

**Abstract of the Research work:**

The main purpose of this thesis has provided a plentiful study about the metal nanoparticles (MNPs) anchored graphene-based supported catalysts. The catalytic aptitude of metal nanoparticles (MNPs) is vastly dependent on the variety of support. In addition, the nature of particle size stabilization in dropping down the spontaneous growth of small MNPs, the key role of the support is to assist by providing competent ways, which lead to the target product. Other uniqueness of the support is to afford a large surface area, strapping metal-support interaction, and the presence of active sites as well that take part in the reaction mechanism. The modern accessibility of graphene oxide (GO), reduced graphene oxide (rGO), and other graphene-based materials have offer new potential for the development of supported MNPs as heterogeneous catalysts. As supports, graphene-based materials provide various constructive properties i.e. single carbon atom in thickness, which approaches the physical limit for a two-dimensional (2D) surface in which MNPs can be deposited that are not observed in conventional solid supports. This research work is limelighted on the synthesis and characterization of transition metal nanoparticles incorporated on graphene-supported multifaceted catalysts for various in-situ multi-steps organic transformations viz. hydrogenolysis of benzyl alcohol,  $A^3$ -coupling reaction, Knoevenagel condensation reaction, Henry and Aldol condensation reactions, and Henry-Michael reaction.

In concluding remarks, the thesis is involved of eight chapters as revealed below:

- 1) The essential aspects and current scenario of the catalysts, type of catalysts, their advantages and disadvantages, and begins materials on the industrial perspectives were systematically discussed in Chapter 1. The plentiful solid supports, which are available for constructing heterogeneous catalysts from the homogeneous counterparts and the preeminent one amongst these (i.e. carbonaceous support), have been chosen in this work.
- 2) As outline carbonaceous supports (in Chapter 1), particularly, graphene-based materials, among them graphene oxide (GO) was synthesized using

the modified Hummers' method and its reduction counterpart i.e. reduced graphene oxide (rGO) was prepared by chemical reduction method (Chapter 2). These multifaceted graphene-based materials were substantiated through various analytical techniques.

- 3) Chapter 3 shown a greener viewpoint for *in situ* syntheses of MNPs immobilized on reduced graphene oxide (MNPs@rGO) (where MNPs = Metal nanoparticles such as VO, Ni and Cu] nanocatalysts. These composite materials were well corroborated through diverse physicochemical techniques. Noticeably, MNPs@rGO promoted hydrogenolysis of benzyl alcohol (BzA) with triethylsilane ( $\text{Et}_3\text{SiH}$ ) as a reductant bestowing exceptional activity to provide synthetically valuable hydrocarbon product i.e. toluene. Amongst them, CuNPs@rGO shown significantly enhanced catalytic efficacy leading to 81.2% BzA conversion (TOF:  $222 \text{ h}^{-1}$ ) with exceptional 99.9% toluene selectivity. Furthermore, CuNPs@rGO catalyst could be easily recycled and reused without momentous loss of activity in the fifth cycle tests.
- 4) In Chapter 4, we have synthesized and fully characterized ZnONPs@rGO nanocatalysts. The as-synthesized ZnONPs@rGO catalysts have shown exceptional catalytic activity for one-pot  $\text{A}^3$ -coupling (Biginelli) reaction using various aldehydes, ethyl acetoacetate and/or urea, giving excellent yields of dihydropyrimidinone product. The plausible catalytic mechanism for this condensation reaction has also been included in this chapter. ZnONPs@rGO has shown remarkable stability, recyclability and leaching-resistant performance with recycled up to five times without significant loss of activity.
- 5) In Chapter 5, FeNPs tethered on amino-modified rGO (FeNPs/Am@rGO) [where FeNPs = Fe nanoparticles; Am = Primary aromatic amine derivatives such as p-phenylenediamine (PPD) and/or aniline (AN)] as bifunctional nanocatalysts were prepared and characterized through various physicochemical techniques. These nanocatalysts have promoted a one-pot Knoevenagel condensation reaction with different aromatic

aldehydes and active methylene compounds conferring excellent activity to offer synthetically valuable multifunctional benzylidene derivatives. Amongst them, FeNPs/PPD@rGO has shown superior catalytic results i.e. 100% benzaldehyde conversion with exceptional 100% yield of product (TON and TOF ( $\text{h}^{-1}$ ) values are 350.8 and 100.2, respectively).

- 6) Chapter 6 shown the synthesis and characterization of FeNPs/DETA@rGO as a bifunctional nanocatalyst. FeNPs/DETA@rGO was effectively employed for the  $\beta$ -nitrostyrene synthesis (with a high yield up to 99.8%) for the Henry reaction using various substituted benzaldehydes with nitromethane under solvent-free condition. Moreover, it was also checked for Aldol condensation reaction by employing various substituted benzaldehyde with acetone under solvent-free condition giving high yield (96.7%) of benzylidene acetone product. The catalyst is recyclable up to four consecutive cycles without momentous loss of activity.
- 7) In this Chapter 7, we have discussed the synthesis and characterization of transition metal immobilized on amino-functionalized rGO-based bifunctional catalysts (MNPs/Am@rGO) (where M = Fe and/or  $\text{Nb}_2\text{O}_5$ ; Am = ED and/or PPD). These bifunctional catalysts shown amino-based organic derivatives on rGO nanosheet showing basic nature whereas, FeNPs and/or  $\text{Nb}_2\text{O}_5$  NPs immobilized on the surface of rGO contributing Lewis acid behaviours. Among them,  $\text{Nb}_2\text{O}_5$  NPs/PPD@rGO has shown astonishing results with 90.6% and 88.9% conversions of benzaldehyde and  $\beta$ -nitrostyrene, respectively together with 93.2% of 2-(2-nitrophenylethyl)malononitrile product selectivity in one-pot multi-steps Henry-Michael reaction. In recyclability tests for multi-steps reaction, the conversions of benzaldehyde and  $\beta$ -nitrostyrene with 2-(2-nitrophenylethyl)malononitrile product selectivity in the fresh run are 90.6%, 88.9% and 93.2%, respectively. However, a little bit dropped in the conversions as well as product selectivity was shown after each run. Overall, the catalyst has shown excellent stability, recyclability and

leaching-resistant performance with recycled up to five times without significant loss of activity.