A

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in

Applied Chemistry

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Subject	**:**	**Applied Chemistry**
Faculty	**:**	**Technology & Engineering**
Title of Thesis	**:**	**Metal Nanoparticles Decorated on Carbonaceous Solid Supports: Towards The Development of Heterogeneous Catalysts**
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Introduction

The 21st century is now going to witness for the era of nanotechnology. There are wide-range of potentialities and feasibilities like nanomagnets will be useful for data storage in nimble computers, [1] nanowires will twine in conjunction with nano-circuits, [2, 3] the contemporary drug will convert by nanomachines [4] and nanocatalysts reveal new paths to a range of products. [5, 6] In all these kinds of applications, nanomaterials in particular metal nanoparticles play a vital role. Metal nanoparticles present inimitable properties somewhere between the molecular state and bulk solid, having its small magnitude, a high range of surface atoms, leading to increased its catalytic activity.[7] In some instances, where all catalysts face deactivation and mislaying their activity, therefore, such material has to be either replaced or reactivated. The field of catalysis, particularly in heterogeneous catalysis, metal nanoparticles have been used since last 60 years.

According to the literature survey, the contribution of supported catalysts has been utilized approximately more than 90% by the industry in a number of industrial processes. Besides this, the supported catalysts have also been pointed up in many diverse fields such as polymers, pharmaceuticals, agrochemicals, and petrochemicals owing to their low cost, easier separation from the reaction mixture, recyclable, need of non-hazardous conditions as well. In continuation with the aforementioned benefits, they also possess high surface area, porosity and a variety of surface defects that prevents the agglomeration of active sites on its surface. [8-9] With unique properties like tunable porosity and surface chemistry, the carbonaceous materials such as activated carbon (AC), carbon black (CB), single- and multiwall carbon nanotubes (CNTs), graphene-based materials are now-a-days in a great demand as supported materials in various catalytic processes. The study on surfaces of carbonaceous materials is a powerful tool that can be easily modified with various scaffolds such as organic and inorganic moieties, polymeric materials, acid-base compounds, transition metals, free ions, coordination metal complexes, clusters, and nanoparticles. [10-13]

In the contemporary age, graphene based research has got tremendous eye-catching grip on the account of its large specific surface area (~2630 m^2/gm), rich oxidative debris (like –OH, -COOH, -C-O-C, -C=O groups) (Fig. 1) as well as intriguing electronic, mechanical and thermal properties. [14-15]

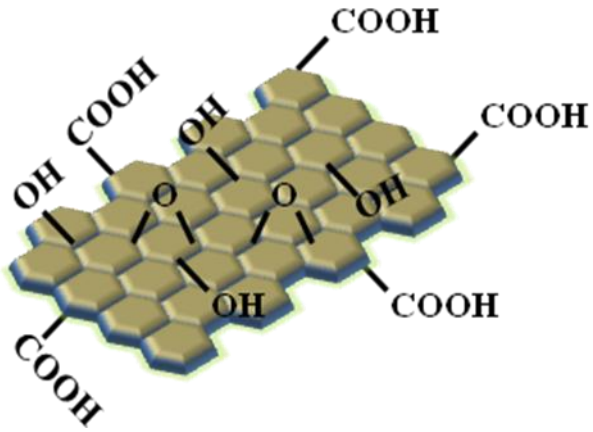

Figure 1 The Structure of Graphene oxide (GO)

Scope of the research study

In these days and age, the field of supported heterogeneous catalysis has been focused of attention in the frontier scientific and technological research that can be dexterously applied in variety of industrially important catalytic reactions, providing meliorate outcomes (in terms of yield) and stability besides the first-rate conversion with the desired selectivity. As per the literature scanning, numerous types of heterogeneous systems have been entrenched such as mesoporous titanosilicate, super paramagnetic mesoporous bi-metallic oxides, MCM-41 silica, nanocrystalline ceria-zirconia, chitosan hydrogel, acrylic resin immobilized lipase, IRMOF-3, and ZIF-8. [17-19] However, these solid catalysts have been suffered from a number of detriments like low selectivity, elevated temperature, longer reaction time, and laborious work-up methods. The selectivity and activity of many heterogeneous catalysts permit for the preparation of high added value chemicals from simple and economic substrates by means of processes with high atom economy, diminishing the formation of residues and, therefore, with a minimum environmental impact. The aim of this research work is to develop varied metal nanoparticles (MNPs) anchored onto carbonaceous supports with their applications in sustainable chemical processes. We have been addressed the synthesis and characterization of newfangled vanadium, iron, nickel, copper, zinc and niobium metal and/or metal oxide based nanoparticles (MNPs) embedded onto carbonaceous (reduced graphene oxide (rGO) or activated carbon (AC)) supports viz. MNPs@rGO and/or MNPs@AC. The as-synthesized catalysts have been substantiated by various physicochemical techniques such as ICP-OES, elemental analysis, (FT-IR, Raman) spectral studies, BET, field emission scanning electron micrographs (FE-

SEMs), high resolution transmission electron microscope (HRTEMs), X-ray photoelectron microscope (XPS), thermal analysis and X-ray powder diffraction (XRD) patterns. To attain the strategic goal of this work, the catalytic aptitudes of the as-synthesized catalysts have been tested over diverse industrially imperative organic transformations such as hydrogenolysis reaction, Biginelli coupling reaction, Knoevenagel condensation (C-C formation) reaction, Henry-Micheal addition (homo-coupling) reaction and Henry-Micheal addition- reduction reaction through optimization of various parameters like mole ratio, catalyst amount, varying reducing agents and/or active methylene compounds, temperature, time, solvents, derivatives. Besides this, the organic products formed during the catalytic reactions are the key intermediates in a variety of industries including foods, pharmaceuticals, fuels, and construction.

Summary of Research Work

The thesis is formulated by presenting the investigation comprises of eight chapters as shown below: Chapter 1 – Introduction, Chapter 2 – Experimental - Synthesis and characterization of graphene oxide (GO), Chapter 3 –Synthesis, characterization and catalytic aptitude of MNPs@rGO (where M= Cu, Ni or VO) over Hydrogenolysis reaction, Chapter 4 – Synthesis, characterization and catalytic aptitude of MNPs@rGO (where M= ZnO, CuO) over Biginelli reaction, Chapter 5 Synthesis, characterization and catalytic aptitude of FeNPs/Am@rGO (where Am = p-phenylenediamine (PPD) and/or aniline (AN)) over Knoevenagel condensation reaction, Chapter 6 Synthesis, characterization and catalytic aptitude of FeNPs/Am@rGO (where Am = aliphatic amine group) over Henry and Aldol condensation reactions, Chapter 7 – Synthesis, characterization and catalytic aptitude of MNPs/Am@rGO (where M = Fe or Nb; Am = p-phenylenediamine (PPD) and/or ethylene diamine (ED)) over Henry-Micheal-reduction reaction, Chapter – 8 Summary and conclusions.

Chapter 1

This chapter of the thesis deals with bird-view of general introduction, a brief historical background, fundamental aspects and contemporary scenario of the catalysts, types of catalysts, their advantages and disadvantages and emerging materials on the industrial perspectives. Numerous solid supports are available for heterogenization of the homogeneous counterparts and the preeminent one amongst these (i.e. carbonaceous support) chosen for this work is discussed here.

Chapter 2

The narrative of the oxidative debris of graphene oxide (GO), their reduction counterpart i.e. reducing graphene oxide (rGO) via ample of reducing agents and their chore in the heterogeneous solid supports are discussed in this chapter. It also comprises of synthesis and characterization of graphene oxide (GO) (via modified Hummer's method [20]) and rGO (via chemical reduction method [21]). The various analytical techniques used for the characterization of the synthesized materials are also included in this chapter.

Chapter 3

The details concerning greener protocol for *in situ* synthesis of metal nanoparticles embedded on rGO nanosheet (MNPs@rGO) (where M = Cu, Ni, VO) as nanocatalysts and were corroborated via assorted physicochemical techniques such as ICP-OES, elemental analysis, (FT-IR, Raman, UV-Vis) spectral studies, thermogravimetric analysis, XPS, FESEM, HRTEM and XRD patterns are incorporated in this chapter. MNPs@rGO promoted over hydrogenolysis of benzyl alcohol (BzA) with triethylsilane (Et_3SiH) as a reductant conferring distinctive activity to cater synthetically valuable hydrocarbon product. The distinct experimental variables like mole ratio of BzA to Et_3SiH, catalyst amount, reaction time and solvents have examined and are included in this chapter.

Chapter 4

This chapter describes the synthesis and characterization of CuO, ZnO, CuONPs/rGO and ZnONPs/rGO nanocomposites. Furthermore, the catalytic aptitude of these nanocomposites was tested over Biginelli reaction using three constituents viz. benzaldehyde, urea and ethyl acetoacetate to achieved 3, 4- dihydropyrimidin-2(1H)-one (DHPM) as a sole product with excellent isolated yield. The effect of experimental variables such as the optimal catalysts, amount of catalyst, reaction time, varying temperature and solvents on the conversion benzaldehyde was analyzed and also checked for other derivatives with good number of recyclability.

Chapter 5

The chapter deals with synthesis of immensely working bifunctional FeNPs embedded on amino-modified reduced graphene oxide (FeNPs/Am@rGO) (where Am = Primary aromatic amine derivatives such as p-phenylenediamine (PPD) or aniline (AN)) nanocatalysts via simple and facile route. These bifunctional nanocatalysts have been characterized thoroughly using various physicochemical techniques such as ICP-OES, (FTIR, Raman and electronic) spectra, Transmission

electron microscopy (TEM), Scanning electron microscope (SEMs), X-ray photoelectron spectroscopy (XPS), X-ray diffraction patterns (XRD) and Thermogravimetric analysis (TGA). FeNPs/Am@rGO notably acts as bifunctional nanocatalysts in the one-pot Knoevenagel condensation reaction with different aromatic aldehydes and active methylene compounds giving venerable results. To monitor discrete parameters such as optimal catalysts, catalyst dosages, various mole ratios, solvents, varying temperature and time has also been examined. Besides this, it could be effortlessly recycled and reused without significant loss of its catalytic activity in a six cycles test.

Chapter 6

This chapter describes the synthesis of atypical highly active nanocatalyst FeNPs anchored on amino functionalized reduced graphene oxide (FeNPs/Am@rGO) (Where, Am= Aliphatic amine derivatives) with acid-base dual-site activation. These nanocatalysts have been analyzed by diverse physicochemical techniques such as ICP-OES, elemental analysis, (FT-IR, Raman, UV-Vis) spectral studies, thermogravimetric analysis, XPS, FESEM, HRTEM and XRD patterns are included in this chapter. FeNPs/Am@rGO nanocatalyst have employed for the Henry and Aldol condensation reactions with different aldehydes under solvent free conditions. The impact of distinct parameters influencing catalytic activity has been checked and included in this chapter. We have monitored recyclability of the as-prepared catalyst as well.

Chapter 7

This chapter delineates synthesis of newfangled MNPs implanted on amino-functionalized reduced graphene oxide (MNPs/Am@rGO) (where M = Fe or Nb; Am = p-phenylenediamine (PPD) and/or ethylene diamine (ED)) nanocatalysts. The as-prepared nanocatalysts have been successfully corroborated by assorted physicochemical techniques as described above. We have first time reported MNPs/Am@rGO nanocatalysts and tested over one pot Henry-Michael-reduction reaction, achieving exceptional results. We have also checked catalytic aptitude over various aromatic aldehydes and active methylene compounds and are included in this chapter.

Chapter 8

The comprehensive systematic investigation of our results on the development of the aforesaid nanocatalysts and to find the optimal catalysts for the relevant catalytic reactions has been summarized in this chapter. As a concluding point, the brief discussion on possible futuristic work of this thesis is also incorporated in this chapter.

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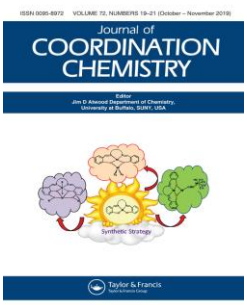
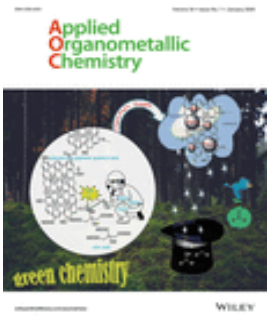
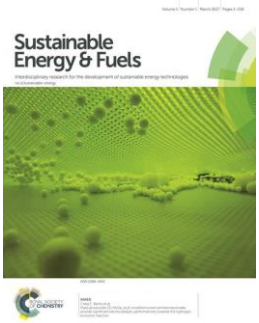
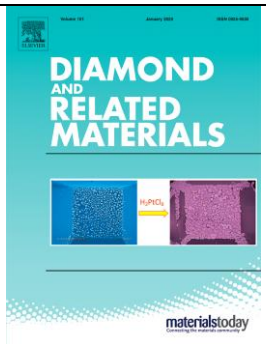
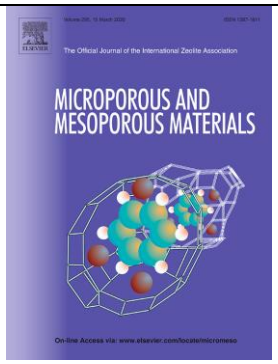
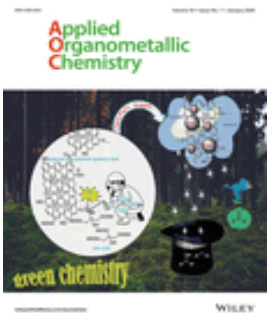
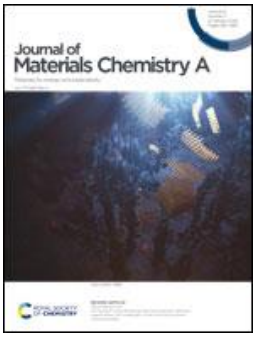
List of Publications (Related to Thesis)

1		Highly efficient FeNPs embedded hybrid bifunctional reduced graphene oxide for Knoevenagel condensation with active methylene compounds **Dikin Patel**, Ravi Vithalani, Chetan K. Modi **New J. Chem.** (Online Published-15th January2020) **DOI: 10.1039/C9NJ05821D** **I. F. = 3.069**
2		Green protocol for the synthesis of MNPs embedded on rGO nanosheet for hydrogenolysis of benzyl alcohol **Dikin S. Patel,** Ravi S. Vithalani, Chetan K. Modi, Nitin V. Bhate, Prafulla K. Jha, Sanjeev R. Kane **J. Coord. Chem.** (Under review) **Manuscript no**.: GCOO-2019-0511; **I. F. = 1.685**

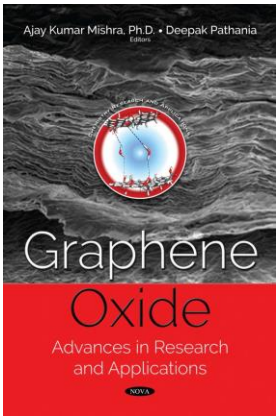
List of Publications (Non-related to Thesis)

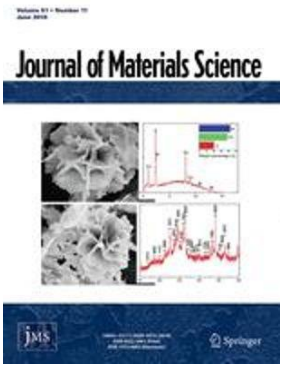
1		Graphene Oxide Supported Oxovanadium (IV) Complex for Catalytic Peroxidative Epoxidation of Styrene: An EyeCatching Impact of Solvent Ravi Vithalani, **Dikin S. Patel**, Chetan K. Modi, Vaishali Sharma, Prafulla K. Jha **Applied Organometallic Chemistry** (Online Published-22nd January 2020) **doi.org/10.1002/aoc.5500** **I. F. = 3.259**

2		Harnessing the N-dopant ratio in carbon quantum dots for enhancing the power conversion efficiency of solar cells Bhavita Mistry, Hiren K. Machhi, Ravi S. Vithalani, **Dikin S. Patel**, Chetan K. Modi, Meha Prajapati, Kiran R. Surati, Saurabh S. Soni, Prafulla K. Jha and Sanjeev R. Kane **Sustainable Energy Fuels**, 2019, 3, 3182 **I. F. = 4.912**
3		Enhancing the potency of surface hydroxyl groups of graphene oxide for selective oxidation of benzyl alcohol Ravi Vithalani, **Dikin Patel**, Chetan K. Modi, Narayan N. Som, Prafulla K. Jha, S.R. Kane **Diamond & Related Materials** 90, 2018, 154–165. **I. F. = 2.290**
4		Zeolite-Y entrapped metallo-pyrazolone complexes as heterogeneous catalysts: synthesis, catalytic aptitude and computational investigation Chetan K. Modi , Ravi S. Vithalani, **Dikin S. Patel**, Narayan N. Som,Prafulla K. Jha **Micropor. Mesopor. Mater.** 261 (2018) 275–285 **I. F. = 4.182**
5		Baeyer-Villiger oxidation of cyclopentanone over zeolite Y entrapped transition metal-Schiff base complexes Chetan K. Modi, Naresh Solanki, Ravi Vithalani, **Dikin Patel** **Applied Organometallic Chemistry,** 2017, 3910. **I. F. = 3.259**

6		Ionic liquid infiltrated within metal loaded zeolites for Baeyer–Villiger oxidation reaction under solvent-free condition Chetan K. Modi, Sabeeyabanu Panwala, Ravi Vithalani, **Dikin Patel** **J Porous Mater**, 25(3) (2017) 871-883 **I. F. = 1.947**
7		Carboxylic acid group activation induced synthesis of graphene oxide supported solid heterogeneous catalyst: Understanding the aptness of oxidative site for functionalization in catalytic application Ravi S. Vithalani, **Dikin S. Patel**, Chetan K. Modi, Vaishali Sharma, Prafulla K. Jha, Himanshu Srivastava **Journal of Materials Chemistry A** (Under Review) **Manuscript no.:** TA-ART-01-2020-000541 **I. F. = 10.733**

List of Book Chapter and Review Article

Book Chapter:		
1		An Immense Uprising: Functionalization and Fine-Tuning of 2D Graphene Designed for Heterogeneous Catalysis to Make Things Greener Chetan K. Modi, Ravi Vithalani, **Dikin Patel** Ch. No. 9 (2018) pp. 217-244 **Book Title**: Graphene Oxide: Advances in Research and Applications **Publisher**: NOVA Science Publishers, USA **ISBN**: 978-1-53614-169-6

Review Article:		
2		Glowing Photoluminesce Carbon Nanodots: Current State and Future Perspectives Ravi Vithalani, **Dikin Patel** Chetan K. Modi **Journal of Materials Science** (Under Consideration) **Manuscript no**.: JMSC-D-20-00379 **I. F. = 3.442**

Work presented in Conferences/ Seminars/ Workshops

1		Green synthesis of metal nanoparticles (MNPs) decorated on reduced graphene oxide (rGO): as efficient heterogeneous catalysts for reduction of benzyl alcohol **Dikin S. Patel**, Ravi Vithalani, Chetan K. Modi* **National Conference** on Recent Developments in Chemical Sciences (RDCS-2018), Mumbai on 8-9th March 2018. **Presented Session: ORAL**
2		One pot Synthesis of Fe nanoparticles decorated on reduced graphene oxide in an ionic liquid for A^3- coupling reaction **Dikin S. Patel**, Ravi Vithalani, Chetan K. Modi* **International Conference** on Multifunctional Advanced Materials (ICMAM-2018), Nagpur on 5-7th October 2018. **Presented Session: ORAL**

3		Reduced Graphene oxide based materials as base catalysts for Knoevenagel condensation reaction **Dikin S. Patel**, Ravi Vithalani, Chetan K. Modi* **International conference** on Advanced Functional Materials for Energy, Environment and Health care (AFMEEHC-2019), Mysore on 18-20th March 2019. **Presented Session: POSTER**
Achievement: Received **2nd Best Poster Presentation Award** at the **International Conference** on Advanced Functional Materials for Energy, Environment and Health Care (**AFMEEHC-2019**), University of Mysore, Mysuru, Karnataka, India on 18-20th March 2019.		
4		Solvent free Henry and Aldol condensation reactions over FeNPs supported on amino functionalized reduced graphene oxide as bifunctional catalysts **Dikin S. Patel**, Ravi Vithalani, Chetan K. Modi* **International conference** on 7th Asian Network & Unnatural Materials (ANNUM-VII-2019), Ahmedabad on 27-29th September 2019. **Presented Session: POSTER**
5		Ionic liquid immobilized FeNPs on reduced graphene oxide: A bifunctional nanocatalyst used for coupling reaction under solvent free conditions **Dikin S. Patel**, Ravi Vithalani, Chetan K. Modi* **National conference** on Current Trends and Advances in chemical science (NCBKM-2020), BKM Science College, Valsad on 12th January 2020. **Presented Session: ORAL**

Participated:		
6		**Dikin S. Patel**, Ravi Vithalani, Chetan K. Modi* National Conference on Recent Scenario in Science and Technology (RSST-2016), Vadodara on 27th February 2016.
7		**Dikin S. Patel**, Ravi Vithalani, Chetan K. Modi* National conference on Frontiers in Heterogeneous Catalysis (HETCAT-2016)- Vadodara 10th December 2016.
8		**Dikin S. Patel**, Ravi Vithalani, Chetan K. Modi* National Symposium on Advances in Chemical Research (ACR-2019), Vadodara on 24th February 2019.
9		**Dikin S. Patel**, Ravi Vithalani, Chetan K. Modi* Workshop on Applications of X-Ray Techniques - XRF, XPS, Auger, Vadodara on 9th March 2019.

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