Summary

Awareness among the people about the growing/ rising environmental adversity is being the foundation of new era of research. Modern research is aiming to attain and conserve the clean and green environment. An archaic industrial production involved many hazardous chemicals, high temperature, high pressure, elevated time and toxic precursors to boost up the reaction was modernized by encouraging the exercise of catalysts. Transition metal ions are very well recognized for their characteristic use as a selective catalyst and potential catalytic support. However, amongst two most important classes of catalysts, the pitfalls of such homogeneous catalysts restrict its applicability. Consequently, for the catalytic driven industrial production, heterogenization of homogeneous catalyst has been adapted.

In this approach, transition metal ions are grafted onto the solid support. A numerous supports including composite stuffs and chemically modified surfaces are accessible. However, in the process of selecting the right support, the optimal performance of the support during the chemical reaction is at the centre-of-heart. For the desirable outcome, the support must survive successfully during the ordeal of harsh chemical reaction. Support must have important characteristics as shown below:

- **High surface area:** As the active phase of the catalyst is dispersed on the surface of the support, higher the surface area of the support is advantageous.
- **Thermal stability:** For all the chemical reaction to make happen, it must have to surmount the activation barrier. A chemical reaction may be exothermic, hence, in this situation, support should not undergo transformations. For this reason, thermal stability is vital factor.
- **Prevention of agglomeration:** At higher temperature, the particles of active species experience a chaotic motion over the support and coalesced leading to reduce a number of active sites. It can be averted by either support acts as heat sink or support has functional groups where the active species tethered covalently.

Afterwards, compete for the superior support commences and plenty of supports with diverse features have been found to date. However, amongst the all accessible supports, graphite and/or GO have emerged as a potential catalytic support which possesses all of the above mentioned characteristics. GO holds two-dimensional hexagonal crystal lattice with unique features such as high surface area, promising high thermal and mechanical properties with discrete high calibre virtue, greater resistivity towards acidic and basic media, promotes high mass transfer. It also possesses various oxidative functional groups like hydroxyl, epoxy, carbonyl and carboxylic acid on its surface. The site of these functional groups makes the GO more attention-grabbing material for the researchers to tailor according to his/her own interest. These functional groups can successfully be functionalized with appropriate organic and/or inorganic moieties. This is also one of the reasons for choosing the GO to support the catalytically active centres. The hasty modernization recommends to adopt and to have in-depth perception of inexpensive though potent ligands. Schiff base is a multi-dentate ligand which forms a stable chelate with metal ions. Ligand alters the electronic properties of the metal and regulates the steric environment surrounding the metal centre. This combine approach has proven more potent to remedy the inadequacy of homogeneous catalysts.

In this research work, we have successfully oxidized the graphite flakes to GO using modified Hummers' method. Afterwards, we have selectively functionalized the –OH and –COOH groups of GO using APTMS and $SOCl_2$, respectively. This was followed by grafting of ligand and metals in case of –OH functionalized GO nanosheets, however, –COOH functionalized GO nanosheets were modified with metal-salen complexes (i.e. Co-salen, VO-salen and Cu-salen). Successful syntheses of both these oxygenated functional groups modified GO supported heterogeneous catalysts were corroborated by various physico-chemical techniques as discussed below:

FTIR analysis confirms the successful oxidation of graphite to GO by exhibiting characteristic peaks of all the oxidative debris at 3389, 1722, 1623 and 1057 cm^{-1}. Successful silylation reaction with APTMS was confirmed by arisen of peaks at 3219 and 1575 cm^{-1} for N-H stretching vibrations. Two new peaks at 1115 and 1037 cm^{-1} atrributed to the stretching vibrations of Si-O-Si and Si-O-C, confirms the successful attachement of APTMS moiety. Grafting of ligand and metal ions are also substantiated peaks observed at 1613, 1614 and 1596 cm^{-1} in –OH modified catalysts. In case of –OH groups modification, it is also proved that –OH is the only site of functionalization when functionalized with APTMS. However, in case of –COOH groups modification, formation of –COCl bond on reaction of GO nanosheet with $SOCl_2$ is confirmed by peaks arisen at 785 cm^{-1}. During this functionalization intensity of –OH groups at 3389 cm^{-1} was seen to be decreased indicating the substitution of some of the –OH groups by chloro groups of $SOCl_2$. Furthermore, grafting of metal-salen complexes is also validated by disappearing of C-Cl peak in thr FTIR spectra of catalysts. Forn these results, it can be concluded that in when GO nanosheet is reacted with $SOCl_2$; it not only activated carboxylic acid groups but also substitutes various –OH groups.

Electronic spectra shows the two characteristic bands of GO in the range of 200 – 300 nm attributed to $\pi \rightarrow \pi^*$ transition of aromatic C=C bond, and $n \rightarrow \pi^*$ transition of conjugated aromatic C=O bond, respectively. A peak at 230 nm in GO was experienced blue shift due to formation of sp^2 carbon indicating the covalent bonding between amino groups of APTMS and GO nanosheet. Moreover, modification by Schiff base ligand and the metal ions this peak further shifted to blue region while another peak (at 300 nm) exhibited red shifting validating successful attachment of ligand and metal ions in case of –OH group modification. However, in case of –COOH group modification, grafting of metal-salen complexes showed the red shifting of the spectra (280 and 323 nm for Co-*f*-GO; 275 and 309 nm fro VO-*f*-GO and 285 and 336 nm for Cu-*f*-GO) due to ILCT and LMCT transitions confirming the successful functionalization with $SOCl_2$ and grafting of metal-salen complexes onto Cl-*f*-GO.

Raman spectrum of GO showed two distinct peaks of D and G band at 1334 and 1578 cm^{-1} corresponding to the disorder (out of plane vibrations of breathing mode) and ordered (in-plane vibrations of E_{2g} phonon) structure of sp^2 bonded carbon atoms in the two dimensional lattice. However, intensity ratio of D and G band (*ID/IG*) demonstrates the degree of defects in the as-prepared samples. *ID/IG* ratio calculated for GO is 0.84 and it experienced the rising trend on functionalization (1.04, 1.04 and 0.9 for CuL-*f*-GO, CoL-*f*-GO and VOL-*f*-GO, respectively) owing to increase in disorder due to formation of sp^3 carbon. This increase in disorder suggests the successful functionalization with APTMS, ligand and metal ions. Moreover, grafting of metal ions causes the red shift of G band due to effective charge transfer from GO to metal ion and no alteration in the properties of the sample was seen in case of –OH groups modification. In case of –COOH groups modification, *ID/IG* ratio increases after the reaction with $SOCl_2$ (1.04), but on grafting of metal-salen complexes it was seen to be reduced (0.88, 0.98 and 0.99 for Co-*f*-GO, VO-*f*-GO and Cu-*f*-GO, respectively). On grafting of metal-salen complexes the intensity of D and G bands were found to be declined suggesting the reduction in defects. This suggests the alteration in the properties as well as polycrystalline nature of the samples which also confirmed by the XRD and HRTEM analysis.

XRD pattern of GO exhibited characteristic planes of hexagonal structure with increased inter-planar distance than in graphite due to insertion of oxidative debris on its basal plane and edges. A characteristic peak at $2\theta = 42.2°$ due to the defects caused by residual trace MnO_2 suggested the multilayered structure of GO. However, on functionalization with APTMS, peak at 2θ = 11.2º was diminished distinctly indicating the removal of –OH groups from the basal plane. Owing to surface gets rid of –OH groups, GO losses its hydrophilicity and as a result roughness was increased. However, on grafting ligand and metal ions, peak at around 2θ = 26.5º in the XRD spectra of GO and characteristic peak of A-*f*-GO was experienced blue shift due to more disordered layers of GO nanosheets. But no alteration in the properties of GO was seen. After the reaction of GO with $SOCl_2$, XRD pattern of Cl-*f*-GO exhibited a broad peak at 2θ = 25.01° with inter-planar distance of 3.55 Å. This reduction in inter-planar distance was believed to be due to formation of –COCl group by substituting hydroxyl groups of –COOH at the edges besides some of the –OH groups lying on the basal plane and these results were in good accordance with DFT calculations. However, XRD patterns of as-prepared heterogeneous catalysts (in case of catalysts synthesized by modifying –COOH groups) showed characteristic diffraction peaks of metal ions at around 36.9º, 38.6º, 44.8º, 55.7º, and 59.3º for Co-*f*-GO were assigned to indices (311), (222), (400), (422) and (511) indicating the presence of Co as Co_3O_4; minor peaks at around 20.2º, 21.6º, 26.1º, 32.3º, 37.1º, 41.9º, 45.2º and 57.9º for VO-*f*-GO were attributed to (001), (101), (110), (011), (401), (102), (411) and (221) planes of vanadium oxide, whereas peaks at around 29.8º, 36.8º, 42.7º and 61.8º for Cu-*f*-GO were assigned to (110), (111), (200) and (220) planes of Cu_2O and minor peaks at around 35.7º, 39.9º, 47.8º and 60.9 which were ascribed to (002), (111), (202) and (113) planes of CuO. On functionalization with $SOCl_2$ and metal-salen complxes, reduction was experienced in the amorphous nature of the smaples indicating the polycrystalline nature of the samples which was also validated by HRTEM analysis. We have calculated the estimated nanocrystallite size from XRD data using Debye-Scherrer equation for all the catalysts.

Metal content in the as-synthesized catalysts of both series had been estimated as 23.01, 4.456 and 10.736 ppm for V, Co, and Cu, respectively in case of catalysts synthesized by modifying –OH groups while it was 47.496, 35.39 and 32.397 ppm for Cu, V and Co, respectively in case of catalysts synthesized by modifying –COOH groups, through ICP-OES results. Surface area of the catalyst synthesized by modifying –OH groups has been measured as 94.23, 40.70 and 33.37 m^2/g for GO, A-*f*-GO and catalysts, respectively, using BET analysis, while temperature programmed desorption of ammonia was performed to interpret the distribution of acid site strength on the surface of solid heterogeneous catalysts synthesized by modifying –COOH groups.

The bonding of metal ions of functionalized GO sheet had been investigated through XPS analysis. Existence of all the elements in the as-prepared heterogeneous catalysts had been confirmed by observing the characteristic peaks at definite eV in the survey spectra. Characteristic signals at 286.1 and 533.3 eV was confirme the presence of C and O; while peak at 400.2 eV confirms the existence of N, peak at 101.4 eV was emerged due to presence of Si. However, peaks at around 933.5, 952.8, 780.5, 796.3, 516.1 and 523.01 eV were corresponds to Cu $2p_{3/2}$, Cu $2p_{1/2}$, Co$2p_{3/2}$, Co$2p_{1/2}$, VO $2p_{3/2}$ and VO $2p_{1/2}$, respectively. Moreover, high resolution C1S, O1S, N1S, Co2P, VO2P and Cu2P spectra provide detailed information of bonding environment of the elements. Hence, successful insertion and attachment of the metal ions to GO nanosheets had been authenticated by XPS analysis in both the cases.

The HRTEM analysis revealed the multi-layered structure of GO nanosheets and homogenous distribution of the metal ions to GO surface. Since oxidative functional groups were primarily unite together via dangling bonds in GO, the thickness of GO nanosheets observed more pronounce at the edges. However, in the –COOH modified catalysts, the thickness at the edges was found to be further increase due ruputuring of edges by $SOCl_2$. Besides this, some of the –OH groups of the basal plane was also seen to be functionalized resulting in more stacked packing arrangement of the layers. SAED patterns of –OH modified catalysts divulged the retention of its amorphous nature during the course of action which supports the conservation of structural and morphological characteristic of the material during synthesis. Whereas SAED patterns of –COOH modified catalysts was revealed the alteration on the surface morphology after the grafting with metal-salen complexes and exhibited its polycrystalline nature. In addition to this, average particle size was also calculated for the catalysts of both the series using Image J software.

In order to accurately investigate the structural and electronic properties, binding mechanism of amino groups of APTMS and chloro groups of $SOCl_2$ over GO with different functional groups like –O–, –OH and –COOH, first principles-based density functional theory (DFT) calculations had been performed. Besides this, other parameters such as different global reactivity descriptors, i.e., electronegativity (χ), chemical potential (μ), global hardness (η), global electrophilicity index (ω) and global softness (S) were also calculated. The results of DFT study were in good accordance with our experimental outcomes that APTMS functionalized only –OH groups of the GO surface; while $SOCl_2$ functionalized mainly hydroxyl groups of –COOH together with –OH groups of the GO surface.

To check the catalytic competency of the as-synthesized heterogeneous catalysts, they had been weighed up against diverse oxidation reactions, for instance, selective oxidation of benzyl alcohol, epoxidation of styrene, epoxidation of norbornene and oxidation of glucose. The results demonstrated that amongst the catalysts synthesized by selective modification of –OH groups of GO, CuL-*f*-GO for selective oxidation of benzyl alcohol, VOL-*f*-GO for epoxidation of styrene, VOL-*f*-GO for epoxidation of norbornene and CuL-*f*-GO for oxidation of glucose had been proven as best suited catalysts. However, amongst the catalysts synthesized by selective modification of –COOH groups of GO, Cu-*f*-GO for selective oxidation of benzyl alcohol, Cu-*f*-GO for epoxidation of styrene, VO-*f*-GO for epoxidation of norbornene and Cu-*f*-GO for oxidation of glucose had been proven as best suited catalysts. We have also checked the low mesh sized graphite flakes for the fabrication of transition metal grafted GO supported heterogeneous catalyst (via modification of –OH groups) and applied for the selective oxidation of benzyl alcohol. From the results of this study, we came to the conclusion that higher mesh size of the flake graphitewas appropriate and profitable for the synthesis of GO supported heterogeneous catalysts as dicussed in chapter 4 as point no 4.1.10.

At the end, the results of these catalytic studies had been systematically compared in chapter 6. From the outcome this comparative study and summarization of all the data, it can evidently be articulated that the –OH modified catalysts are the constructive and best suited catalysts and –OH oxidative debris as the “site of choice for the modification to fabricate transition metal grafted heterogeneous catalysts for oxidation reactions”.

7.1. Suggestion for future work

The present research work is focused on the synthesis and characterization of transition metal grafted graphene oxide supported heterogeneous catalysts for the choice of selective oxidation reactions viz. benzyl alcohol, styrene, norbornene and glucose.

There are ample opportunities for graphene and graphene oxide in the manufacturing of numerous organic syntheses. In addition to this, graphene oxide can be converted to graphene by the reduction of the oxidative debris present on its surface followed by the dispersion of transition metal nanoparticles, metal oxides and rare earth oxides for variety of catalytic reactions. Systematic investigation demonstrates that graphene possessing exceptional electronic and other stupendous properties being a promising material for a wide range of applications. Graphene oxide can also be used for the synthesis of graphene quantum dots (GQDs). Doping with a choice of doing agent(s) one can tune the electronic properties of graphene which has broad spectrum application such as in the fabrication of solar cells, environmental applications, sensors, various biological motives and variety of biocompatible instruments. Graphene can also be tailored for the burning issue of air purification and water decontamination.

There is plenty of research left to be done, for the bulk production of graphene, a novel reduction method that reduces the residual oxidative debris to possible maximum level. Recently, a nascent form of graphene, 3D graphene, due to its outstanding absorbance property is becoming an eye-catching area for the researchers. Above and beyond to these areas of research, one most vital and thrust field of precise characterization techniques is optimistically and ardently awaiting for new findings.

This “magical material” that turns all the curiosity and fantasy of researcher to a reality and endow with a new line of attack to deal with complex situations for societal challenges in terms of green and sustainable developments along with environment fortification. It is a blessing material with an “art of exciting” the spirit of quest in expert and neophyte researchers.