conditions: The reaction conditions were optimized in each case by investigating the effect of each of the reaction parameters viz., **nature of solvent, reaction temperature, reaction time, ratios of amounts of catalyst : substrate as well as substrate : oxidant on the product selectivity, yield and rate of conversions**.

C.2 The products obtained will be analyzed and characterized by GC, GC-MS and HPLC techniques, IR, UV-Vis, NMR spectroscopy and melting point / boiling determination,.

C.3 Catalytic efficiency in terms of turn over number (TON) and turn over frequency (TOF) were determined.

C.4 Test for stability of the catalyst – catalyst recyclability: Stability of the catalysts in terms of their regeneration and reusability were assessed. For practical utility of a catalytic process the longevity of the catalyst and its potential for regeneration and reusability are of fundamental importance.

Scalability: Suitability of the developed protocols for larger scale application were explored by conducting the reactions under optimized conditions.

ANNEXURE II

Detailed analysis of Results : (contributions made towards increasing the state of knowledge of the subject)

1. Niobium(V)-amino acid complexes supported on organic polymers as sustainable catalysts for solventless olefin epoxidation and sulfide oxidation

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 confirm the successful anchoring of triperoxidoniobium(V), **$[Nb(O_2)_3]^-$** to the host polymer via the pendant amino acid groups. Our findings are summarized in the following Figure.

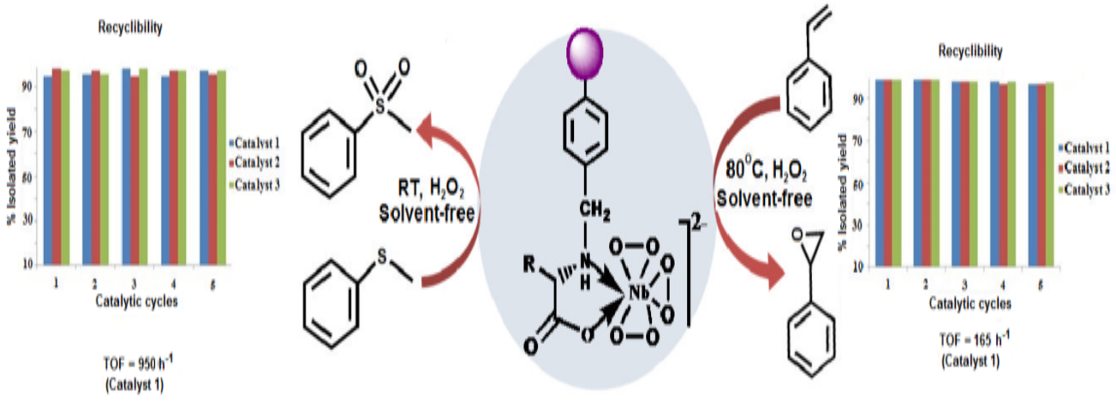


Figure 1 : Solventless olefin epoxidation and sulfide oxidation catalyzed by Niobium(V)-amino acid complexes supported on organic polymers.

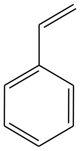
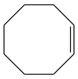
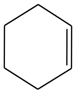
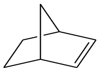
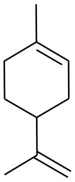
- The supported catalysts exhibited excellent performance in epoxidation of styrene and a range of cyclic and terpenic compounds under environmentally acceptable solvent-free condition with aqueous H_2O_2 as oxidant. The catalytic protocols provided high conversion to the desired epoxide (up to 100%) with selectivity > 99%, TOF as high as

1330 h^{-1} and high H_2O_2 utilisation efficiency (92-97%). The results are depicted in Table 1.

- Moreover, the catalysts efficiently facilitated chemoselctive solvent-free oxidation of variety of thioethers to sulfones with H_2O_2 at room temperature.

- Simple operational strategy, easy recyclability for multiple reaction cycles with consistent activity-selectivity profile are the additionl significant attributes of the developed catalytic processes

Table 1: Epoxidation of various alkenes with H_2O_2 catalyzed by compounds **1,2**[a]

			Catalyst 1			Catalyst 2		
Entry	Substrate	Time (h)	Conversion/ Epoxide Selectivity (%)	TON	TOF (h^{-1})	Conversion/ Epoxide selectivity (%)	TON	TOF (h^{-1})
1		6	99/99[b]	990	165	99/99[b]	990	165
		6	97[c]/99[b]	970	162	98[c]/99[b]	980	163
		6	99[d]/ 99[b]	990	165	99[d]/ 99[b]	990	165
2		0.75	100/100	1000	1333	100/100[e]	1000	1000
3		0.5	100[f]/39[g]	1000	2000	100[f]/34[g]	1000	2000
4		1.5	100/97[h]	1000	667	100/91[h]	1000	667
5		8	93/ 63[i,j]	930	116	95/67[i,j]	930	119

[

a] All reactions were carried out with 5 mmol alkene, 10 mmol 30% H_2O_2, solvent-free, T = 80ºC, catalyst (0.005 mmol of Nb). [b] Other product: benzaldehyde. [c] % conversion for 5th reaction cycle. [d] % conversion of scaled-up reaction (5.7 g). [e] Reaction time: 1 h. [f] Reaction at room temperature. [g] Other products: 2-cyclohexen-1-one+2-cyclohexen-1-ol, [h] Other product: Norbornanone. [i] Limonene1,2-epoxide, [j] Other products: Carveol+Carvone.

2. Tantalum(V) peroxides immobilized on asparagine or arginine grafted polymer resin as highly selective heterogeneous catalysts for organic oxidations under eco-compatible reaction conditions

Polymer supported heterogeneous peroxotantalum(V) catalysts were developed by anchoring Ta(V)-diperoxo species to chloromethylated poly(styrene-divinylbenzene) resin functionalized with amino acids, asparagine and arginine. The structurally well-defined catalysts, $[Ta(O_2)_2(L)_2]^{-}$-MR, [L =asparagine (**Catalyst 1**) or arginine (**Catalyst 2**) and MR=Merrifield resin] (Figure 1) displayed excellent activity and selectivity in alkene epoxidation as asparagines as well as sulfoxidation with aqueous 30% H2O2 under mild condition.

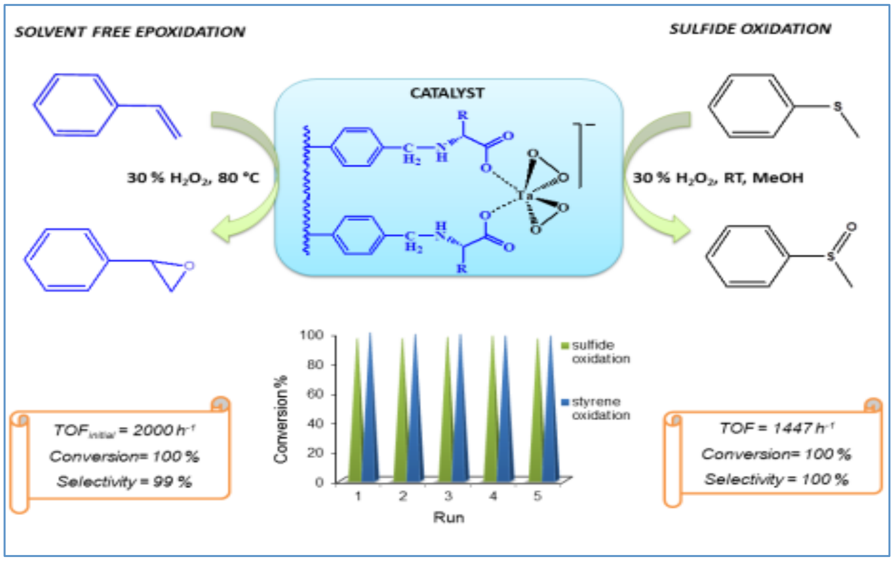


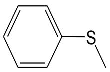
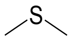
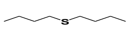
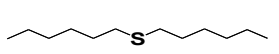
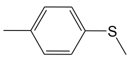
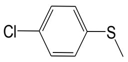
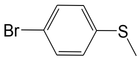
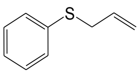
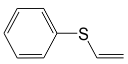
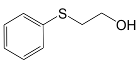
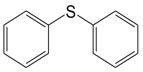
Fig . 2. Tantalum(V) peroxides immobilized on asparagine or arginine grafted polymer resin as highly selective heterogeneous catalysts for organic oxidations with H_2O_2

- **Solvent-free epoxidation of olefines with aqueous H_2O_2 :** The catalysts mediated epoxidation of olefins under solvent –free condition with high TOF and TON. We examined the performances of the catalysts with respect to their selectivity, reusability, TON and TOF and environmental compatibility. The oxidation of olefins *viz*, styrene, cyclohexene and norbornene has been achieved under solvent-free condition. No report appears to exist pertaining to alkene epoxidation catalyzed by Ta-based heterogeneous catalysts under solvent-less condition.

- **Selective oxidation of sulphides to sulfoxides:** The heterogeneous **catalysts 1** and **2** also facilitated chemoselective oxidation of a broad range of organic sulphides to the desired sulfoxides in methnol, a relatively safer organic solvent, at ambient temperature. (Table 2) .

- **Recyclability of the supported peroxotantalum catalysts:** The immobilized catalysts are remarkably robust affording easy recyclability for epoxidation as well as sulfoxidation up to a minimum of five reaction cycles in each case with stable selectivity/activity profile. (Figure 1)

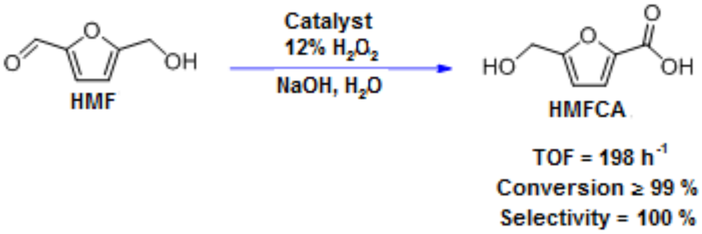
Table 2. Selective oxidation of sulfides to sulfones with H_2O_2 catalyzed by catalysts **1** and **2** under solvent-free condition[a]

Entry	Substrate	Catalyst **1**			Catalyst **2**		
		Time (min)	Isolated Yield (%)	TON	Time (min)	Isolated Yield (%)	TON
1		60	95	950	65	98	980
		60	97[b]	950	65	96[b]	960
		60	96[c]	960	65	97[c]	970
2		40	98	980	45	95	950
3		60	95	950	65	96	960
4		80	95	950	90	97	970
5		55	96	960	60	96	960
6		90	96	960	95	97	970
7		80	97	970	85	95	950
8		140	94	940	145	97	970
9		315	95	950	325	93	930
10		205	98	980	210	97	970
11		260	92	920	270	94	940

[a] All reactions were carried out with 5 mmol substrate, 10 mmol oxidant, and catalyst (0.005 mmol of Nb) at RT and without solvent. [b] % conversion for 5th reaction cycle. [c] Scale-up data (7.5 g of thioanisole).

3. **Merrifield resin supported Nb(V) and Ta(V) complexes as efficient heterogeneous catalysts for selective oxidation of biomass derived HMF to HMFCA**

Highly selective oxidation of biomass derived 5-hydroxy methyl-2-furfural (HMF) to 5-hydroxy methyl-2-furan carboxylic acid (HMFCA) using a set of peroxido complexes of Nb and Ta supported on amino acid functionalized Merrifield resin (MR) as catalysts. Results obtained after investigating a number of important reaction parameters demonstrated that under optimized condition it was possible to attain nearly 99% HMF conversion with 100% HMFCA selectivity within 30 min of reaction, using 12% H_2O_2 as oxidant at 60 ^{0}C, in water. The maximum TOF was observed to be of 198 h^{-1} . Thus compared to several reported methods on metal catalyzed HMFCA synthesis from HMF, our catalytic protocols offered a number of advantages with respect to conversion, selectivity and reaction conditions employed, as shown in the following **Scheme 1**.



Scheme 1 : Oxidation of HMF to HMFCA by H_2O_2 using catalyst **[Nb(O_2)$_3$(valine)]- MR.**

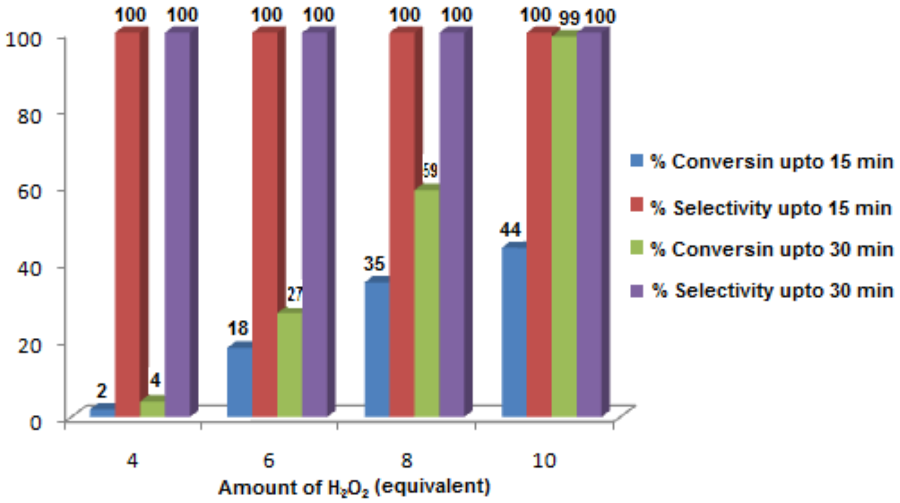
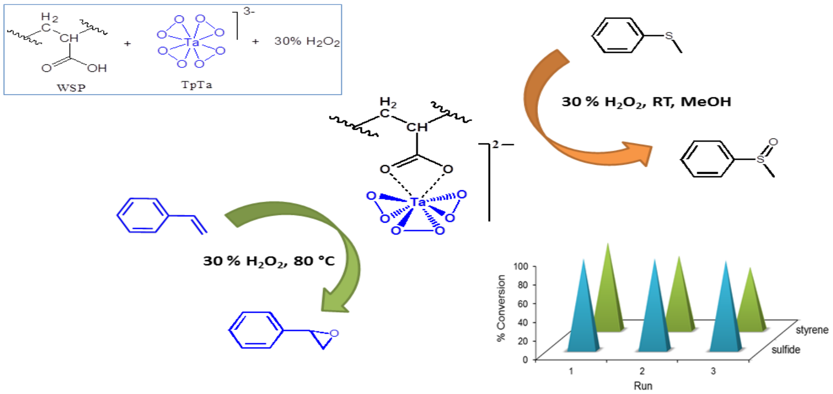


Fig 3. % HMF conversion vs. amount of H_2O_2 (eq.) for catalyst **[Nb(O_2)$_3$(valine)]- MR**. Reaction condition: 0.4 mmol of HMF (50 mg), catalyst(0.004 mmol of Nb, 13.3 mg), 1.6 mmol of NaOH (dissolved in 3 mL H_2O), 60 ^{0}C in 3 mL water.

4. Macromolecular Nb(V) and Ta(V) anchored to water soluble polymer supports and their application as homogeneous catalysts in organic oxidations

In this work, we have synthesised new water soluble polymer supported niobium and tantalum derivatives, [Nb(O_2)$_3$(sulfonate)$_2$]-PSS [PSS = poly(sodium styrene sulfonate)] (catalyst **1**), [Ta(O_2)$_3$(carboxylate)]-PA, [PA= poly(sodium acrylate)] (**PATa**) and [Ta(O_2)$_3$(sulfonate)$_2$]-PSS, PSS= poly(sodium 4-styrene sulfonate) (**PSSTa**). The catalytic activities of the compounds were studied on two different organic oxidations- alkene epoxidation and sulfide oxidation under eco-compatible conditions. Apart from being high-yielding (maximum TOF OF 9600 h^{-1} obtained for dimethyl sulfide oxidation) and operationally simple, the additional environmentally significant characteristics which enhance the sustainability of the water-based oxidation protocol include: chemoselectivity of the catalysts towards oxidation for sulfides and easy recyclability of the catalyst with consistent activity and selectivity for several cycles of oxidation (Figure 4).

Fig. 4. Macromolecular Nb(V) and Ta(V) anchored WSP supports as homogeneous catalysts in organic oxidations



- The macromolecular complexes efficiently catalyzed selective epoxidation of three different alkene substrates, *viz.* styrene, cyclohexene and norbornene with 30% H_2O_2 under solvent-less condition.

- Moreover, All the catalysts afforded oxidation of a number of structurally different sulfides substrates with impressive yield and turn over frequency under mild condition.

- Another salient feature of the catalysts is its chemoselectivity towards sulfur group in presence of other oxidation prone functionalities such as –C=C- and –OH group.
- The methodologies developed for both the oxidation reactions were devoid of organic co-solvent, co-catalysts or any other toxic auxiliaries to adhere to the green concept.
- The catalysts were recyclable with respect to sulfide oxidation with undiminished activity and selectivity, while in case of styrene oxidation, the activity of the catalysts were observed to decline after each run.

5. Peroxo compounds of Nb (V), Ta(V) and Mo(VI) anchored to biopolymer chitosan. Synthesis characterization and activity as heterogeneous catalyst for selective sulfoxidation in water

Heterogeneous water-compatible and recyclable catalysts has been developed by immobilizing peroxometalates on natural biopolymer, chitosan for chemoselective and ecologically sustainable oxidation of sulphides to high purity sulfoxide in aqueous medium at room temperature (Scheme) . The oxidation protocol is high yielding, straightforward and halogen-free.

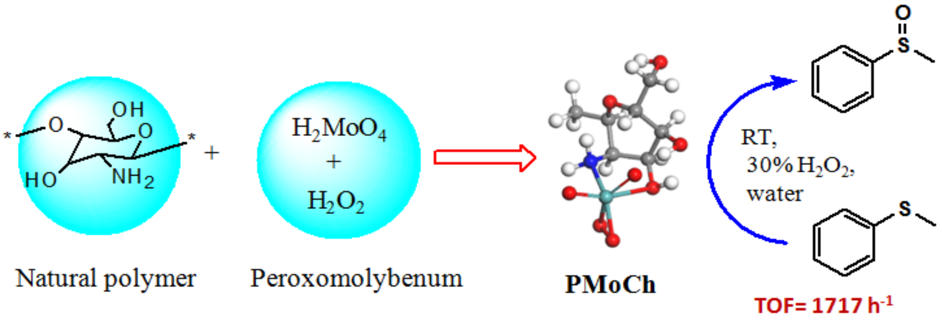


Fig. 5 Chitosan supported Mo(VI) complex catalyzes selective sulfoxidation of thioethers

6. Water-soluble polymer anchored peroxotitanates as environmentally clean and recyclable catalysts for mild and selective oxidation of sulfides in water with H_2O_2

- Anchoring of peroxotitanium species to non-cross linked linear polymers, poly(sodium acrylate) (PA) and poly(sodium methacrylate) (PMA) led to the successful synthesis of a pair of new, water-tolerant and recyclable catalysts of the type **$[Ti_2(O_2)_2O_2(OH)_2]$-L (L=PA or PMA),** highly active in chemoselective sulfoxidation of organic sulfides with 30% H_2O_2 in aqueous medium at ambient temperature.
- The catalytic protocol, in addition to being high yielding (TOFs up to 11538 h^{-1}) and operationally simple, is free from halogenated solvent and is environmentally clean and safe. The catalysts are sufficiently stable to afford easy recyclability for at least 10 consecutive reaction cycles of sulfoxidation with consistent activity selectivity profile. Oxidation of thioethers and dibenzothiophene (DBT) to respective high purity sulfoxide or sulfone could also be accomplished using the same catalysts by variation of reaction conditions.

Considering the mild reaction conditions the TOF values obtained in the present study, reaching up to a highest value of 11,280 h^{-1}, are indeed remarkable in comparison to most of the water-based catalytic sulfoxidations reported so far. Both the catalysts displayed high functional group tolerance towards sensitive groups such C=C and OH. Thus allylic and alcoholic sulfides were chemoselectively oxidized to yield targeted sulfoxide without affecting any other functional group transformation under the optimized condition.

7. Synthesis, structure and catalytic activity of new oxovanadium(V) complexes with deferiprone and N,N-donor ligands

A pair of new water-soluble oxovanadium(V) complexes comprising of deferiprone (def) and N,N-donor ligands, 2,2′-bipyridine (bpy) or 1,10-phenanthroline (phen), $[VO_2(def)(bpy)]$□H_2O (**1**) and $[VO_2(def)(phen)]$□$4H_2O$ (**2**) were synthesized. The complexes were characterized by elemental analysis, spectral studies and single crystal X-ray diffraction analysis. The X-ray crystal structures of **1** and **2** reveal that both the complexes possess distorted octahedral coordination geometries with O_4N_2 coordination sphere around the vanadium center, and the deprotonated deferiprone occupying the equatorial plane. The complexes **1** and **2** efficiently catalyzed selective epoxidation of styrene with 30% H_2O_2 under ecologically sustainable organic solvent-free conditions, at ambient temperature. The catalysts afforded good styrene conversion and high TON value along with excellent epoxide selectivity (>99%). Recyclability of the catalysts at least up to three consecutive cycles without significant alteration in activity or selectivity, is an additional remarkable feature of the developed catalytic protocol.

GFR 12 – A
[(See Rule 238 (1))]
UTILIZATION CERTIFICATE (UC) FOR THE YEAR (1/4/2020 – 17/8/2020)
in respect of *NON-RECURRING*
as on 31ST March, 2019, to be submitted to SERB

Is the UC....Audited.................... *(Provisional/Audited)*
(To be given separately for each financial year ending on 31st March)

1. Name of the grant receiving Organization : Tezpur University
2. Name of Principal Investigator(PI) **Dr. Nashreen S.Islam**
3. SERB Sanction order no. & date ... SERB No: **EMR/2016/003158 Dt. 20-Jul-2017**
4. Title of the Project : "Development of Polymer SupportedNiobium and Tantalum Based catalysts for Organic Oxidations under Ecologically Sustainable Reaction Conditions"
5. Name of the SERB Scheme : CRG......(CRG/NPDF/ECR etc.)
6. Whether recurring or non-recurring grants : ***NON-RECURRING***
7. Grants position at the beginning of the Financial year

(i)	Carry forward from previous financial year	: Rs.**1,00,752/-**
(ii)	Others, If any (INTEREST EARNED)	**Rs, 6754/-**
(iii)	**Total** :	**Rs. 1,07,506/-**

8. Details of grants received, expenditure incurred and closing balances: (Actuals)

Unspent Balance of Grants received previous years [figure as at Sl. No. 7(iii)] (Rs.)	Interest Earned thereon (Rs.)	Interest deposited back to the SERB	Grants received during the year			Total Available funds (1+2-3+4) (Rs.)	Expenditure incurred (Rs.)	Closing Balances (5-6) (Rs.)
1	2	3	4			5	6	7
1,00,752/-	**6754/-**		Sanction No. (i)	Date (ii)	Amount (iii)	**1.07,506/-**	**Nil**	**1,07,506/-**
			DST letter No. EMR/2016/ 003158	07-Feb-2020	Nil			

Component wise utilization of grants:

Grants-in-aid- General	Grant-in-aid-creation for capital assets	Total
Nil	**Nil**	**Nil**

Details of grants position at the end of the year

(i)	Balance available at end of financial year :	**Rs. 1,07,506 /-.**
(ii)	Unspent balance refunded to SERB (If any):	**Rs. 1,07,506/-**
(iii)	Balance (Carried forward to next financial year) if applicable:	NA

GFR 12 – A
[(See Rule 238 (1))]
UTILIZATION CERTIFICATE (UC) FOR THE YEAR 2019 - 2020
in respect of *NON-RECURRING*
as on 31ST March, 2021, to be submitted to SERB

Is the UC....Audited.................... *(Provisional/Audited)*
(To be given separately for each financial year ending on 31st March)

Certified that I have satisfied that the conditions on which grants were sanctioned have been duly fulfilled/are being fulfilled and that I have exercised following checks to see that the money has been actually utilized for the purpose for which it was sanctioned:

(i) The main accounts and other subsidiary accounts and registers (including assets registers) are maintained as prescribed in the relevant Act/Rules/Standing instructions (mention the Act/Rules) and have been duly audited by designated auditors. The figures depicted above tally with the audited figures mentioned in financial statements/accounts.

(ii) There exist internal controls for safeguarding public funds/assets, watching outcomes and achievements of physical targets against the financial inputs, ensuring quality in asset creation etc. & the periodic evaluation of internal controls is exercised to ensure their effectiveness.

(iii) To the best of our knowledge and belief, no transactions have been entered that are in violation of relevant Act/Rules/standing instructions and scheme guidelines.

(iv) The responsibilities among the key functionaries for execution of the scheme have been assigned in clear terms and are not general in nature.

(v) The benefits were extended to the intended beneficiaries and only such areas/districts were covered where the scheme was intended to operate.

(vi) The expenditure on various components of the scheme was in the proportions authorized as per the scheme guidelines and terms and conditions of the grants-in-aid.

(vii) It has been ensured that the physical and financial performance under **CRG**................ **(CRG/NPDF/ECR.....etc.)** (Name of the scheme has been according to the requirements, as prescribed in the guidelines issued by Govt. of India and the performance/targets achieved statement for the year to which the utilization of the fund resulted in outcomes given at Annexure – I duly enclosed.

(viii) The utilization of the fund resulted in outcomes given at Annexure – II duly enclosed (to be formulated by the Ministry/Department concerned as per their requirements/specifications.)

(ix) Details of various schemes executed by the agency through grants-in-aid received from the same Ministry or from other Ministries is enclosed at Annexure –II (to be formulated by the Ministry/Department concerned as per theirrequirements/specifications).

Date: 22.12.2021

Place: Tezpur

N. S. Jalan **Signature of PI :** 22.12.2021	04/1/2022 **Signature with Seal:.................** **Name: ....** **Chief Finance Officer (Head of Finance)** Finance Officer Tezpur University	4/1/22 **Signature with seal.......................** **Name: ....** **Head of Organisation** Registrar Tezpur University

(Strike out inapplicable terms)

GFR 12 – A
[(See Rule 238 (1))]
UTILIZATION CERTIFICATE (UC) FOR THE YEAR <u>(1/4/2020 to 17/8/2020)</u>
in respect of *RECURRING*
as on 31ST March, 2020, to be submitted to SERB

Is the UC....Audited.............................. *(Provisional/Audited)*
(To be given separately for each financial year ending on 31st March)

1. Name of the grant receiving Organization : Tezpur University
2. Name of Principal Investigator(PI) **Dr. Nashreen S.Islam**
3. SERB Sanction order no. & date … SERB No: **EMR/2016/003158 Dt. 20-Jul-2017**
4. Title of the Project : "Development of Polymer SupportedNiobium and Tantalum Based catalysts for Organic Oxidations under Ecologically Sustainable Reaction Conditions"
5. Name of the SERB Scheme : CRG……(CRG/NPDF/ECR etc.)
6. Whether recurring or non-recurring grants : ***RECURRING***
7. Grants position at the beginning of the Financial year

(i) Carry forward from previous financial year : Rs. **5,54,773/-**
(ii) Others, If any (INTEREST EARNED) **Rs, Nil**

(iii) **Total** : **Rs. 5,54,773/-**

8. Details of grants received, expenditure incurred and closing balances: (Actuals)

Unspent Balance of Grants received previous years [figure as at Sl. No. 7(iii)] (Rs.)	Interest Earned thereon (Rs.)	Interest deposited back to the SERB	Grants received during the year			Total Available funds (1+2-3+4) (Rs.)	Expenditure incurred (Rs.)	Closing Balances (5-6) (Rs.)
1	2	3	4			5	6	7
5,54,773/-	**Nil**	NA	Sanction No. (i)	Date (ii)	Amount (iii)	**5,54,773/-**	**6,50,888/-**	**(-) 96,115**
			DST letter No. EMR/2016/ 003158	07-Feb-2020	**Nil**			

Component wise utilization of grants:

Grants-in-aid- General	Grant-in-aid-creation for capital assets	Total
Rs. **6,50,888/-**	**Nil**	Rs. **6,50,888/-**

Details of grants position at the end of the year

(i) Balance available at end of financial year : **Rs. (-) 96,115**

(ii) Unspent balance refunded to SERB (If any): …… ………

(iii) Balance (Carried forward to next financial year) if applicable: **Rs. (-) 96,115**

GFR 12 – A
[(See Rule 238 (1))]
UTILIZATION CERTIFICATE (UC) FOR THE YEAR 2019 -2020
in respect of *RECURRING*
as on 31ST March, 2019, to be submitted to SERB

Is the UC.......Audited.............................*(Provisional/Audited)*
(To be given separately for each financial year ending on 31st March)

Certified that I have satisfied that the conditions on which grants were sanctioned have been duly fulfilled/are being fulfilled and that I have exercised following checks to see that the money has been actually utilized for the purpose for which it was sanctioned:

(i) The main accounts and other subsidiary accounts and registers (including assets registers) are maintained as prescribed in the relevant Act/Rules/Standing instructions (mention the Act/Rules) and have been duly audited by designated auditors. The figures depicted above tally with the audited figures mentioned in financial statements/accounts.

(ii) There exist internal controls for safeguarding public funds/assets, watching outcomes and achievements of physical targets against the financial inputs, ensuring quality in asset creation etc. & the periodic evaluation of internal controls is exercised to ensure their effectiveness.

(iii) To the best of our knowledge and belief, no transactions have been entered that are in violation of relevant Act/Rules/standing instructions and scheme guidelines.

(iv) The responsibilities among the key functionaries for execution of the scheme have been assigned in clear terms and are not general in nature.

(v) The benefits were extended to the intended beneficiaries and only such areas/districts were covered where the scheme was intended to operate.

(vi) The expenditure on various components of the scheme was in the proportions authorized as per the scheme guidelines and terms and conditions of the grants-in-aid.

(vii) It has been ensured that the physical and financial performance under **CRG**................ **(CRG/NPDF/ECR.....etc.)** (Name of the scheme has been according to the requirements, as prescribed in the guidelines issued by Govt. of India and the performance/targets achieved statement for the year to which the utilization of the fund resulted in outcomes given at Annexure – I duly enclosed.

(viii) The utilization of the fund resulted in outcomes given at Annexure – II duly enclosed (to be formulated by the Ministry/Department concerned as per their requirements/specifications.)

(ix) Details of various schemes executed by the agency through grants-in-aid received from the same Ministry or from other Ministries is enclosed at Annexure –II (to be formulated by the Ministry/Department concerned as per theirrequirements/specifications).

Date: 22.12.2021

Place: Tezpur

N.S. Islam **Signature of PI :** 22.12.2021	04/1/2022 **Signature with Seal:**................. **Name:** .... **Chief Finance Officer (Head of Finance)** Finance Officer Tezpur University	4/1/22 **Signature with seal**....................... **Name:** .... **Head of Organisation** Registrar Tezpur University

(Strike out inapplicable terms)

Annexure -II

Statement of Expenditure
For the Financial Year : 2020-2021, From 1 April, 2020 to 17.8.2020

Sl. No. (I)	Sanctioned Heads (II)	*Total Funds Allocated (sanctioned) in Rs (III)	Expenditure Incurred in Rs				Total	Total Expenditure till 17.8.2020 (VII = IV + V + VI+ VII) (Rs)	Balance as on 17/8/2020 (VIII = (III-VII) + Interest (C)	Requirement of Funds up to 17-08-2020)	Remarks (If any)
	Recurring heads (A)		**1st Yr (IV) (17-06-2017 to 31-03-2018)**	**2nd Year** (V) (1.04.18-31.3.2019)	**3rd Yr (VI) 1.04.19 – 31.3.2020**	3rd yr cotd. (VII) 1.04.20-17.8.20)		**A : Recurring heads** **24,86,121**	**(-) 96,115 (A)**		
1	Manpower cost	**21,79,600**	92,867	1,68,000	1,54,000	61871	4,76,738				
2	Consumables		3,57,948	3,87,559	2,20,464	4,52,362	**14,18,333**				
3	Travel		3,054	58,368	67,561	17,780	1,46,763				
4	Contingencies		77,077	39,325	0.00	33,322	**149,724**				
5	Overhead expenses	**4,10,660**	1,23,455	85,555		85,553	2,94,563				
	Total (Recurring)	**25,90,260**	**6,54,401**	**7,38,807**	**4,42,025**	**6,50,888**	**24,86,121**				
6	**Non-Recurring heads(B) Equipment**	**19,27,000**			Nil	Nil		**B: Non-Recurring** **18,54,385**	**1.07,506**	………… …	
	(a) HPLC system		NA	**15,79,603**			**18,54,385**				
	(b) Minor equipment		1,87,682								
	(c) Laser Printer		10,200								
	(d)Laptop/computer		76,900								
	Total (Non-Recurring)	**19,27,000**	**2,74,782**	**15,79,603**	Nil						
	Total cost of the project (A+B)	**45,17,260**	**9,29,183**	**23,18,410**	**4,42,025**	**6,50,888**	**43,40,506**				
8	**Interest (C)**	**61,447**	-	-	-			-			
9	**Total**	**45,78,707**						**43,40,506**	**11,391**		

N. S. Islam

Name and Signature of Principal Investigator

Date: 22.12.2021 (With Seal)

Dr. Nashreen S. Islam
Professor
Department of Chemical Science
Tezpur University

04/1/2022

Signature of Competent Financial Authority

(With Seal)***Date of start of Project**: 18/08/2017

Finance Officer
Tezpur University