
Polymer Immobilized Peroxido Complexes of Titanium(IV) and Molybdenum(VI): Synthesis, Characterization and Application as Eco-compatible Catalysts in Organic Oxidations

The present thesis deals with the results of studies involving synthesis and characterization of series of new peroxide containing macro complexes of titanium and molybdenum immobilized on polymer supports. The thesis also provides an account of the activity of the developed supported peroxidometallates as versatile and highly efficient homogeneous or heterogeneous catalysts in variety of organic oxidations accomplished under environmentally acceptable reaction conditions. The contents of the thesis have been distributed over six chapters. The outline of the thesis is described below.

Chapter 1 presents a general introduction along with literature review relevant to the work embodied in the thesis. The chapter describes the background and scope of the present study in light of the current status of peroxidometal chemistry of the chosen metals. Also provided in this chapter is a brief overview of various aspects related to immobilization of metal complexes on polymer matrices highlighting the importance and utility of insoluble cross-linked polymers, water-soluble polymers (WSP) as well as natural chelating polymers as supports in the field of catalysis. Attention has been drawn to the fact that, despite the enormous progress in the domain of metal containing polymers, there is a dearth of information on preparation and application of well-defined polymer supported peroxidometallates as catalysts in organic oxidations.

Chapter 2 presents the details of the methods of the elemental analyses and techniques used for characterization and structural assessment of the newly synthesized compounds. Also, methods used for studies on the catalytic activities of the complexes in oxidation reactions are described herein.

In **Chapter 3**, we have introduced a set of novel peroxidotitanium(**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 the type, $[\text{Ti}_2(\text{O}_2)_2\text{O}_2(\text{OH})_2(\text{carboxylate})]$ -PA (**PATi**) (**3.1**), $[\text{Ti}_2(\text{O}_2)_2\text{O}_2(\text{OH})_2(\text{carboxylate})]$ -PMA (**PMATi**) (**3.2**) and $[\text{Ti}_2(\text{O}_2)_2\text{O}_2(\text{OH})_2(\text{sulfonate})]$ -PSS (**PSSTi**) (**3.3**) were synthesized by reacting freshly

prepared titanate acid, with 30 % H₂O₂ in presence of the respective **WSP**. The pH of the reaction medium was maintained at *ca.* 4 which was found to be crucial for the formation of the μ -oxido peroxidotitanium(IV) complexes and their co-ordination to the pendant functional groups such as carboxylate or sulfonate, of the polymer chain.

The synthesized compounds were comprehensively characterized by elemental analysis (ICP-OES, CHN and energy-dispersive X-ray spectroscopy), spectral studies (IR, Raman, UV-Vis and ¹³C NMR studies), thermogravimetric analysis (TGA) as well as SEM studies. The structure of the complex [Ti₂(O₂)₂O₂(OH)₂(carboxylate)]-PA (**PATi**) has also been verified by density functional theory (DFT) method. A structural feature common to each of these immobilized compounds was observed to be the presence of a dimeric hydroxido-peroxido Ti(IV) moiety with a Ti₂O₂ core linked to the respective polymer chain *via* its pendant ligand groups. Di- μ -oxido titanium complexes with Ti₂O₂ core have been reported in variety of ligand environment which is known to impart stability to the peroxidotitanium(IV) complex species.

This chapter also describes the catalytic activity of the compounds **3.1-3.3** in chemoselective oxidation of variety of sulfides to high purity sulfoxides and sulfones with 30% H₂O₂ in aqueous medium at ambient temperature. The catalytic protocol is high yielding (TOF up to 11,280 h⁻¹), operationally simple as well as environmentally clean and safe, being free from halide, or any other toxic auxiliaries. Furthermore, the catalysts are remarkably robust in the reaction medium as evident from their easy recyclability up to 10 reaction cycles of sulfoxidation without significant change in activity.

Chapter 4 elaborates the development of a new heterogeneous catalyst prepared by immobilization of oxido-peroxido molybdenum(VI) species on natural bio-polymer, chitosan which displayed excellent activity, stability and chemoselectivity for the oxidation of a wide variety of sulfides to the respective sulfoxides by 30% H₂O₂ in water, at ambient temperature. The chitosan peroxidomolybdenum catalyst, MoO₂(O₂)(OH)(NH₂)-chitosan (**PMoCh**) (**4.1**) has been characterized by elemental analysis, spectral studies (FTIR, Raman, solid-state ¹³C NMR and diffuse reflectance UV-Vis), PXRD, Brunauer-Emmett-Teller (BET), SEM, EDX and TGA-DTG analysis. The density functional theory (DFT) method has been employed to study the structure of the synthesized complex.

Also reported in this chapter is the activity of a set of previously reported water soluble polymer supported peroxidomolybdenum(VI) compounds of the type, $[\text{MoO}(\text{O}_2)_2(\text{sulfonate})]\text{-PS}$ [PS = poly(sodium vinyl sulfonate)] (**PSMo**) (4.2) and $[\text{Mo}_2\text{O}_2(\text{O}_2)_4(\text{carboxylate})]\text{-PA}$ [PA = poly(sodium acrylate)] (**PAMo**) (4.3) as homogeneous catalysts in oxidation of sulfides to sulfoxides by 30% H_2O_2 at room temperature in aqueous medium.

The versatility of the afore mentioned homogeneous as well as heterogeneous **pMo** based catalytic systems in sulfoxidation was further evident from their high compatibility in organic solvents as well. Furthermore, the results obtained from this study showed that under similar reaction conditions, homogeneous catalysts (**PAMo** and **PSMo**), exhibit superior catalytic activity over its heterogeneous counterpart. Both sets of catalysts are sufficiently stable to afford easy recyclability of sulfoxidation with consistent activity selectivity profile.

Chapter 5 illustrates the synthesis, characterization and catalytic performance of a pair of Merrifield resin (**MR**) immobilized dioxidoperoxidomolybdenum(VI) compounds, $[\text{MoO}_2(\text{O}_2)(\text{L})]\text{-MR}$, (L = L-Asparagine) (**MRAsnMo**) (5.1) and $[\text{MoO}_2(\text{O}_2)(\text{L})_2]\text{-MR}$, (L = Nicotinic acid) (**MRNAMo**) (5.2). The functionalized polymers **MRAsn** and **MRNA** were prepared by reacting chloromethylated polystyrene cross-linked with 2% DVB with the respective ligands (L-asparagine or Nicotinic acid) in methanol and in presence of pyridine as a base. The reaction of the respective functionalized resin with H_2MoO_4 and 30% H_2O_2 subsequently led to the synthesis of the heterogeneous catalysts **MRAsnMo** (5.1) and **MRNAMo** (5.2).

The synthesized compounds were characterized by elemental analysis (CHN, inductively coupled plasma analysis (ICP) and energy-dispersive X-ray spectroscopy), spectral studies (FTIR, Raman, solid-state ^{13}C NMR, diffuse reflectance UV-Vis and XPS analysis), Brunauer–Emmett–Teller (BET), XRD, thermogravimetric analysis (TGA) as well as SEM studies.

The catalysts displayed excellent activity in epoxidation of various olefins such as styrene, cyclooctene, norbornene and cyclohexene with 30% H_2O_2 under solvent free condition, providing high conversion and 97-100% epoxide selectivity, with high TON values obtained ranging between 800-1000. The catalysts also efficiently mediated selective oxidation of a series of structurally diverse sulfides to their corresponding

sulfoxides with 30% H₂O₂ or sulfones under solvent-free reaction condition. The heterogeneous catalysts could be recovered simply by filtration and reused for a number of consecutive cycles without any significant loss in activity or selectivity in both epoxidation as well as sulfide oxidation reactions.

The results of our investigation presented in **Chapter 6** demonstrated that the peroxidotitanium complexes [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**), could serve as aqueous-phase catalysts for selective oxidation of 5-hydroxymethylfurfural (HMF) to 5-hydroxymethyl-2-furancarboxylic acid (HMFCa) with 12% H₂O₂. HMF, a heterocyclic furanoic molecule, substituted in 2,5-position with hydroxyl and aldehyde functional groups, is regarded as a promising platform chemical. The **pTi** systems showed a remarkable tendency towards catalyzing the selective oxidation of aldehyde functional group of HMF to yield HMFCa as the sole oxidation product. The product selectivity was found to remain unchanged in organic solvents as well. A variety of reaction parameters viz., catalyst amount, solvent, reaction temperature, were examined in order to optimize the reaction condition.

The chapter also describes the catalytic performance of the supported peroxidotitanium(**pTi**) compounds **3.1-3.3** as reusable catalysts in selective epoxidation of styrene and cyclooctene using 30% H₂O₂ under solvent free reaction condition. Both the substrates were epoxidized with >99% selectivity. All the three catalysts were recyclable under solvent free condition for three consecutive reaction cycles without appreciable change in selectivity. However, gradual decrease in product conversion was noted in subsequent reaction cycles.

The majority of work described in chapters 3-6 has been published and the rest is under communication.