Summary

Supported metal particles play an important role in heterogeneous catalysis. It has been shown that the supported metal catalysts has a profound effect on the catalytic activity, thus necessitating the need for synthesis methods aimed at a strict control of the metal crystallite size in these catalysts. The controllable preparation of heterogeneous catalysts is a gentle art, and various procedures are at the disposal of chemists to efficiently elaborate supported catalysts for improving reaction rate and selectivity.

The present work describes our studies with alumina supported ruthenium, silica supported copper as well as palladium nanomaterials were applied as a catalyst and catalytic activity results are discussed. The thesis is comprised of six chapters. Chapters I and II discuss the general introduction about colloidal metal nanoparticles as catalysts in homogeneous, heterogeneous catalysis and various methods adopted and materials used in thesis. In chapter III, use of \( \gamma \)-Al\(_2\)O\(_3\) as a catalytic support for ruthenium nanoparticles and used for the oxidation of sulfides into sulfoxides and tertiary amines are discussed. In chapter IV, the functionalized silica as support for copper nanoparticles used for the synthesis of 1,2,3-triazole and thioethers. In chapter V, the same amine functionalized silica as support for palladium nanoparticles, is employed as versatile catalyst Suzuki, Heck and Sonogashira coupling reactions. In chapter VI, highly branched polymer as support for gold nanoparticles used as a homogenous catalyst for reduction of nitro compounds using ice cold NaBH\(_4\) by kinetic methods.

Chapter I

Introduction

This chapter deals with various aspects of synthesis of homogeneous and heterogeneous catalyst and their catalytic applications have been discussed. Metal salt reduction method to use to synthesis various metal colloids and these nanocolloids were immobilization on the surface of metal oxides as a catalytic support.
Chapter II

Methods and Materials

In this chapter, detailed accounts of various materials were used in Ru, Cu, Pd and Au nanocatalyst preparations. Synthesis of amine functionalized silica colloids have been detailed discussed. Experimental details for the synthesized, Ru, Cu and Pd colloids were immobilized on a suitable catalytic support for the heterogeneous catalyst. Highly branched polymer capped Au nanoparticles for the homogeneous catalyst and also various instruments used are discussed in detail.

Chapter IIIA

Alumina supported nanoruthenium as efficient heterogeneous catalyst for the selective $\text{H}_2\text{O}_2$ oxidation of aliphatic and aromatic sulfides to sulfoxides

Oxidation of aromatic aliphatic sulfides is important, fundamental reactions are paramount importance in organic synthesis. In particular, oxidation of aromatic sulfides has evoked great contemporary interest as they are prime precursors for organic transformations. The $\gamma$-$\text{Al}_2\text{O}_3$ is an irreducible oxide (similar to MgO and SiO$_2$), which was traditionally regarded as a good support for Ru. Alumina is not a transition metal oxide (TMO), which lacks the d-states. The empty d-states were shown to play important roles in activating $\text{H}_2\text{O}_2$ for oxidation on Ru/Al$_2$O$_3$. In the present work, a mild and efficient protocol for the selective oxidation of alkyl and aromatic sulfides has been achieved by employing Ru/Al$_2$O$_3$ as a catalyst using 30% $\text{H}_2\text{O}_2$ oxidizing agent in CH$_3$CN medium (Scheme 1).

\begin{center}
\textit{Scheme 1. Oxidation of sulfides using Ru(PVP)/$\gamma$-Al$_2$O$_3$.}
\end{center}
Summary

The proposed mechanism involves the adsorption of both the oxidant (H\textsubscript{2}O\textsubscript{2}) and the substrate (sulfide) on the adjacent sites of Ru(0) surface and the efficient coupling of reactants to form the product sulfoxide selectively. Interestingly this report seems to be a novel and simple method for the oxidative conversion of sulfides to sulfoxide using H\textsubscript{2}O\textsubscript{2} as the oxidant and Ru nanoparticles loaded on \(\gamma\)-Al\textsubscript{2}O\textsubscript{3} as the catalyst (Ru(PVP)/\(\gamma\)-Al\textsubscript{2}O\textsubscript{3}). The catalyst (Ru/Al\textsubscript{2}O\textsubscript{3}) is synthesized and well characterized by XRD, HRTEM, BET, H\textsubscript{2} chemisorption, SEM-EDX, AFM, FT-IR, and UV-vis spectral techniques.

Chapter IIIB

Alumina supported nanoruthenium catalyzed N-oxidation of tertiary amines by using H\textsubscript{2}O\textsubscript{2}

The chemistry and applications of N-oxides have recently received much attention due to their usefulness as synthetic intermediates and their biological importance. Heterocyclic N-oxides are also useful as protecting groups, auxiliary agents, oxidants, ligands in metal complexes and catalysts. The N-O moiety of pyridine N-oxides possesses a unique functionality which can act effectively as a push electron donor and as a pull electron acceptor group. This strong push-pull property has an essential chemical consequence; it accounts for the equally easy synthesis of 4- substituted derivatives of pyridine N-oxides with donor as well as acceptor groups.

In continuation to our oxidation studies (Previous chapter), here we applied the catalyst I for the oxidation of tertiary amines to the corresponding N-oxides with 30\% H\textsubscript{2}O\textsubscript{2} in high yields. The title reaction is represented in Scheme 2.

Scheme 2. N-oxidation of amines using catalyst I.
Here we applied the same catalyst (Ru/Al$_2$O$_3$) used for N-oxidation of aromatic amines in CH$_3$CN medium. The catalyst is reused without any loss in its activity. The reaction takes place at room temperature the yields is very low as well as take much more time to accomplish the reaction. It readily takes place at 80°C in short time with good yields. Other advantages include much simpler experimental conditions, ease of recovery and reuse of catalyst.

Chapter IV

Highly dispersed silica-supported nanocopper as efficient heterogeneous catalyst: Application in the synthesis of 1,2,3-triazoles and thioethers

In this chapter, we report the synthesis of amine modified SiNPs (silica nanoparticles) by sol-gel method and the role of synthesized SiO$_2$ as a solid support for the nanocatalyst CuNPs (copper nanoparticles). In this Chapter we design and development of new, highly efficient catalyst systems for the cycloaddition and C-S coupling reactions using copper nanocatalysts which can be recycled and reused several times with little loss of their catalytic activity. The catalytic activities of nano Cu/SiO$_2$ (Catalyst II) for the 1,3-dipolar cycloaddition and C-S coupling reactions as detailed in Scheme 3 are investigated and presented in this chapter.

Scheme 3. Synthesis of 1,2,3-triazoles and thioether using catalyst II.
The nanocatalyst is characterized by XRD, HRTEM, BET, AFM, SEM, EDX, UV-vis, FT-IR and TGA techniques. The effect of different solvents and bases are used to optimization of the Click and C-S coupling reactions. The Cu/SiO$_2$ (catalyst II) serves as an efficient heterogeneous nanocatalyst exhibiting high catalytic activity for the synthesis of a series of 1,4-disubstituted-1,2,3-triazoles and thioethers. The catalyst II can be recycled and reused several times without any significant loss of catalytic activity proved by XRD and HRTEM techniques.

Chapter V

Synthesis and characterization of silica-supported palladium nanoparticles and role as potential catalyst in Suzuki, Heck and Sonogashira coupling reactions

We have demonstrated that synthesized silica supported PdNPs was successfully employed in the Suzuki, Heck and Sonogashira coupling reactions. The PdNPs were synthesized using highly branched PEI as a capping agent and ascorbic acid as a reducing agent in aqueous solution at 95°C. The catalyst Pd/SiO$_2$ is employed as an efficient catalyst in coupling reactions and is catalytic role is schematically represented in Scheme 4.

Scheme 4. Pd/SiO$_2$ catalyzed Suzuki, Heck and Sonogashira coupling reactions.

Comparison of our catalytic system with different nanocatalysts in published literature. For the bromo-and iodo halobenzenes are involved in Suzuki coupling...
reaction to carried out in aqueous media and afforded good yields. The solvents DMF and ethylene glycol are used in Heck and Sonogashira coupling reactions and good catalytic activity. The catalysts were characterized by XRD, HRTEM, BET, SEM-EDX, AFM, FT-IR, and UV-vis spectral techniques.

Chapter VI

Highly branched polymer capped gold nanoparticles as efficient active catalyst for catalytic reduction of aromatic nitro compounds by kinetic method

The work presented in this chapter is focused on the synthesis of gold nanoparticles (AuNPs) using highly branched polyethylenimine (PEI) and acylated polyethylenimine (PEI-C$_{12}$) as reducing as well as stabilizing agent. In this work, we have investigated the catalytic activity of PEI and PEI-C$_{12}$ stabilized AuNPs as catalyst in the reduction of 4-nitrophenol (4-NP) with NaBH$_4$ to produce 4-aminophenol (4-AP) as a model reaction in Scheme 5. The catalytic performance in terms of the rate constant and the induction period is discussed through the comparison with the PEI and PEI-C$_{12}$ capped AuNPs catalysts reported so far. Our catalysts appear to exhibit the best performance.

Scheme 5. Reduction of 4-nitrophenol (4-NP) to 4-aminophenol (4-AP) using the AuNPs as catalyst as a model reaction.

The AuNPs are characterized by XRD, TEM, HRTEM, AFM, UV-vis and FT-IR techniques. The AuNPs, in a PEI matrix, is found to be a stable and active catalyst for the selective reduction of nitro compounds using NaBH$_4$ under mild reaction conditions. This catalytic system is stable for several months without any obvious colloidal aggregation.