ABSTRACT

The thesis entitled "*Development and Catalytic Studies on Novel Main Group, Transition Metal and Organometallic Catalysts for Oxidation of Alcohols and Amines*" presents the results obtained from the research work carried out on the development, characterization and application of novel main group, transition metal complexes and organometallic compounds as catalysts for the oxidation of alcohols and amines to value-added chemicals. The accompanied research work has been divided into the nine chapters.

Chapter 1 The work described in this thesis centers around the development of novel catalytic systems based on main group elements and ions, transition metal complexes and organometallic compounds and their application for oxidation of alcohols and amines to value-added chemicals. The first chapter of the thesis deals with a brief discussion on the literature around C-H functionalizations using directing group strategies and possible methods to remove the directing groups from the metal sandwich compounds. This is be followed by a detailed discussion on use of water as solvent in organic reactions and the oxidation of alcohols and amines to value-added chemicals using water soluble catalysts. Following this a brief background for the catalytic olefination using benzyl alcohols and benzylamines has been provided. In the last section of this chapter, a brief background of recent developments on artificial switchable catalysts has been portrayed.

The chapter ends with the scope of the present of work carried out and reported in the thesis.

Chapter 2 describes the general experimental procedures adopted in the synthesis of new compounds and details of characterization techniques utilized. Specific synthetic details of the starting materials described in the thesis are also presented.

Chapter 3 describes sp^2 C–H bond activation and sp^3 C–H bond oxidation studies on metal sandwich compounds using picolinamide as the directing group. In addition to the C-H bond activation and functionlization, this study has resulted in a novel method to remove the direction group via oxidation of $-CH_2$ unit bound to the Cp-ring of the metal sandwich compounds. Identities of the palladacycle intermediate and some C-H functionalized metal sandwich compounds were confirmed by single crystal XRD studies. The reaction mechanisms for both the C-H bond activation and C-H bond oxidation reactions were also proposed by taking in account the literature reports and control experiments.

Chapter 4 describes a sustainable method of oxidation of benzylamines to the corresponding imines using Co(II)bpb, (bpb = *N,N′*-bis(2'-pyridinecarboxamide)-1,2-benzene) an inexpensive water soluble transition metal complex as the catalyst, water as the solvent and air as the green oxidant. The substrate scope showed the applicability of this reaction in presence of electron-donating as well as electron withdrawing substrates. Mixture of two amines gave the cross-coupled imine products in moderate to good yields. The rate and order of the reaction was also determined by kinetic experiments.

Chapter 5 describes the oxidation of alcohols and aldehydes to carboxylic acids in water medium using molecular iodine as catalyst and ter-butylhydroperoxide (TBHP) as the oxidant. In addition to substrates scope, detailed mechanistic studies have also been carried out to find out the active catalyst, role of water and the possible reaction pathway.

Chapter 6 deals with the topic of earth/sea abundant anionic catalyst for oxidation of alcohols and amines. We have for the first time developed a novel catalytic system using Cl^-, the most abundant, ubiquitous and inexpensive anion for oxidation of alcohols to acids and amine to imines in water. The substrate scope showed the applicability of this metal free, sustainable and economical oxidation method. The rate and order of the reaction w.r.t benzyl alcohol as well as benzylamine was also determined by kinetic experiments.

Chapter 7 describes oxidative olefination of methyl substituted N-heteroarenes with benzylamines and alcohols in water medium using NaCl as the catalyst and aq. TBHP as the oxidant. A detailed optimization of the mentioned method has been discussed in the thesis. Substrate scope of the methyl substituted N-heteroarenes, benzylamines and benzyl alcohols were investigated and the mechanism of the reaction was also proposed by taking in account the literature reports and control experiments.

Chapter 8 describes the development of a water soluble switchable bifunctional bi-state Ru-catalyst for dehydrogenation of alcohols and hydrogenation of aldehydes. Substrate scope of benzyl alcohols and benzaldehydes were investigated and the mechanism of the reaction was also proposed by taking in account the literature reports.

Chapter 9 gives the overall conclusions of the entire work carried out in the present study.