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**Debris: Towards The Development**
**of Conventional Catalysts**
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## Introduction

In chemistry, we regularly require catalysts to execute reactions at considerable speeds. A catalyst is a substance that boosts the rate of a reaction by coming up with an alternative pathway for the breaking and making of bonds without being used up itself. The contemporary industrialization would not be imagined without catalysts. The advancement of chemical products is only be technically, economically, and ecologically possible by means of precise catalysts. As per one approximation almost 90% of the production processes are catalyst-based. Accordingly, comprehensive and in-depth research is being carried out in this field.

## Motivation and Definition of the problem

Chemical transformations may be performed in homogeneous or heterogeneous phase. Though in homogeneous catalytic reactions, the distribution of active sites is equal in all respects and also the collision of molecules eventuate without any difficulty, on working up the reaction mixture, the catalyst cannot be regenerated. Homogeneous catalytic reactions, therefore, are not beneficial from the economical and ecological point of view. Consequently, the thought of its substitution potently inspires the scientists. Embedded the active sites on the solid support is one of the probable approach by means of solving this problem so the chemical reaction takes place under heterogeneous conditions. Heterogeneous catalysts are more advantageous rather homogeneous one. Primarily, it is easily separable from the reaction mixture by means of simple filtration or decantation. Furthermore, activity and selectivity is relatively high and hence the efficiency of heterogeneous catalysts is also high. Besides these, it also drop downed the waste and adverse environmental footprint and enhances the inherent process safety.[1] Sometimes it can be used in solvent-free condition and more importantly it can be regenerated and reused several times[2] making their applications more economical. In spite of this, heterogeneous catalyst also unexpectedly experiences the hindered diffusion and non-uniform distribution of active sites.

In this epoch, a range of solid catalyst supports are available, for instance, cation exchange resin, molecular sieves, silica, natural clays, heteropoly acids, metal oxides, zeolites etc.[2] Even though cited catalysts, of course, prevail over numerous deficiencies but most of them are inapt due to deactivation (leaching)[3], internal mass transfer[4], high mass transfer resistance and most importantly high cost. The quest for heterogeneous acid catalysts, apt to encounter the majority of the above stated complexities, has resulted in the deliberation of carbon based nanomaterials (CNMs)[5-6]. Until the 20th century, the carbon family was being prevalent only with eminent materials like diamond, fullerenes, CNTs and graphite. Amongst them fullerenes were found to be toxic[7] besides high price. However, bulk synthesis and purification of CNTs are still quite difficult procedure. This era was worked-out with graphite and single layer graphene since the pioneering work of Brodie[8] and seminal report of the Geim and Novoswlov[9].

In the contemporary age, graphene oxide (GO) based research has got hold of awe-inspiring impetus on account of their latent applications predominantly as catalysts and catalytic supports in the field of catalysis[10-11] owing to its exceptional characteristic such as 2D monolayer hexagon structure with $sp^2$ bonded carbon atoms, densely packed carbon atoms in a honeycomb shaped nanosheets, high thermal stability and elevated tensile strength, high-calibre virtues for instance, huge surface area, high mass transfer facilitation, inherent low mass and prevention of agglomeration.[12] Moreover, GO possesses hole defects all over the scaffold holding plenty of functional groups like carboxylic acid, carbonyl, hydroxyls and epoxides, fastened to both the side of the sheet on its basal planes and edges as shown in Fig.1.

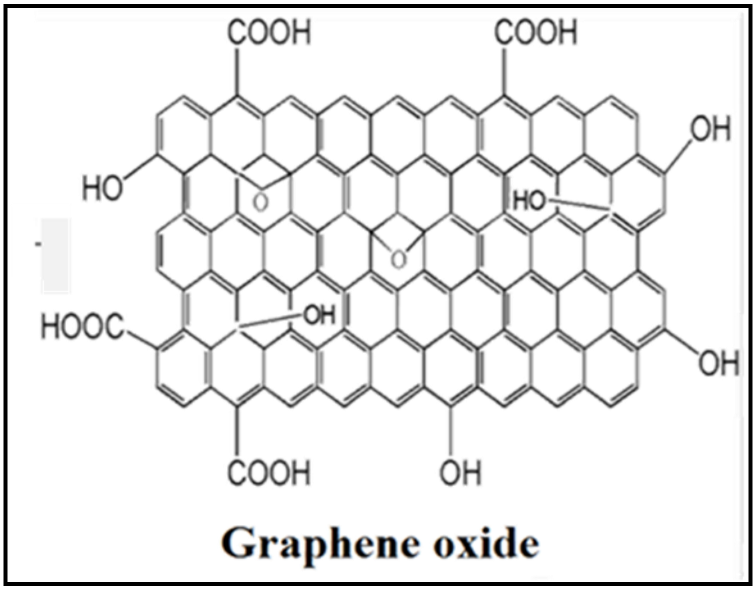

**Fig. 1 Graphene oxide surface decorated with oxidative debris**

## Scope of the research study

To remedy the shortcomings of homogeneous catalysis, implementation of transition metal complexes onto the GO nanosheets via covalent grafting has been proved to be a proficient approach[13]. Transition metal ion is eminent well for its catalytic characteristics owing to the extremely captivating electron-transfer properties. Transition metal exerts modifying catalytic properties as a result of varying coordination environment surrounding it. Ligand, possessing number of donor sites, can tune the properties of the complexes for oxidation, reduction and hydrolysis reactions as well.[14] Hence, reactive species can readily access the active sites with limited mass transfer resistance and therefore remarkable catalytic performance of GO supported metal complexes have been observed. However, much fundamental and applied research has been carried out to find how catalyst works and to develop their efficacy by industries and academia. If it possible to improve the catalytic activity of the catalyst, it may be possible to lower the temperature and/or pressure and other parameters at which the reaction operates and thus can save the fuel, one of the major costs in large-scale productions.

It is an extremely demanding to recognize the key intermediates and make use as value-added chemicals. An appreciable rise in the literatures related to production of these intermediate chemicals was seen during the past decade for instance, oxidation of benzyl alcohol. However, gluconic acid and its salts are chief compounds in pharmaceutical, food and chemical industries. Epoxides are the crucial precursors in the production of a variety of important substances like plasticizers, perfumes, epoxy resins, etc, and hence epoxidation reaction assumes to be of considerable importance**.** Epoxidation of styrene is commercially vital reaction for the manufacturing of styrene oxide; an important organic intermediate while the derivatives of norbornane like epoxy norbornene and diol have extensive applications in polymers synthesis, pharmaceutical intermediates, general organic synthesis, etc.

## Literature review

The catalytic activity of $TiO_2$/GO is reported as a heterogeneous solid catalyst in the oxidation of styrene using TBHP as an oxidant in acetonitrile at 70 °C by B. Sakthivel and co-workers[15]. It leads to the formation of benzaldehyde and styrene oxide as primary products. Moreover, it was noticed that the selectivity of styrene oxide increases with increasing the wt%

of $TiO_2$ on GO under the same reaction conditions. The polymer supported Mn(II) complexes were employed for the oxidation of norbornene with tert-butyl hydroperoxide (TBHP) as a terminal oxidant by S. A. Patel and co-workers[16]. After 24 h of reaction they got maximum 45% selectivity of the epoxide. Gluconic acid was prepared by oxidation of glucose with $H_2O_2$ at 80 °C for 70 min. by Y. M. MAO[17]. He observed that the yield was affected by the reaction time, temperature and $H_2O_2$ concentration.

In this research work, we have targeted -OH and –COOH functional groups located onto the GO nanosheet, to modify with suitable organic and/or inorganic moiety in the first stage. In the second stage, it was grafted with Schiff base ligands, viz. 2-hydroxyacetophenone and N,N'-(salicylaldehyde)ethylenediamine for functionalization at –OH and –COOH groups, respectively. In the final step, this Schiff base ligand grafted GO nanosheet was treated with varying metal salts; $M(X)_n \cdot mH_2O$ (where M = $VO^{4+}$, $Co^{2+}$, $Cu^{2+}$; X = $NO_3^-$, $Cl^-$, $SO_4^{2-}$; m = 1,2,3…) to prepare GO supported heterogeneous catalysts [M(L)n-*f*-GO].

We have substantiated the best attachment site from all the oxidative functional groups on the GO nanosheet through DFT study. Selective functionalization at –OH and –COOH groups with the control of surface composition was also validated by theoretical calculations.

To attain the strategic aims of the research study, the catalytic competence of as-synthesized catalysts have been tested over assorted oxidation reactions, for instance, oxidation of benzyl alcohol, glucose and norbornene besides epoxidation of styrene through optimization of various parameters like mole ratio, catalyst amount, temperature, time, solvents, amount of solvent, varying oxidants etc.

To determine the best suited catalyst for oxidation of benzyl alcohol and in epoxidation of styrene to provide plausible reaction pathway, we performed DFT calculations viz. HOMO, LUMO, energy gap, global hardness and softness, etc.

## Summary of Research Work

The present thesis comprises of six chapters as arranged in following manner.

Chapter 1 – Introduction, Chapter 2 – Objectives and experimental work, Chapter 3 – Results and discussion, Chapter 4 – Catalytic aptitude of –OH functionalized catalysts, Chapter 5 – Catalytic aptitude of –COOH functionalized catalysts, Chapter 6 – Summary and Conclusions.

**Findings from Chapter 1**

The general introduction on current scenario about the catalysts, types of catalysts, importance of catalysts and improvement in traditional catalysts are discussed in this chapter. Even the efforts have been made for the development of traditional catalysts so far is also covered in this section. A numerous solid supports available for the heterogenization of homogenous catalysts and the best one amongst this and support chosen for this work along with the description of the functionalization of oxidative debris of GO, ligands and metal complexes used for the fabrication of GO supported transition metal grafted heterogeneous catalysts are discussed here.

**Findings from Chapter 2**

The fabrication as stated heterogeneous catalysts has been done in two ways: (i) by functionalizing the –OH groups and (ii) by functionalizing the –COOH groups. The strategic objectives and experimental work of the present research work are discussed in this chapter.

**Objectives of the research study**

- Synthesis and characterization of graphene oxide (GO) and functionalized GO (*f*-GO) nanosheets.
- Synthesis and characterization of covalent tethering of transition metal complexes on GO [$M(L)_n$-*f*-GO]
- To study the catalytic competence of synthesized catalysts over possible diverse catalytic reactions.
- Optimal catalyst will be developed and chosen for scale-up reactions.

**Experimental section**

**Synthesis of GO:** GO nanosheet had been synthesized by the oxidation of graphite flakes using modified Hummer's method. [18]

**Functionalization at –OH groups**: Surface hydroxyl groups of the GO nanosheet were modified using 3-aminopropyltrimethoxysilane (APTMS) under $N_2$ atmosphere. This $NH_2$-modified GO nanosheet (A-*f*-GO) was further grafted with 2-hydroxyacetophenone ligand. In the final step, this Schiff base ligand grafted GO nanosheet was treated with varying metal salts; $M(X)_n \cdot mH_2O$ (where M = $VO^{4+}$, $Co^{2+}$, $Cu^{2+}$; X = $NO_3^-$, $Cl^-$, $SO_4^{2-}$; m = 1,2,3…) to synthesize transition metal complex covalently grafted to $NH_2$-modified graphene oxide as heterogeneous catalysts [M(L)n-*f*-GO].

**Functionalization at –COOH groups**: In the first step, surface carboxyl groups lie at the edges of GO nanosheet were functionalized with thionyl chloride ($SOCl_2$). Furthermore, transition metal Schiff base (derived from salicylaldehyde and ethylene diammine in 2:1 ratio) complexes $M(L)_n$ [where M = $VO^{4+}$, $Co^{2+}$, $Cu^{2+}$ ; $H_2L$ = N,N'-(salicylaldehyde)ethylenediamine] were prepared in the second step. In the final step, the $SOCl_2$-modified GO nanosheet (Cl-*f*-GO) was treated with metal Schiff base M(L)n complexes to synthesize M(L)n-*f*-GO heterogeneous catalysts.

## Findings from Chapter 3

To validate the successful synthesis of M(L)n-*f*-GO catalysts, numerous characterization techniques were employed. The presence of various functional groups was validated by FTIR analysis. Thermal stability of as synthesized heterogeneous catalysts was investigated using TG analysis. Furthermore, successful formation of GO and catalysts could be evaluated by RAMAN analysis. On the other hand, with the help of SEM and HRTEM analysis it could be substantiated that the material is nanocomposite besides the study of surface morphology and surface functionalization. Furthermore, productive information about the elemental composition and bonding environment could be acquired through XPS analysis. Crystalline nature of these heterogeneous catalysts was corroborated by the XRD analysis. Moreover, BET analysis was being helpful to corroborate the successful functionalization and surface area alongside the porous nature of the heterogeneous catalysts. The successful grafting of transition metal complexes onto GO nanosheet and metal percentage was confirmed by the ICP-OES analysis. UV/Vis analysis was also carried out to substantiate the fruitful functionalization and fabrication of the heterogeneous catalysts. Successful selective functionalization at –OH and –COOH groups was corroborated by DFT studies as well.

**Findings from Chapter 4**

As prepared M(L)n-*f*-GO catalysts were evaluated against the catalytic oxidation reactions to examine the catalytic efficiency. Transition metal complex covalently grafted to $NH_2$-modified graphene oxide as heterogeneous catalysts [M(L)n-*f*-GO] were weighed-up against the catalytic oxidation of benzyl alcohol, epoxidation of styrene, epoxidation of norbornene and oxidation of glucose. To develop the optimal catalyst, various parameters like mole ratio, catalyst amount, temperature, time, solvents, amount of solvent, oxidants etc has been investigated. We have succeeded in in achieving the highest conversion and selectivity with good number of recyclability.

For the selective oxidation of benzyl alcohol, we were able to predict the catalysts that would exhibit the excellent performance for this transformation, with the help of DFT study. As a result of the computational investigation and detailed examination of the elements by DFT, we could be inferred that CuL-*f*-GO will exhibit a better catalytic activity in terms of reactivity and stability. To provide the plausible reaction pathway for the epoxidation of styrene, we have calculated the binding energy of oxidant to catalysts and to reactant. Based on the result obtained from the DFT calculations, we inferred that this reaction would move forward by the formation of radical metal-peroxo species. We also validate this belief by confirming the generation of metal-peroxo species through UV/Vis. and Resonance Raman analysis.

**Findings from Chapter 5**

$SOCl_2$-modified GO nanosheet (Cl-*f*-GO) treated with transition metal Schiff base M(L)n complexes to synthesize M(L)n-*f*-GO heterogeneous catalysts were tested over the catalytic oxidation of benzyl alcohol, epoxidation of styrene, epoxidation of norbornene and oxidation of glucose. To develop the optimal catalyst, various parameters like mole ratio, catalyst amount, temperature, time, solvents, amount of solvent, oxidants etc has been investigated. We have succeeded in in achieving the highest conversion and selectivity with good number of recyclability.

## Findings from Chapter 6

The detailed systematic investigation of our results on the development of GO supported heterogeneous catalysts and to find the optimal heterogeneous catalysts for the given catalytic reactions has been summarized in this chapter. It can be concluded from the obtained results that [M(L)n-*f*-GO] catalysts (derived from transition metal complex covalently grafted to $NH_2$-modified GO nanosheet) exhibited better catalytic activity without using any precursor and with lesser amount of catalyst, however, M(L)n-*f*-GO catalysts (derived from $SOCl_2$-modified GO nanosheet with transition metal Schiff base complexes) required precursor in oxidation of benzyl alcohol and needed higher amount for the epoxidation of styrene. It was concluded that it is advisable to modify the surface –OH groups of GO nanosheet to fabricate the heterogeneous catalysts via ligand spacer. The existence of –COOH groups on the surface of GO responsible to provide the acidity to the catalysts which is very useful in oxidation reactions. As a final point, the brief discussion on possible future work of this thesis has been concluded.

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## List of Publications Related to Thesis

1. 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.
2. Graphene supported oxovanadium (IV) complex for catalytic peroxidative epoxidation of styrene: An eye catching impact of solvent
   **Ravi Vithalani**, Dikin Patel, Chetan K. Modi*, Narayan N. Som, Prafulla K. Jha
   Appl. Organometal. Chem. Manuscript ID: AOC-19-0868 (Under Review).

### 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

## List of Publications Non-related to Thesis

1. State-of-the-art catalytic hydrogenolysis of aromatic C-O bond: A key step towards greener tactics
   Dikin Patel, **Ravi Vithalani**, Chetan K. Modi, Prafulla K. Jha, S.R. Kane
   Appl. Organometal. Chem. Manuscript ID: AOC-19-0729 (Under Review).
2. Harnessing the N-Dopant Ratio to Carbon Quantum Dots for Enhancing the Power Conversion Efficiency of Solar Cell
   Bhavita Mistry, **Ravi S. Vithalani**, Dikin S. Patel, Hiren K. Machhi, Chetan K. Modi*, Meha Prajapati, Kiran R. Surati, Saurabh S. Soni*, Prafulla K. Jha, Sanjeev R. Kane

Sustainable Energy & Fuels Manuscript ID: SE-ART-05-2019-000338 (Under Review)

3. Baeyer-Villiger oxidation of cyclopentanone over zeolite Y entrapped transition metal ‐ Schiff base complexes

   Chetan K. Modi*, Naresh Solanki, **Ravi Vithalani**, Dikin Patel

   Appl Organometal Chem. 32(1) (2017) e3910. Doi. 10.1002/aoc.3910
4. Ionic liquid infiltrated within metal loaded zeolites for Baeyer–Villiger oxidation reaction under solvent-freecondition

   Chetan K. Modi*, Sabeeyabanu Panwala, **Ravi Vithalani**, Dikin Patel

   J Porous Mater, 25(3) (2017) 871-883.
5. 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.

**Book Chapter**

1. Glowing Photoluminesce Carbon Nanodots: Current State and Future Perspectives

   Chetan K. Modi*, **Ravi Vithalani**, Dikin Patel **(Accepted)**

   **Book title**: Green Nanocomposites: Advances and Applications in Environmentally Friendly Carbon Nanomaterials

   **Publisher**: Pan Stanford, Singapore.

## List of Conferences/ Seminars/ Workshops Related to Thesis

1. Covalent tethering of transition metal complexes onto graphene oxide nanosheets heterogeneous catalysts

   Chetan K. Modi*, **Ravi Vithalani**

   International Conference on Science: Emerging scenario & Future Challlenges (SESFC), Dharamshala, 2016.

   Absrtact ID: PMS15, Page No.: 126 – Oral presentation

2. DFT Assisted Investigation of Selective Oxidation of Benzyl Alcohol over Amine Substituted Graphene Oxide as Heterogeneous Catalysts
   **Ravi Vithalani,** Dikin Patel, Som Narayan, Prafulla Jha, Chetan K. Modi*
   International Conference on Advances in Chemical Science and Allied Fields of Science, Health, Education and Environment: ACAEE 2018, Bhopal, 2018.
   Abstract ID: acaeeC88, Page No.: 119 – Oral presentation
3. Surface Hydroxyl Group Modified Graphene Oxide as Heterogeneous Catalysts for the Epoxidation of Styrene
   **Ravi Vithalani**, Dikin Patel, Chetan K. Modi*, Narayan N. Som, Prafulla K. Jha
   National symposium on Advances in Chemical Research (ACR), Vadodara, 2019.
   Abstract ID: pp-31.

## List of Conferences/ Seminars/ Workshops Non-related to Thesis

1. Encapsulation of ionic liquid skeleton within metal loaded zeolites via ship-in-a-bottle synthesis for Baeyer-Villiger oxidation reaction under solvent-free condition
   Chetan K. Modi*, **Ravi Vithalani**, Sabeeha Panwala, Dikin Patel
   National Seminar on Frontiers in Heterogeneous Catalysis (HETCAT), Vadodara, 2016.
   Abstract ID: pp-03.
2. Workshop on Applications of X-Ray Techniques - XRF, XPS, Auger
   Department of Chemistry, The Maharaja Sayajirao University of Baroda, Vadodara, 2019.

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