

Chapter 1

Introduction

In 1836 Berzelius introduced the term catalyst; according to him catalyst is a substance which enhances the rate of reaction without being consumed. Catalysis plays an important role in production of bulk chemicals and fuels. They are important in the economic and environmental perspective. Main advantage of using catalyst in a chemical reaction is selectivity. Currently there are technologies available for the design and development of catalyst mainly by the discovery of atom scale measurements, and high resolution spectroscopic techniques. Catalysts are divided into three types; homogeneous, heterogeneous and enzymatic, each employed with a single aim to enhance the rate of chemical reaction.

Environmental concern encourages the chemical community to search for more environmentally benign processes for chemical synthesis. Two important issues in this regard are development of recyclable heterogeneous catalysts and use of less toxic solvents and reagents. “Green chemistry” is a common word having twelve distinct principles which explores the use of no solvent or green solvent and green catalyst for synthetic purpose. The weakness of using non-green solvent and catalyst made the researchers to think about the “green” strategy. Water is taken as the commonly used “green solvent”. A catalyst should be cost effective, environment friendly, highly active, easily recyclable, and easy to recover from reaction medium. Heterogeneous catalysis became more relevant as it satisfies the crucial objectives of “green chemistry” minimizing waste and optimizing the use of resources thereby leading to sustainability. Now a days, merging of two fields like catalysis and organic synthesis became more prominent due to economic and environmental reasons.

One of the objectives of the present research work is the development of efficient, cost effective and green catalytic system for the synthesis of 1,2,3-triazole *via* click reaction. For this we developed two catalytic systems, one using copper supported polymer which can be prepared by suspension polymerization followed by complexation with copper and the second one by using nanoparticles prepared using

Myristica fragrans fruit extract. Our next aim was to develop a simple but efficient synthesis of *N*-heterocyclic carbene complex starting from 1,2,3-triazole and its application in catalysis as well as biological activity.

The thesis is divided into 6 chapters. A review on the CuAAC synthesis of 1,4-disubstituted 1,2,3-triazole are highlighted in chapter 2. In the review, more priority has been given to the importance of heterogeneous catalysts in triazole synthesis.

1,2,3-triazoles are important class of heterocyclic compounds because of their wide range of biological activities and applications in industry. Huisgen's 1,3-dipolar cycloaddition commonly called click reaction is used to assemble this scaffold. Click reactions are mainly of two types, copper catalyzed azide-alkyne cycloaddition (CuAAC) reaction and thiol-ene reaction. CuAAC leads to the formation of 1,4-disubstituted 1,2,3-triazoles by the reaction between terminal alkyne and azide in the presence of copper(II). The uncatalyzed reaction requires high temperature and lacks regioselectivity in products. Heterogeneously catalyzed click reaction takes more benefits compared to the homogeneous one including simplicity in product isolation, recyclability and reducing environmental concerns.

Chapter 3 describes the synthesis of *N,N'*-methylene bis-acrylamide cross linked *N*-vinyl-2-pyrrolidone (PVPNNMBA). The polymer matrix can reduce Cu(II) to Cu(I) and can stabilise the later within the polymer matrix, preventing further reduction. Techniques like FTIR, XRD, EDS, SEM, XPS, ICP-AES, TGA-DTA etc. were used to characterize the polymer. The copper supported polymer catalyst was used for the efficient synthesis of 1,4-disubstituted 1,2,3-triazole and optimization of catalyst was carried out in terms of solvent, temperature and catalyst loading. The catalyst performs well in water as solvent with minimum catalyst loading. The products were characterized using ¹H NMR, ¹³C NMR, GC-MS. The study demonstrated that copper supported polymer material is an excellent heterogeneous catalyst for the azide-alkyne click reaction.

Chapter 4 explains the preparation and characterization of copper oxide and silver nanoparticles from *Myristica fragrans* fruit extract. Hydrothermal method was adopted for the preparation of the fruit extract. Bioreduction of copper acetate produces copper oxide nanoparticless. Phytoconstituents present in the fruit extract are responsible for the metal reduction. Light induced reduction of silver nanoparticle

was carried out in presence of *Myristica fragrans* fruit extract. Color change observed during the reaction indicates the formation of silver nanoparticles and the same was confirmed by UV-visible absorption spectroscopy. FTIR provides an indication of the functional groups present in the phytoconstituents. Powder X-ray diffraction studies were used for phase identification and size of copper oxide nanoparticles. Nano size of the copper oxide was confirmed using FEG-SEM, and HR-TEM. EDS was used to find out the elemental composition of the nanoparticles entrapped in phytoconstituents. Copper oxide and silver nanoparticles have been tested for its potential as a heterogeneous catalyst for CuAAC click reaction in water.

Catalytic activity of silver nanoparticle was also investigated for azide-alkyne cycloaddition reaction (AgAAC). Silver nanoparticles were not suitable for the regioselective synthesis of 1,4-disubstituted triazoles. As the metallic silver is known to possess biological activities, antibacterial properties of synthesized silver nanoparticles were studied. The antibacterial activity largely depends on the size and shape of the nanoparticle and its influence on the activity was also studied.

In organometallic catalysts a central metal is bonded to organic ligands. Properties of the catalyst are determined by both the central metal atom and the coordinated ligands. The success of organometallic catalysts depends on the relative ease of catalyst modification by changing the ligand environment. Simply by changing the ligands around the metal centre, one can tune its catalytic properties.

Over the last two decades, *N*-heterocyclic carbenes (NHCs) have emerged as ligands for a variety of transition metals. After the isolation of the first “bottleable” NHC by Arduengo in 1991, a large variety of NHCs have been synthesized. Among these, imidazolylines and triazolylidenes have become more popular. Initially, NHCs were considered as phosphine mimics, the difference between phosphine and NHCs becomes more apparent now. *N*-heterocyclic carbene complexes have application in several fields. In Medicinal field they have application as antimicrobial and antitumor agents. It can be used as a homogeneous catalyst for a variety of chemical reactions like transfer hydrogenation, C-C bond forming cross coupling reactions like Heck, Suzuki-Miyaura and Sonogashira reactions.

Chapter 5 describes the synthesis of 1,2,3-triazoles and their palladium *N*-heterocyclic carbene complexes. We have synthesized palladium triazole/triazolylidene complexes

with different bonding pattern. These complexes were characterized by ^1H NMR, ^{13}C NMR, and SXRD. The catalytic efficiency of the palladium *N*-heterocyclic complexes containing C-Pd-N bonding pattern shows better catalytic activity towards Suzuki-Miyaura cross coupling reaction in water and compared to its activity with other synthesized complexes. The Cytotoxicity of these complexes has been studied and the carbene complex with C-Pd-N bonding pattern was found to have good activity compared to other palladium complexes. A summary and conclusion of the work is presented in Chapter 6.