CHAPTER-8

CONCLUSION

AND

FUTURE PERSPECTIVES

The primary objective of this thesis has provided a comprehensive study about the metal nanoparticles (MNPs) immobilized graphene-based supported catalysts. The catalytic aptitude of metal nanoparticles (MNPs) is highly reliant on the kind of support. Besides the nature of particle size stabilization in dropping down the unprompted development of small MNPs, the key role of the support is to assist by giving competent pathways which lead to the target product. Other characteristics of the support are to provide a large surface area, strapping metal-support interaction, and the presence of active sites as well that take part in the reaction mechanism. The recent accessibility of graphene oxide (GO), reduced graphene oxide (rGO), and other graphene-based materials have afforded new possibilities for the development of supported MNPs as 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 spotlighted on the synthesis and characterization of transition metal nanoparticles embedded 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 comprised of eight chapters as shown below:

1) The rudimentary aspects and contemporary scenario of the catalysts, kinds of catalysts, their merits and demerits, and emanating 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 preferred in this work.

2) As delineated carbonaceous supports (in Chapter 1), especially, graphene-based materials, among them graphene oxide (GO) was fabricated using the modified Hummers' method and its reduction counterpart i.e. reduced graphene oxide (rGO) was synthesized by chemical reduction method (Chapter 2). These multifaceted graphene-based materials were corroborated through various analytical techniques.
3) Chapter 3 demonstrated a greener perspective for *in situ* syntheses of MNPs embedded 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 (Et_3SiH) as a reductant bestowing exceptional activity to provide synthetically valuable hydrocarbon product i.e. toluene. Amongst them, CuNPs@rGO demonstrated significantly enhanced catalytic efficacy leading to 81.2% BzA conversion (TOF: 222 h^{-1}) with exceptional 99.9% toluene selectivity. In addition to this, 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. In particular, XRD patterns of ZnONPs@rGO nanocatalyst, the diffraction peaks were observed at 31.7º, 34.4º, 36.1º, 47.6º, 56.7º, 62.9º, 68.0º and 70.9º, which are more compatible with those of (1 0 0), (0 0 2), (1 0 1), (1 0 2), (1 1 0), (1 0 3), and (1 1 2), respectively, pointing towards the hexagonal wurtzite structure of ZnO (JPCDS 36-1451). The as-synthesized ZnONPs@rGO catalysts have shown exceptional catalytic activity for one-pot A^3-coupling (Biginelli) reaction using various aldehydes, ethyl acetoacetate and/or urea, giving admirable yields of dihydropyrimidinone product. The plausible catalytic mechanism for this condensation reaction has also been discussed and is 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 anchored 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 synthesized 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 give 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 (h^{-1}) values are 350.8 and 100.2, respectively).
6) Chapter 6 depicted the synthesis and characterization of FeNPs/DETA@rGO as a bifunctional nanocatalyst. The catalyst acquired easily accessible active metal sites with having Lewis acid behaviour and the basic sites engendered through the functionalization of –COOH groups present on GO via amino groups derived from DETA. FeNPs/DETA@rGO was effectively used for the β-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 tested for Aldol condensation reaction by employing various substituted benzaldehydes with acetone under solvent-free condition affording high yield (96.7%) of benzylideneacetone product. The catalyst is recyclable up to four consecutive cycles without momentous loss of activity.
7) In this Chapter 7, we have described the synthesis and characterization of transition metal immobilized on amino-functionalized rGO-based bifunctional catalysts (MNPs/Am@rGO) (where M = Fe and/or Nb_2O_5; Am = ED and/or PPD). These bifunctional catalysts exhibited amino-

based organic derivatives on rGO nanosheet showing basic nature whereas, FeNPs and/or Nb_2O_5 NPs immobilized on the surface of rGO contributing Lewis acid behaviours. Among them, Nb_2O_5 NPs/PPD@rGO has shown astonishing results with 90.6% and 88.9% conversions of benzaldehyde and β-nitrostyrene, respectively together with 93.2% of 2-(2-nitro-phenylethyl)malononitrile product selectivity in one-pot multi-steps Henry-Michael reaction. In recyclability tests for multi-steps reaction, the conversions of benzaldehyde and β-nitrostyrene with 2-(2-nitro-phenylethyl)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 observed 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.

Future perspectives

Graphene and graphene-based multifunctional catalysts have been developed over the last ten to fifteen years, and it is no doubt that such materials can catalyze many industrially productive organic reactions. Graphene-based multifunctional catalysts have emerged as valuable catalysts for a wide range of organic transformations. In particular, graphene-supported metal nanoparticles catalyzed C-C and C-X coupling reactions have opened up a new horizon in the organic multi-steps synthesis owing to their extensive synthetic efficacy in the preparation of the most important compounds and intermediates.

About the uniqueness of graphene and it's pioneering as a catalyst to the perturbed field of studies in the contemporary years, there are a number of researches should be highlighted about that as a road map ahead to its heuristic applications. Notwithstanding the fact that graphene-based materials have gained immense attraction as a next-generation material, which is having distinctive

fascinating properties such as mechanical characteristics, excellent electrical conductivity and better thermal conductivity as contrasted with other similar materials. In addition, the next-generation materials of modified graphene materials including activated graphene, graphene quantum dots (GQDs), N, S-doped graphene quantum dots (N, S-GQDs), and polymer/graphene composites are ample opportunities for nanoelectronics, composite materials, energy technology, and sensors.

This ‘next-generation material’ which turns all interested and new researchers towards reality and bring out an idea for resolving difficult situations in terms of green and sustainable developments together with environmental issues.