Abstract

Majority of the catalytical processes employed in industries involve homogeneous catalyst due to high efficiency and selectivity offered by them. However, the recovery and separation of homogeneous catalyst has so far remained a considerably challenging task. Therefore, chemical processes involving many of these homogeneous catalyst poses serious environment threat that must be addressed for a sustainable future. In this context, heterogeneous solid catalysts are gaining interest because of their easy post reaction separation and thus reducing waste [1]. In addition to that, processes involving heterogeneous catalysts are atom economic and thus indirectly also helps in waste management process. These advantages of the heterogeneous catalysts over their homogeneous counterparts accentuate their relevance towards development of green and economically profitable chemical technology [2,3]. In this regard, enhancing the efficiency, recyclability and selectivity of heterogeneous catalysts to match their homogeneous counterparts has emerged as one of the most pressing challenges for furthering their industrial applications. Current outburst of activities to address this concern primarily relies on tuning the surface area and electronic characteristics of active catalytic species either by particle size miniaturization or by manipulating interaction with support surface. A fascinating assortment of highly efficient heterogeneous catalyst, prepared by immobilization of metal nanoparticles over a wide array of solid supports, e.g., carbon-based materials [4], silicious materials [5], polymers [6], metal–organic frameworks [7,8] have already been reported. Many of these heterogeneous catalysts can be easily recycled and repeatedly used, afford products in high yields within a reasonably short reaction time, require mild reaction conditions in green solvent medium or even under solventless conditions. Nonetheless, in terms of catalyst recyclability, efficiency and uniformity of catalytically active sites over the solid support there still remains considerable scope of advancement. However, heterogeneous catalytic systems are available for only a handful of chemical transformations and further they lack the selectivity or high degree of activity usually observed for homogenous catalytic systems. Moreover, tuning the catalyst activity to obtain optimum productivity has remained a major challenge for heterogeneous catalytic systems.

Recently, metal organic frameworks (MOFs) have emerged as a potential candidate that can bridge the advantages for both homogeneous and heterogeneous catalysts. MOFs are an extensive class of porous crystalline polymeric materials having metal centre or a metal cluster as the nodes and organic ligands as linkers. Due to polymeric nature, MOFs are usually insoluble in common solvents and thus can be regarded as heterogeneous.

Abstract

Many of the MOFs reported so far display intriguingly high internal and external surface area together with the extraordinary degree of variability for both the organic and inorganic components of their structure. There materials have characteristically high surface area which can be tuned depending upon the organic linker as well as the inorganic cluster; high porosity, which can be tuned to micro, macro and mesopores depending upon the organic linkers and comparatively easy preparation methods [9]. Moreover, the ability to modify the chemical or physical properties of the voids by employing suitable organic linkers allows one to assemble catalytically active MOFs with the ability to tune the catalyst activity or selectivity. Traditionally, organic polycarboxylate compounds are the most preferred choice of linkers for MOF synthesis, primarily due to the high crystallinity of the final polymeric frameworks which greatly aid in their structural characterization. However, most of the carboxylate-based MOFs are moisture sensitive due to the weak metal carboxylate bonds which tend to hydrolyse under ambient conditions. The lack of stability in air and water remains a significant problem if they are to be used in industrial or commercial applications. Therefore, development of hydrolytically stable MOFs remains one of the most pressing challenges that needs to be overcome for their eventual application in industry.

Layered phosphonate frameworks are one of the extraordinary classes of metal organic frameworks, having layered structure [10]. These systems are highly stable considering their robust structure and often surpass carboxylate-based metal organic frameworks in terms of chemical and thermal stability. The higher acidity of oxygen in phosphate group compared to oxygen in carboxylate group enables the phosphonate group to have a stronger interaction with the electropositive metal molecule with respect to carboxylate-based MOFs [11]. Also, presence of three possible coordination sites in the phosphonate group makes the framework more intact and stable than the carboxylate-based frameworks. Carboxylate based MOFs are more vulnerable to degradation under extreme pH environment or even in aqueous medium because of considerably weak oxygen-metal (O-M) bonds of carboxylates in harsh chemical and thermal environment, which thus involves greater O-M bond interaction in case of phosphonates. Phosphonate based MOFs with Sn(IV) and Zr(IV) are profoundly porous in nature (determined by the organic linkage present), stable and considerably robust, mostly insoluble in regularly utilized solvents like methanol, water, dichloromethane, acetone and so on, also stable at acidic conditions [12,13]. Besides, these materials form stable systems even in aqua regia. This class of materials with its typical layered structure, possess immense

possibilities in various applications like catalysis including heterogeneous catalyst support, radioactive anion trapper, proton conductor, anion adsorption and gas stockpiling material and so on [14-18].

In view of the above literature, work done during the tenure of the Ph.D. work, primarily focuses on design of catalytic systems with improved efficiency and recyclability. For this purpose, two distinct yet complementary methodologies were employed. The first approach relied on incorporating an additional functionality on a N-heterocyclic carbene (NHC) based organocatalytic system as a hemilabile arm and thereby enhancing 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 six chapters and detailed content of each chapter are described below.

Chapter 1

A detailed introduction on NHC based catalytic systems, their advantages along with current challenges are described in Chapter 1. Further, details of different heterogeneous NHC based catalytic systems developed so far and the limitations of such systems are also discussed in this chapter. Based on the literature survey discussion, the objectives of the thesis are drawn and discussed in this chapter.

Chapter 2

Synthesis, characterization, theoretical calculations, and catalytic application of a series of phosphonate ester functionalized imidazolium salts are elaborated in this chapter. Starting from N-aryl imidazoles, a series of phosphonate ester functionalised imidazolium salts (**5**-**8**) are prepared (Chart 1). All four phosphonate ester functionalized imidazolium salts are characterized by elemental analysis, Fourier-transform infrared spectroscopy (FT-IR), ^{1}H Nuclear magnetic resonance (NMR), ^{13}C Nuclear magnetic resonance (NMR), ^{31}P Nuclear magnetic resonance (NMR) and High Resolution Mass Spectrometry (HR-MS). Density Functional Theory (DFT) calculations were carried out to understand the electronic behaviour of the corresponding N-heterocyclic carbenes obtained from the phosphonate functionalized imidazolium salts.
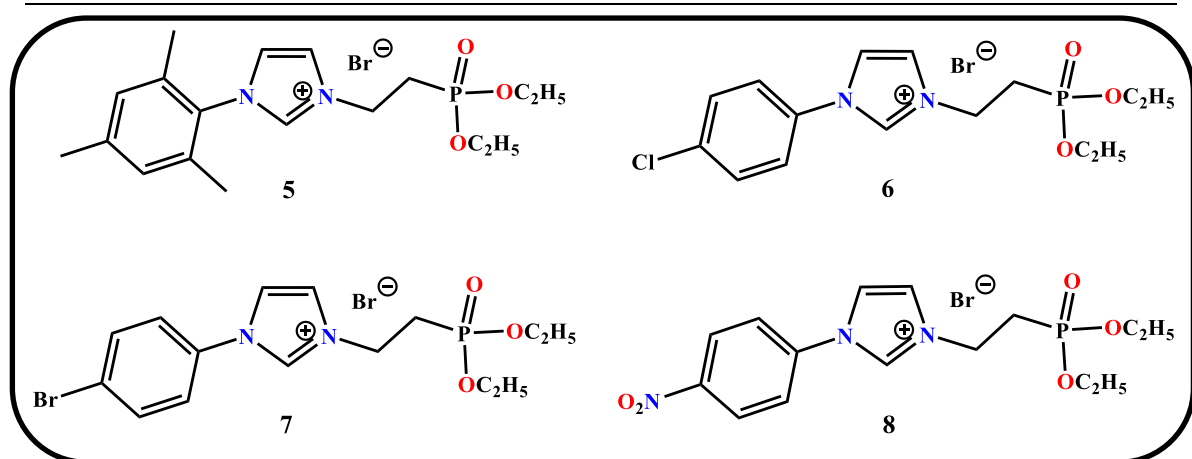
Chart 1: Phosphonate ester functionalized imidazolium salt

The catalytic efficacy of the phosphonate ester functionalised N-heterocyclic carbenes generated from the respective imidazolium salts (**5**-**8**) in esterification of benzaldehyde with two different substrates *viz.* aryl boronic acid and alcohols were investigated (Scheme 3). Density Functional Theory (DFT) calculation were carried out to probe the probable mechanism of these two N-heterocyclic carbene catalysed esterification reaction and decipher the influence of phosphonate ester functionality on the catalytic efficacy.
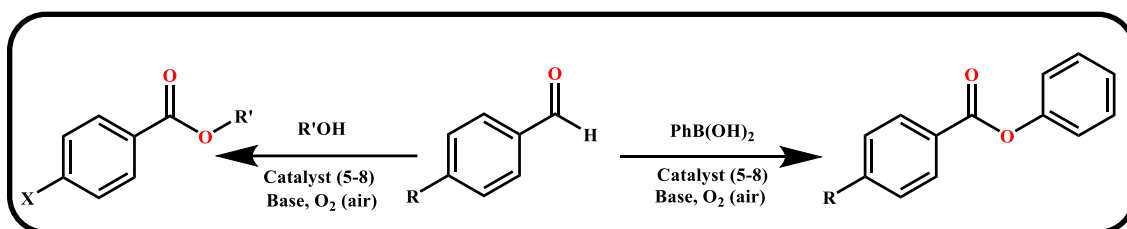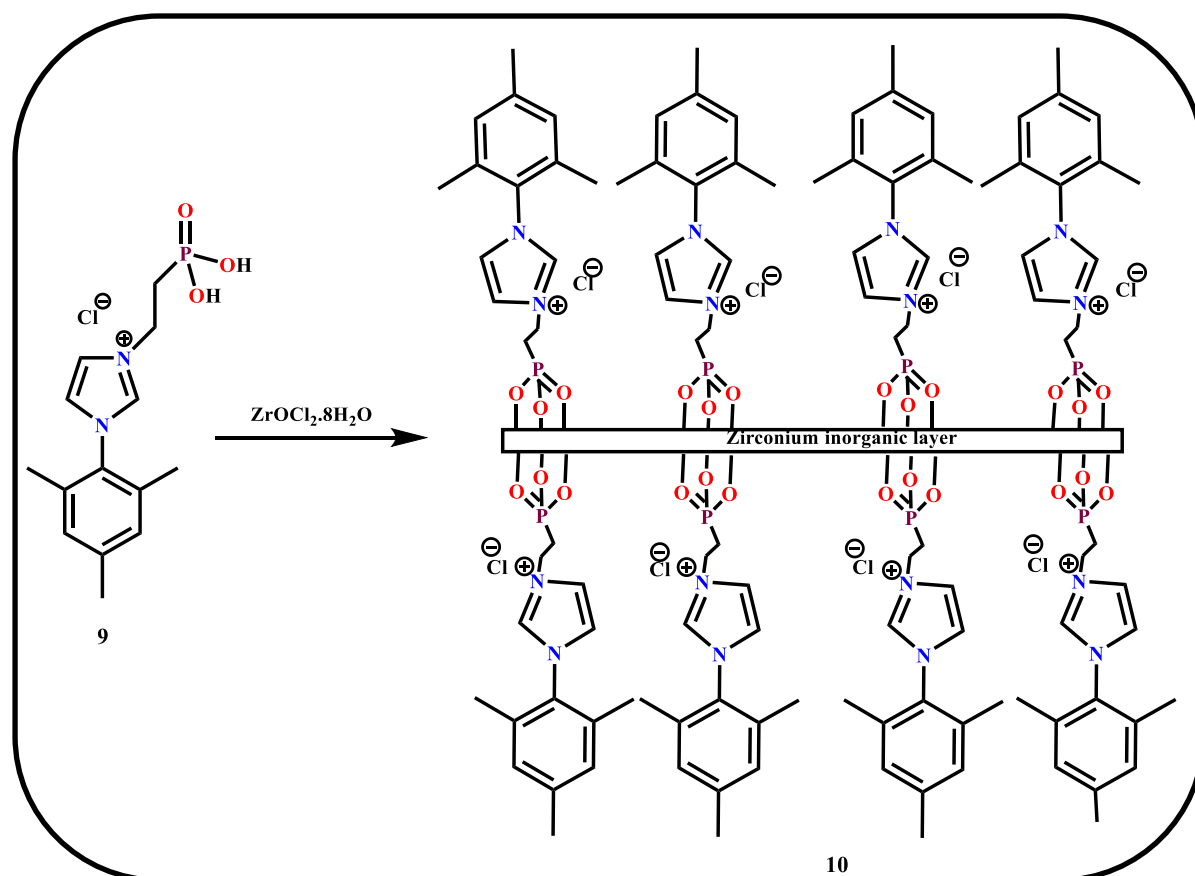

Scheme 3: Esterification of benzaldehyde with aryl boronic acid and alcohols
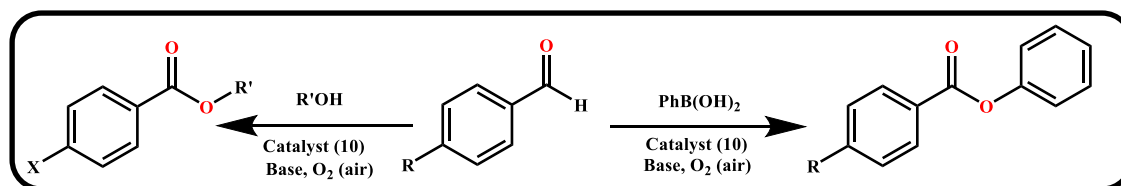
Chapter 3

Synthesis, characterization and organocatalytic application of a zirconium phosphonate supported NHC is reported in chapter 4. By employing the phosphonate ester functionalized imidazolium salt, **5** as precursor, a simple and facile approach to prepare a layered Zr(IV) phosphonate with covalently anchored imidazolium functionality is developed. The phosphonate ester functionalized imidazolium salt can be easily hydrolyzed to result the corresponding phosphonic acid. Reaction of phosphonic acid functionalized imidazolium salt with $ZrOCl_2.8H_2O$ gave quantitative yield of the desired Zr(IV) phosphonate with dangling imidazolium group (Scheme 4). The title compound is

characterized by elemental analysis, Fourier-transform infrared spectroscopy (FT-IR), Thermogravimetric Analysis (TGA), powder-X-ray diffraction (PXRD), solid state ^{13}C MAS NMR (Magic Angle Spinning Nuclear magnetic resonance), ^{31}P MAS NMR (Magic Angle Spinning Nuclear magnetic resonance), X-ray photoelectron spectroscopy (XPS), energy dispersive X-ray spectroscopy (EDS) and Field emission scanning electron microscope (FESEM).

Scheme 4: Preparation of layered Zr(IV) phosphonate with dangling imidazolium group

The heterogenous organocatalytic efficacy of the Zr(IV) phosphonate framework in esterification of benzaldehyde with both aryl boronic acid and alcohols (Scheme 5) are probed. Apart from that investigating the substrate scope of **10** catalyzed esterification reaction, the recyclability of the catalyst is also probed. Further, the integrity of the catalyst recovered after multiple catalytic cycle is investigated to establish its true heterogeneous nature.

Scheme 5: Esterification reaction of benzaldehyde with aryl boronic acid and alcohols using **10** as catalyst

Chapter 4

The possibility to employ α- zirconium phosphate nano-platelets as a heterogenous support for immobilizing CdS quantum dots and thereby improve the photocatalytic efficacy have been explored and the results are detailed in this chapter. A simple and facile technique is developed to immobilize CdS quantum dots of average size 2-6 nm on the surface of α- zirconium phosphate nano-platelets (Scheme 6). A new composite material is characterized by using analytical, spectroscopic, structural and microscopic studies. Chrono-amperometric and electrochemical impedance studies were also carried out to investigate photochemical characteristics of the composite material.
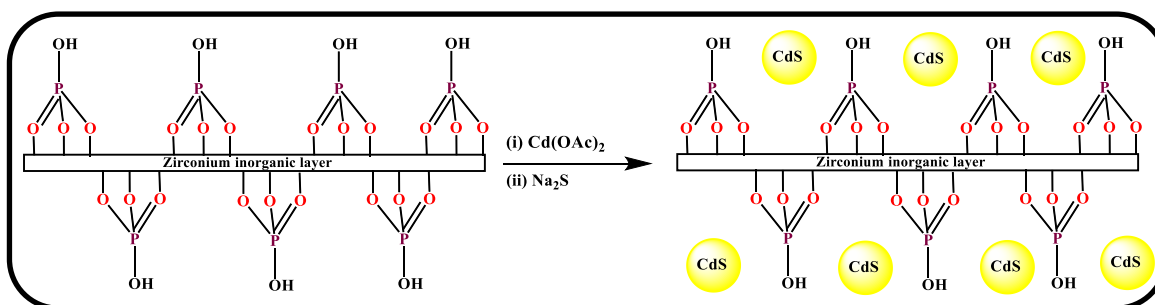
Scheme 6: Synthesis of α- zirconium phosphate nano-platelets supported CdS quantum dots

The photocatalytic behaviour of the CdS@α- zirconium phosphate composite was explored in photochemical oxidation of benzyl alcohol to benzaldehyde. Apart from the catalytic efficacy and selectivity of benzaldehyde formation, the reusability of the composite material in multiple catalytic cycle is also investigated (Scheme 7). Moreover, the mechanism of the photocatalytic reaction is investigated by carrying out the reaction in presence of different scavengers and the results are discussed in this chapter.
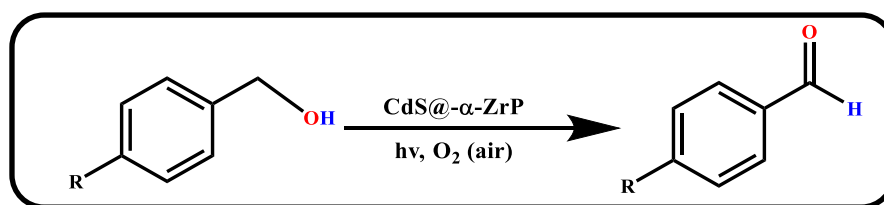
Scheme 7: Photocatalytic reaction of Benzyl alcohol to Benzaldehyde

Chapter 5: Conclusions

Chapter 5 includes the summary of the results found and discussed in chapter 2-4. The important correlations between the investigations carried out in this present work are discussed in this chapter. Based on the salient features of the present thesis work, futures prospective of the work, the possible advancement in this field of research are also discussed in this chapter.

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