

Phosphonate functionalized N-heterocyclic carbenes and zirconium phosphate supported CdS quantum dots: Application in aerobic oxidation reactions

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Gorishmita Borah

Registration No. TZ132964 of 2013



**Department of Chemical Sciences
School of Sciences
Tezpur University
Napaam, Tezpur-784028
Assam, India**

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Chapter 5

Conclusion

5.1. Conclusion

The global environment is rapidly changing due to global warming and climate change. Widespread concern about an unprecedented environmental crisis caused by the relentless production of chemical waste materials like non-degradable polymers, organic dyes and chemicals, medicines, heavy metals, and fossil fuels has propelled efforts to reduce and safely dispose of chemical waste. Thus, there is a surge of activities aiming design of chemical processes that focus on reduction or elimination of hazardous substances using the well-defined principles of Green Chemistry. The present thesis is a humble step towards this comprehensive goal and we endeavoured to design chemical processes for industrially relevant organic transformation by designing efficient catalytic systems. During this work, two distinct yet complementary approaches were adopted to design environmentally benign and sustainable catalytic processes *viz.* introducing additional & supplementary functionality on an organocatalysts to enhance catalytic efficacy and immobilization of catalytically active species on robust solid support to enhance recyclability. The first approach relied on incorporating an additional functionality on a N-heterocyclic carbene (NHC) based organocatalytic system as a hemilabile arm and thereby enhance the efficacy of the catalytic system. In the second approach, a robust, hybrid and crystalline metal organophosphonate support was employed as a solid support to improve the catalytic efficiency and recyclability of two different catalytic system. The thesis embodies a total of five chapters and detailed content of each chapter are described below.

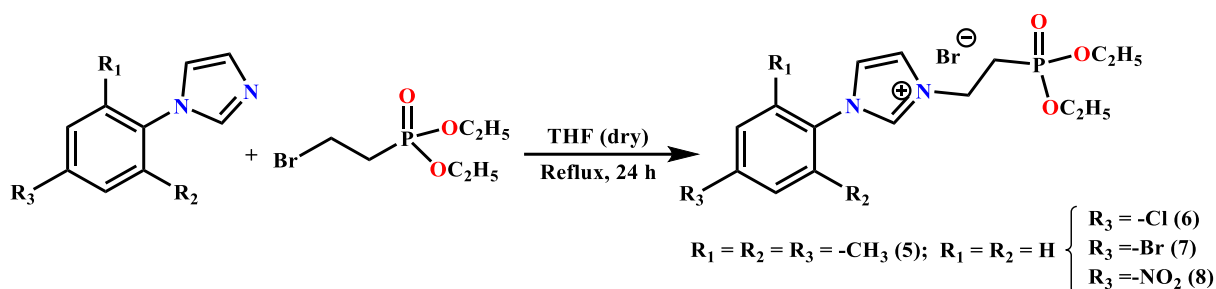
Chapter 1 begins with a general introduction to the importance of catalysis as well as the current challenges that must be addressed on a war footing for sustaining life on earth. Thereafter, a detailed discussion on N-heterocyclic carbenes (NHCs) which are regarded as the next big discovery of the time in the world of catalysis is presented in this chapter. The electronic characteristics of NHCs as well as highly celebrated examples of metal-NHC catalysts are introduced. The relevance and application of NHCs in organocatalytic reactions involving benzaldehyde are discussed. NHCs are well recognized for their ability to invert the polarity of carbonyl carbon atoms and this characteristic has been exploited to catalyse several important organic transformations. The mechanism of this umpolung reaction involving formation of an enaminol intermediate presently recognized as Breslow intermediate as is elaborated. Moreover, approaches to generate different reactive equivalents by employing various carbonyl functionalities along with their application in organocatalysis are discussed. Thereafter, a detailed literature survey

on NHC catalysed oxidative as well as oxygenative esterification of benzaldehyde with different substrates e.g. aryl boronic acid, aliphatic/benzylic alcohol and alkyl bromide is presented in this chapter.

The above discussions are followed by approaches to enhance the catalytic efficacy as well as recyclability of NHCs via introduction of an additional and supplementary functionality and immobilization on solid supports respectively. Literature survey on NHCs containing additional donor functionality and thereby introduce hemilability, chirality or to anchor them onto solid surface is presented. Further, the nature of solid supports that are conventionally employed for immobilization of catalytically active species and their limitations are elaborated. Thereafter, high valent metal organophosphonates are introduced as a highly promising class of solid support for immobilization of catalytically active species. Apart from NHCs, the present thesis also explores the possibility to enhance the recyclability of semiconductor based photocatalysts via immobilization on high valent metal organophosphonate support. Thus, a detailed discussion on photocatalysis followed by literature survey on photocatalytic aerobic oxidation of benzyl alcohol is presented. Finally, based on the discussions, scope of the current work is discussed, and the objectives of the thesis are drawn.

In chapter 2, synthesis, characterization, density functional theory (DFT) calculations organocatalytic efficacy of a series of phosphonate ester functionalized NHCs are described. A strategy is developed for preparation of a novel class of phosphonate ester functionalized imidazolium salts by employing N-aryl substituted imidazole's (**1-4**) as precursors. Four phosphonate ester functionalized imidazolium salts (**5-8**) are prepared by following this strategy and all these compounds are characterized by employing FT-IR, ¹H NMR, ¹³C NMR, ³¹P NMR and high-resolution mass spectrometry (Scheme 5.1). DFT calculations reveal the electronic and donor characteristics of the phosphonate ester functionalized NHCs derived from the corresponding imidazolium salts **5-8**. The catalytic efficacy of the phosphonate ester functionalized NHCs in aerobic oxygenative esterification of benzaldehyde with two different substrates e.g. phenyl boronic acid and aliphatic/benzylic alcohols were investigated. In spite of the presence of less bulky non-aromatic substituent on imidazole N-atom, the present compounds act as highly efficient organocatalysts in both the reactions. When compared to other reported catalysts, the reagents used in the current protocol are less expensive and yield relatively good yields in a much shorter period. Several ester derivatives are isolated in near quantitative yields

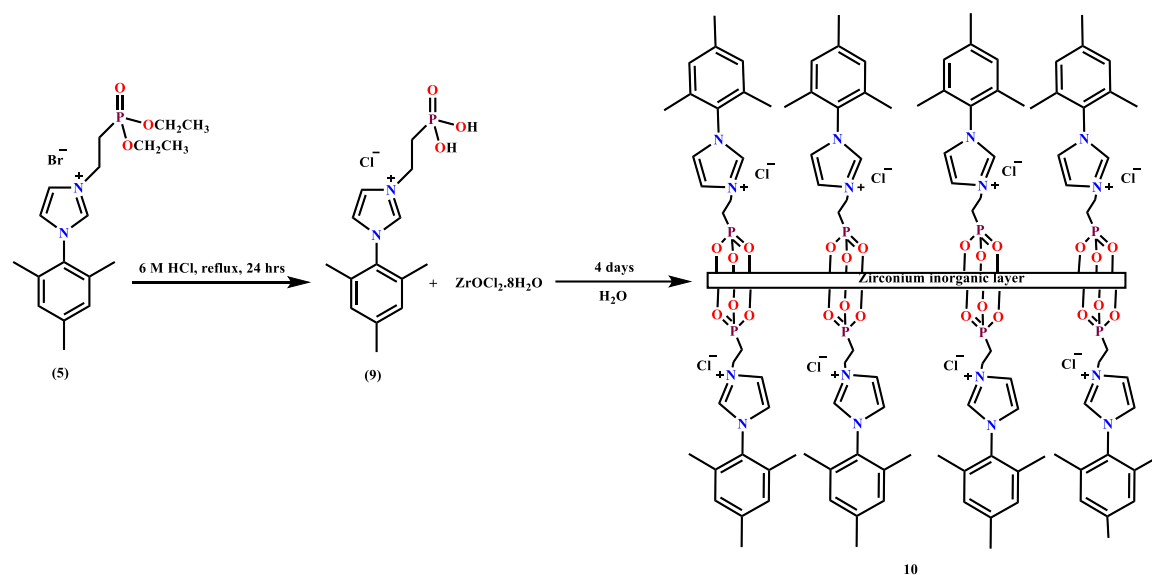
using the current catalytic system, with no undesirable by-products produced. The mechanism of phosphonate functionalized NHC catalysed aerobic oxygenative esterification of benzaldehyde with phenyl boronic acid is probed by DFT calculations establish the thermodynamic feasibility of the proposed reaction pathway. Although no influence of phosphonate ester group on the proposed reaction pathway could be established from DFT calculations, observation of high catalytic efficacy of the present NHCs reveal the importance of phosphonate ester functionality in enhancing their catalytic efficacy.



Scheme 5.1. Synthesis of phosphonate ester functionalized imidazolium salts, **5-8**

In chapter 3, synthesis, characterization and catalytic application of a zirconium(IV) phosphonate framework decorated with pendant imidazolium functionality is elaborated. Acid promoted hydrolysis of phosphonate ester functionalized imidazolium salt, **5** prepared in chapter 2 result the corresponding phosphonic acid functionalized imidazolium salt (**9**) in near quantitative yield (Scheme 5.2). Reaction of this phosphonic acid functionalized imidazolium salt with ZrOCl_2 resulted a layered zirconium(IV) phosphonate framework (**10**) decorated with covalently anchored imidazolium functionality. Compound **10** is characterized by employing analytical, spectroscopic, structural and microscopic studies. Presence of dangling imidazolium substituents on the surface of the layered metal phosphonate framework promoted its application as a recyclable heterogeneous organocatalysts. Investigation of catalytic efficacy of compound **10** in aerobic oxygenative esterification of benzaldehyde with both phenyl boronic acid and aliphatic/benzylic alcohols reveal its high catalytic efficiency as well as recyclability without any appreciable loss of efficacy. The high recyclability of the present catalytic system can be attributed to the robust chemical nature of the zirconium phosphonate solid support as well as the covalent nature of the linkage between the NHC moiety with the phosphonate framework. Moreover, the zirconium phosphonate framework has a layered structure and the NHC moieties are uniformly anchored to this

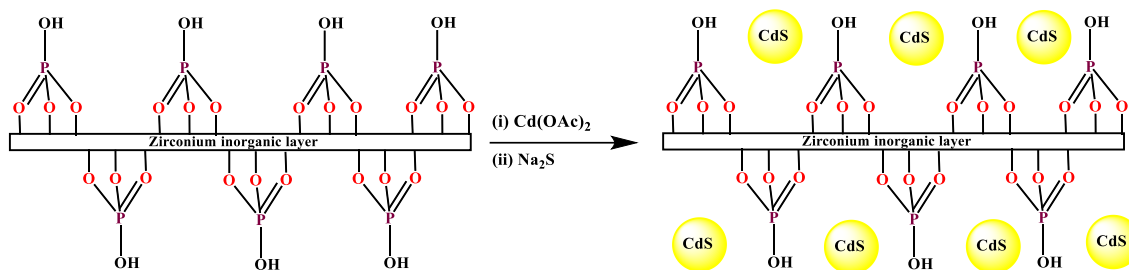
2D structure. This can be attributed to the high catalytic efficacy of the present NHC based heterogeneous organocatalytic system.



Scheme 5.2. Synthesis of zirconium(IV) organophosphonate framework with dangling covalently anchored imidazolium groups

Extensive research has been devoted to the development of photocatalytic materials with the goal of utilizing solar energy and thus addressing the growing global concerns of environmental remediation and clean fuel production. Decades of work have resulted in a diverse range of efficient semiconductor-based photocatalytic materials. However, inhibition of photodegradation of the photocatalyst during photocatalytic reactions remains a major challenge that needs to be addressed by recycling photocatalysts. Immobilization of photocatalyst in inert solid surfaces has emerged as a prolific strategy for inhibiting photodegradation of semiconductor based photocatalysts. High valent metal phosphonates/phosphates typically show high ion adsorption capacity. We exploited this characteristic of a well characterized metal phosphonate phase α -zirconium(IV) phosphate (α -ZrP) to design a composite material with CdS quantum dots. In chapter 4, a simple and bottom up method for immobilizing CdS quantum dots on zirconium phosphate framework by treating Cd(II) exchanged α -ZrP with Na₂S is described. The composite, CdS@ α -ZrP was characterized using analytical, spectroscopic, structural, and microscopic tools. These studies establish that CdS quantum dots of size 2-6 nm are uniformly distributed over the surface of the layered solid support, α -ZrP. The composite demonstrated good photocatalytic activity in the

aerobic oxidation of benzyl alcohol to benzaldehyde and can be recycled up to the fifth cycle without significant efficiency loss.



Scheme 5.3. Synthesis of CdS@ α -ZrP composite

Thus, the current thesis has successfully addressed some of the most important aspects of Green Chemistry and several significant milestones have been achieved during the course of this work. Initially, the focus was on developing NHC based homogeneous organocatalyst and improve their catalytic efficacy by incorporation of an additional functionality. Thus, a series of phosphonate ester functionalized imidazolium salts are developed, and they act as efficient precatalyst in two related NHC catalyzed organic transformations. It is also worth noting that a novel atom-economic and environmentally friendly strategy is developed for preparation of the phosphonate ester functionalized imidazolium salts in good yields. The phosphonate ester substituent augment organocatalytic efficacy of the NHCs as typically imidazole rings containing bulky electron donating substituents on both N atoms act as good organocatalysts. Thereafter, we exploited the phosphonate ester functionality present on the imidazolium salts to design a heterogeneous NHC based organocatalysts. Thus, phosphonate functionalized imidazolium salt was used as precursor to assemble a zirconium phosphonate framework where imidazolium functionalities are covalently anchored on the surface of the layered 2D structure. The Zr(IV) phosphonate framework containing covalently bonded imidazolium exhibits notable catalytic activity in the oxygenative esterification of aromatic aldehyde with boronic acid and alcohols. Thereafter, CdS nanoparticles are embedded over a layered zirconium phosphate framework, α -ZrP to design a robust heterogeneous photocatalyst. The composite acted as a highly efficient and selective photocatalyst in the photocatalytic aerobic oxidation of benzyl alcohol to benzaldehyde. Moreover, the photocatalyst can be recycled several times without any significant loss of photocatalytic activity. Hybrid metal phosphonate/phosphate-based frameworks are easily accessible, and a wide range of functional groups can be incorporated onto these frameworks. As a result, metal phosphonate/phosphate frameworks offer a novel and

intriguing way to modify the physicochemical properties of catalyst and thereby augment their activity and efficiency.

5.2. Future scope

The current thesis work exploited the phosphonate/phosphate functionality for enhancing efficiency as well recyclability of catalytic systems. Several significant milestones have been reached during the course that will undoubtedly enrich the phosphonate chemistry domain. The works described here has immense potential in development of future catalytic systems for various applications, but most of these remain unaddressed due to time constraints. Porosity can be introduced into the zirconium phosphonate frameworks and this can significantly augment both the selectivity as well as efficiency of the heterogeneous catalytic systems developed during this work. Moreover, marriage of the heterogeneous organocatalytic systems with the heterogeneous photocatalytic systems developed during this thesis has immense potential in the development of tandem bifunctional catalytic systems. Our research group is currently actively investigating the aforementioned possibilities in an effort to mitigate chemical waste generation in chemical processes.