ABSTRACT

The fields of catalysis and nanoscience have been inextricably linked to each other for quite some time. Several inorganic or organic materials like mesoporous silica, zeolites, charcoal, graphene oxides as well as organic polymers have been used either to promote surface-mediated reactions or to immobilize metal nanoparticles for catalytic performance. Both mono- and bi-metallic nanoparticles (NPs) embedded with heterogeneous supports exhibit improved catalytic activity and find applications in several industrial processes. Development of more active, versatile and recyclable catalysts has remained the contemporary challenges in this field of chemistry and catalysis. The present thesis entitled "PREPARATION, CHARACTERIZATION OF BIMETALLIC NANOPARTICLES SOAKED ON POLY-IONIC RESINS AND THEIR CATALYTIC APPLICATIONS" has made some efforts to demonstrate new heterogeneous surface-promoted reactions as well as to develop mono- and bi-metallic nanocomposites mainly based on poly-ionic resins and graphene-based carbonaceous materials. These two different heterogeneous supports, either free or embedded with metals, have been utilized in diverse C−C, C−S and S−S bond-forming reactions. The thesis is divided into eight chapters.

Chapter I summarizes a brief review on heterogeneous catalysis, nanocomposites and their catalytic applications.

Chapter II describes the use poly-ionic resin hydroxide (Amberlyst® A-26(OH)), as an efficient heterogeneous base for the preparation of organic disulfides from alkyl and acyl methyl thiocyanates. Further extension of this protocol has been tested using two different organyl thiocyanates to prepare unsymmetrical disulfides. The present protocol shows the advantage of using the heterogeneous base Amberlyst A-26(OH) over some existing homogeneous bases (NaOH, NH_3, K_2CO_3). The recyclability was also checked.

Chapter III delineates a simple procedure for the preparation of poly-ionic amberlite resins embedded with CuO NPs (referred to as CuO@ARF). The as synthesized heterogeneous catalyst CuO@ARF was characterized and successfully applied in C−S cross–coupling reaction under ligand–free and 'on–water' conditions. Low loading of the catalyst, recyclability without leaching and chemoselectivity between aromatic halides are notable features. Further application of the chemoselectivity has been demonstrated in the synthesis of bioactive heterocyclic scaffold phenothiazine.

Chapter IV deals with the bi-metallic nanocomposite material. Cationic and macroporous amberlite resins with formate ($HCOO^-$) as the counter anion (ARF) have been used to prepare a new class of heterogeneous Pd/Cu bimetallic composite nanoparticles (NPs) (Pd/Cu–ARF). The physicochemical characteristics of Pd/Cu−ARF revealed fairly uniform distributions of composite NPs of average size~4.9 nm. The nanocomposite material (Pd/Cu ARF) exhibited high catalytic activity in the Sonogashira cross–coupling reaction between aryl iodide and terminal alkynes. Heterogeneity of the catalytic activity was evidenced from different tests (hot-filtration and catalyst-poisoning) and the recycling ability of the catalyst was examined for five consecutive runs without any significant loss of activity.

Chapter V describes further use of the Pd/Cu bimetallic composite nanoparticles (Pd/Cu ARF) in other cross–coupling reactions like Suzuki–Miyaura and Mizoroki–Heck reactions. The bi-metallic nanocomposite material was much effective as compared to monometallic Pd–ARF catalyst, as prepared in this laboratory previously. The catalyst was also recyclable for seven consecutive runs with excellent conversions.

Chapter VI depicts successful application of graphene oxide (GO) as the metal-free carbocatalysts for (i) sequential dehydration–hydrothiolation reaction from a mixture of secondary aryl alcohols and thiols in toluene and (ii) chemoselective thioacetalization of aldehyde under mild, solvent-free and aerobic conditions.

Chapter VII demonstrates the catalytic activity of Ni(0) nanoparticles supported with reduced graphene oxide (Ni/RGO) in Kumada–Corriu cross–coupling reaction. A detail study of the catalysis was performed by varying the haloarenes and Grignard reagents. Interestingly, this catalyst was found to be equally active for the oxidative addition to the sp^2 C−F bond. The recyclability of the catalyst was examined for six consecutive runs without significant loss of activity. Finally the recovered Ni/RGO was characterized by X-ray diffraction (XRD) and Raman spectroscopy and found to be unaltered.

Chapter VIII describes the use of Ni/RGO nanocomposite in C−S cross–coupling reaction. The catalyst was found to be recyclable for six consecutive runs, as examined.