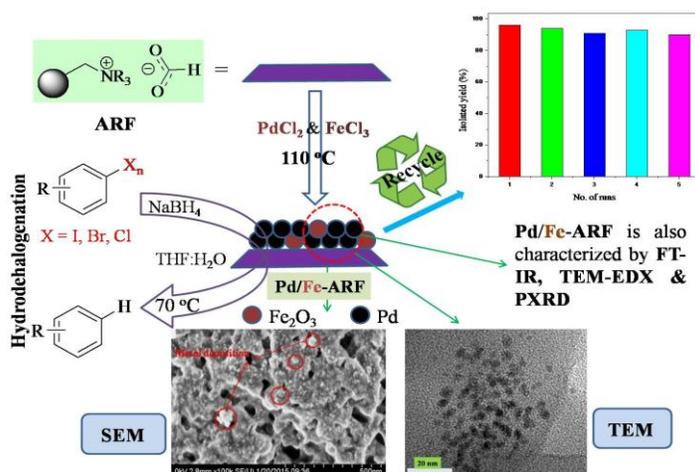


ABSTRACT

The research work embodied in this thesis entitled “**DEVELOPMENT OF ORGANIC REACTION METHODOLOGY USING POLYMER-SUPPORTED REAGENTS, FOCUSED MICROWAVES AND ON-WATER CHEMISTRY**” is primarily focused on polymer-supported heterogeneous catalysis, ‘on-water’ and microwave-assisted organic reactions. The entire works essentially follow some principles of Green Chemistry. The work was initiated in July 2008 as a CSIR-NET-JRF and completed with the support from UGC under faculty development program. Based on different facets and contents of the work, the thesis has been divided into five chapters.

As a prelude to present work, the **Chapter I** covers a brief review on the recent development and trends towards polymer-supported reagents and metal nanoparticle composites as heterogeneous catalysts in organic reactions. Among diverse polymeric supports or assembly, the inorganic polymers mainly utilized as suitable solid supports and metal encapsulating agents and inorganic-organic hybrid materials like Coordination Clusters, Metal Organic Frameworks are used as metal embedding supports and further applications in diverse fields including catalysis. Besides, the organic polymeric materials are discussed quite elaborately since the present work in the next chapter is directed towards the use of organic polymeric resins as the suitable support for the immobilization of mono- and bimetallic species and subsequent applications of the resulting nanocomposites as heterogeneous catalysts. Illuminating examples along with merits and demerits are discussed in this chapter with updated references.

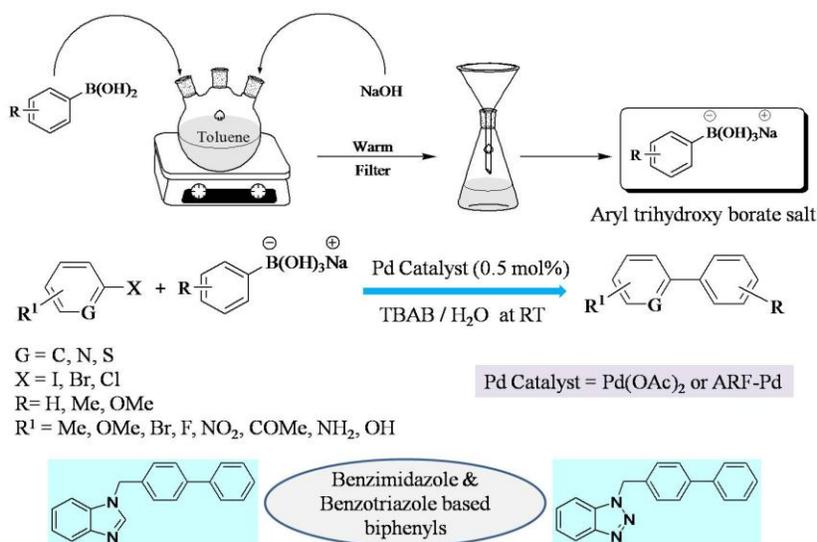
Chapter II describes our works on the preparation of poly-ionic resin embedded with bimetallic (Pd & Fe) nanocomposites, their characterization by FT-IR, powder XRD, AAS, SEM and TEM analyses and subsequent use as catalyst in hydrodehalogenation of aromatic halides in the presence of NaBH₄ in aqueous THF. The new bimetallic nanocomposite consisting of palladium, iron oxide and Amberlite resin formate has been found to be as an efficient, chemoselective and recyclable heterogeneous catalyst. Enhanced catalytic activity has been explained in the light of synergism between two metallic species and a plausible mechanism is proposed accordingly.



The **Chapter III** is divided in three sections: **Section A, B & C**

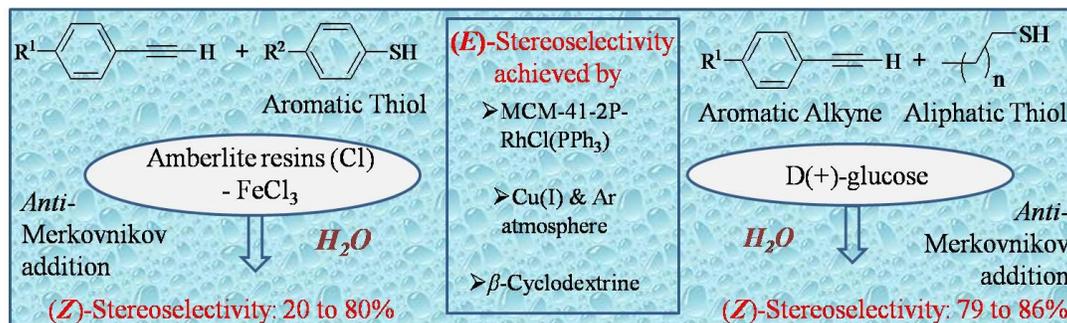
Section A gives a concise background of 'On-water' chemistry in the field of organic synthesis. The primitive reaction developed by Paul Anastus opened a new epoch in the field of organic synthetic methodology. Though organic compounds are insoluble in aqueous medium but in some cases, the reaction rates were found to be increased tremendously. This phenomenon has been explained by two effects. Finally, these section ensembles some metal-catalyzed and without metal catalyzed organic reactions with interesting examples of recent work.

Section B details on Suzuki-Miyaura coupling reaction at room temperature and 'on-water' conditions. In the present work, sodium salt of aryl trihydroxy borate was used as an efficient water soluble organoboron species, which couple with aryl halides under Pd-catalyzed 'on-water' conditions. Other methods using aryl boronic acid/esters under 'on-water' conditions often proceed very slow and/or incomplete conversions along with the difficulty to isolate the products from the reaction mixture. The protocol was established as a general and practical strategy with applications to wide variety of aryl halides. Further extension of this 'on water' protocol was extended towards the preparation of some pharmaceutically important benzimidazole- and benzotriazole-based biphenyl scaffolds with appreciable conversions. A comparison of the reactivity of using homogeneous Pd(OAc)₂ and heterogeneous ARF-Pd catalyst has also been examined and excellent conversions of biaryls were obtained using both types of catalysts.

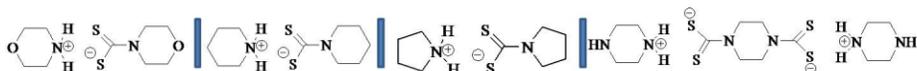
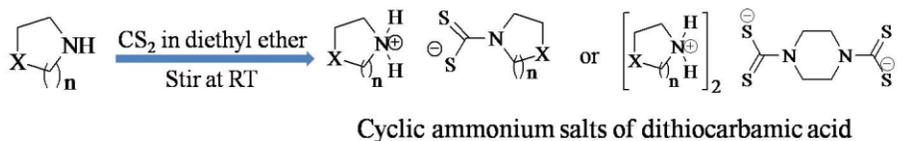
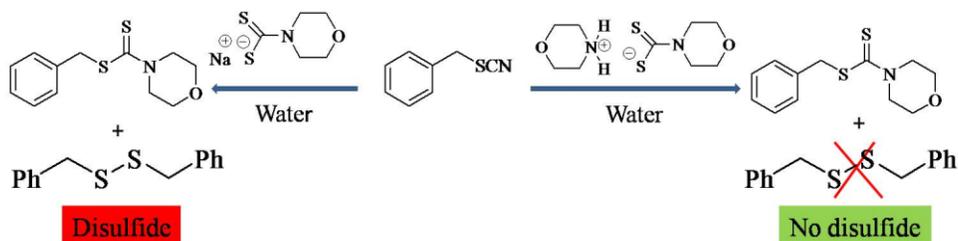


Section C delineates our studies towards the 'click' thiol addition to alkynes leading to the formation of (*E/Z*)-vinyl sulfides, carried out under 'on-water' conditions in the presence of a range of additives. In general, the (*E*)-isomer is formed preferentially. However, the stereochemical outcome has been found to be dependent of the additives, which could be used as 'stereoselective switch' to *E*- or *Z*-vinyl sulfides, though succinct reasons for the selectivity are not understood. While a combination of Amberlite resin Chloride-FeCl₃ leads to maximum *Z*-stereoselectivity for reaction with aromatic thiols, the presence of D(+)-glucose affords

maximum *Z*-stereoselectivity for reaction with aliphatic thiols. Other additives favor usual formation *E*-vinyl sulfides.



The **Chapter IV** describes an efficient and rapid protocol for the synthesis of libraries of carbodithioate esters from organyl thiocyanates by reacting with cyclic amine-based dithiocarbamic acid salts in water. Alkyl thiocyanates, often considered as pseudohalides, are reluctant to undergo substitution reaction with dithiocarbamate nucleophile and usually give rise to the formation of disulfides under basic medium. The protocol is found to be applicable in general to various thiocyanates like benzyl/aroyl methyl/cinnamyl etc. Other notable features include no by-products like disulfides, metal- and alkali-free, aqueous conditions and finally easy and near-quantitative formation of cyclic amine-based dithiocarbamic acid salt as stable alternative reagent.



Chapter V depicts preparation of new CuI-1,3-dithioether coordination polymer complex, characterization by NMR and single crystal X-ray structure determination, and finally its efficient role as catalyst in azide-alkyne cycloaddition (AAC) reaction. Although few examples of other dithioether-based Cu(I) complexes are known in the literature, the present 1,3-dithioether ligand-based Cu(I) complex is not known, and there is no example of such complexes used as the catalyst for the AAC reaction. The present study therefore establishes a

new and convenient catalytic process for the one-pot AAC in multi-component manner, and the catalytic system has been found to be recyclable. The yields of the cycloadducts are excellent in diverse array of reactants. While trying the AAC under microwave irradiation however did not give satisfactory results.

