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Carbocatalytic Activity of Graphene Oxide in Organic Synthesis

Biju Majumdar, Daisy Sarma and Tridib K. Sarma

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Abstract

Nanochemistry has evolved as an important part in catalysis for both academic as well as industrial research. Traditional homogeneous catalytic systems have gained significant importance due to the molecular level analysis of their catalytic activity and the excellent homogeneity of the catalysts and the reactants. However, removal of the catalysts from the reaction mixture without product contamination requires tedious purification steps. With increasing ecological and economical demands towards sustainable chemical synthesis, the recovery and reuse of catalysts has been an important factor. In this drive, various heterogeneous catalytic systems including mesoporous materials, solid catalysts, organometallics, noble-metal nanoparticles, etc. have been developed for photochemical and electrochemical conversion, environmental remediation as well as catalyst for important chemical transformations. Carbon nanomaterial specially graphene oxide and carbon dots have received significant research importance due to their large scale availability, easy surface modification, non-toxicity and other surface properties. Here, we review the continuous progress in the development of graphene based materials and their catalytic activity in organic synthesis.

Keywords: carbocatalysis, graphene oxide, oxygen functional groups, organic synthesis

1. Introduction

In recent years, there has been tremendous focus towards developing greener synthetic methods for the industrial production of fine and commodity chemicals. Towards the development of economical and sustainable routes for large scale synthesis, the ideal protocols are characterized by four parameters: catalytic activity, selectivity, atom-economy and step-selectivity. Among them, development of catalytic systems with high activity and selectivity plays the

most important role. A catalyst provides an alternative pathway with a lower activation energy barrier for an organic reaction without being transformed itself [1]. If there are several products and several reaction barriers, a catalyst can drive the reaction selectivity with a particular product. The efficiency of a catalyst lies on the formation of the desired product with high yield and selectivity at relatively milder reaction conditions. Hence, the search for suitable catalytic systems to achieve green and sustainable production of chemicals is growing continuously, that promotes reduction of toxic and hazardous chemicals, stoichiometric amount of promoter, less consumption of energy, fewer side products and less number of steps involved.

In the past, the main objective of catalysis was to enhance the activity and selectivity of a catalyst, the recovery and reusability of a catalyst was rarely a major concern. Traditional homogeneous organocatalysts, transition metal catalysts as well as bio-catalytic systems are highly efficient because the catalytic activity can be defined on a molecular level. These single site catalysts are highly accessible to reactant molecules, readily soluble in reaction medium and often give rise to high catalytic activity and selectivity even under mild conditions [2]. However, often use of expensive metal salts, expensive ligands, expensive and tedious purification steps as well as recovery of the catalyst is the major issue. A variety of homogeneous and heterogeneous catalysts have been developed, however there is still a vast scope for development of suitable catalysts that not only offers high activity and selectivity, but also provide a greener route. Fabricating single step synthetic methods using heterogeneous catalysts is a challenging goal as it aims at decreasing the energy and time consumption by operation of single step synthesis. This consequently eliminates the need of separation of products from the reaction mixture again and again.

1.1. Nanocatalysis

In the area of heterogeneous catalysis, the primary focus is towards development of materials with high surface area as the reactions involve surface initiated pathway. With exceptional nanodimensional properties (high surface to volume ratio), nanoparticles have produced tremendous interest in wide range of research activities including pharmaceuticals, fine chemicals, renewable energy and biotransformation. The key objective of nanocatalysis research is to produce catalysts with 100% selectivity with extremely high activity, low energy consumption, and long lifetime. This can be achieved only by precisely controlling the size, shape, spatial distribution, surface composition and electronic structure, and thermal and chemical stability of the individual nanocomponents. In addition, surface atoms which are at the edges or in the corners are more active than those in planes, and their number also increases with decreasing particle size. Thus nanoparticles have shown tremendous applicability at the interface between homogeneous and heterogeneous catalysis [3–5]. Homogeneous nanocatalysts are used in the same medium as the reactants. The main concern with homogeneous nanocatalysts is their recovery from the solution for repeated cycles as nanoparticles are extremely difficult to be removed from a solution and the extra steps needed to do so could completely negate the process simplification. If the nanoparticles cannot be recovered, they pose an environmental risk, as well as threatening the profitability of the process. For

easy recovery and recyclability, the active nanocatalysts are often immobilized on a solid inert matrix, which is in a different phase to the reactants. The solid catalysts can in most cases simply be filtered out and used for the next cycle of reactions, making the process economical and ecological. Due to the complex physicochemical properties at the nanometer level and possibility of multiple surface initiated reactions at the active site, synthesis-structure-catalysis performance relationships are poorly understood in many catalytic systems. A variety of heterogeneous catalytic systems based on metal nanoparticles, semiconductors, oxides/sulfides, mesoporous materials, metal-organic framework etc. and their combinations have been developed for photochemical and electrochemical catalysis, environmental remediation as well as catalysis for important chemical conversions. Other metal-free nanomaterials such as fullerene, graphite, graphene oxide (GO), carbon nanotube (CNT) and carbon nanodots (CNDs) have also been studied either as effective carbocatalyst or as support for metal/oxide for various catalytic applications.

In heterogeneous catalysis, the *modus operandi* is through surface mediated reactions. Therefore, availability of large surface area is a prerequisite for high catalytic conversions [6, 7]. Although, unsupported nanoparticles with well-defined surface structure and clean exposed facets are predicted to be highly active for catalysis as shown by several theoretical studies, their applicability in real catalysis is a challenge. Due to high surface energy resulting from the large fraction of atoms present on the surface of NPs, they tend to reduce the surface energy and stabilize themselves through agglomeration and coagulation, resulting in decreased active surface area [7]. This leads to an exponential decrease in the surface area for effective catalysis and the prime objective of using nanoparticles for repeated cycles with high activity is practically lost. For example, in case of Au nanoparticles, size plays a critical role during oxidation reactions, as nanoparticles with the diameter 1–5 nm are highly active, whereas larger nanoparticles becomes inactive. The protection of nanoparticle surface from agglomeration can be achieved by using a surface stabilizing agent or immobilizing the NPs into a solid matrix with high surface areas [8, 9]. Soft organic materials such as polymers, surfactants, dendrimers, and ionic liquids have been used as effective capping agents. These systems often show high catalytic performances [10] e.g. reduction of nitrobenzene, olefin hydrogenation and CO oxidation at low temperatures by Au nanoparticles, C–C coupling or hydrosilylation reactions of olefins by Pd nanoparticles. However, these polymeric supports suffer certain disadvantages such as providing low surface area which limits the interface between the catalyst and the reaction substrate. Moreover, soft nature of the materials and low mechanical stability often leads to separation of the support from the NPs surface after repeated reaction cycles which eventually results in agglomeration of the particles and decrease in catalytic activity. Alternatively, nanoparticles have been immobilized or grafted onto solid supports to improve their stabilization and recycling ability [8]. “Inert” porous solid materials such as zeolites, charcoals, metal-organic frameworks, layered-double hydroxides etc. have been used for immobilization of active metal catalysts. Being inert and hard, these materials are highly stable even under harsh reaction conditions and can be easily recovered from the reaction mixture for further applications. Porous materials also allow control over the nanoparticle growth in the porous matrix, prevents agglomeration and enhances active site exposure [11]. The host support materials stabilizes the nanoparticles, however they have

no role in manipulating the activity of the nanoparticles for catalysis. In the last few years, there has been tremendous focus on the development of “active” supports, which along with stabilizing the nanoparticles also contribute towards overall catalytic activity in synergy with the nanoparticles [12, 13]. For example, the charge state of the Au nanoparticles is known to influence their reactivity, in the case of the negatively charged Au nanoparticles, an extra electron from the gold readily transfers to the anti-bonding $2\pi^*$ orbital of the adsorbed O_2 , which weakens the O—O bond and activates oxygen molecule for further catalytic reaction. On the other hand, the positive charge accumulated on the gold can promote adsorption of some reactants, such as CO and hydrocarbons. An active support can transfer charges to/from the active catalytic surface, hence influencing the activity of the reaction. For example, Au nanoparticles anchored on rutile TiO_2 (110) surface shows high activity for the oxidation of CO to CO_2 . Along with providing significant exposed catalytic active sites for the reaction, TiO_2 also involves in charge transfer process with the Au NPs making the NPs surface highly negative for dioxygen activation leading to oxidation of CO to CO_2 [14]. Recently, research works involving GO as a support for immobilizing active metal nanoparticles have gained attention. GO, not only provides a large surface area with high exposure of active catalysts, but also can influence the catalytic activity [15]. Possible surface to metal electron transfer from GO to nanoparticles activating dioxygen molecule over NPs surface for several oxidation reactions has been reported [15]. Hence, choice of a suitable support for NPs stabilization with possible cooperativity might play an important role in controlling the reaction yield and selectivity of products.

2. Carbocatalysis

Carbon is one of the most abundant elements on earth and is central to life. Hence, catalytic application of carbon is very attractive and both organic and inorganic carbons play a key role in catalysis. A huge amount of organic compounds act as highly efficient homogeneous catalysts, forming a dedicated branch of chemistry “organocatalysis.” Carbon is often the main constituent of the organic ligands surrounding the metallic center in organometallics. In enzymatic catalysis it constitutes the backbone of the active species. In heterogeneous catalysis, carbon materials act as unique catalyst supports by anchoring different active species through its active site and can also act as catalysts by themselves. The physical and chemical properties of carbon materials, such as their tunable porosity and surface chemistry, make them suitable for application in many catalytic processes.

Among the carbon catalysts developed, activated carbon (AC) and carbon black (CB) are the most commonly used carbon supports. The typically large surface area and high porosity of activated carbon catalysts favor the dispersion of the active phase over the support and increase its resistance to sintering at high metal loadings. The pore size distribution can be tuned to suit the requirements of active supports and substrates. The activated carbon shows several advantages owing to their several outstanding properties, such as low cost, resistance to acids and bases, high stability even at elevated temperature, high surface area ($>1000\text{ m}^2/\text{g}$)

and easy removal etc. Moreover, metal salts can be reduced to active metallic forms in these mesoporous materials, making them highly competent as metal supports.

The study of chemical reactions using carbon materials are termed as carbocatalysis. The catalysts are prepared and used in the powder form and hence they are heterogeneous. Carbocatalysis has been known for decades since the first discovery of catalytic activities of carbon materials [16] when Rideal and Wright [17] showed the charcoal catalyzed oxidation of oxalic acid, which was one of the ground breaking discovery of carbocatalysis. Moreover, 45 years earlier also, carbon materials were shown to be effective for the conversion of halogenated hydrocarbon [16].

With the development of fullerenes, the research activities for the growth of nanocarbon materials have gained momentum. Several polytypes of carbon which include fullerenes, nanotubes, graphene, nanodiamonds and amorphous porous carbon and their derivatives represent a rich class of solid carbonaceous materials with environmental acceptability and reusability and all are found to be catalytically active in certain reactions. However, most of these carbon materials are highly hydrophobic without any functional groups on their surface.

Fullerene black is an efficient catalyst for dehydrogenation, cracking, methylation, and demethylation reactions. C_{60} and C_{70} were found to be suitable catalysts for the reduction of nitrobenzene, using hydrogen gas under UV light [18]. Further, several organometallic compounds involving fullerene as a ligand have been developed that showed efficient catalytic activity for several organic transformations.

The 1D and 2D carbon materials such as carbon nanotubes and graphene offered high surface area and continuous efforts are focused on surface functionalization of these materials, both through covalent and non-covalent approach. Oxidation in presence of strong acids and oxidants could introduce oxyfunctionalized groups on the surfaces of these carbon materials, making them hydrophilic and suitable for anchoring several active catalytic groups on their surfaces. The work on the oxidative dehydrogenation reaction by Mestl et al. [19] and Zhang et al. [20] opened a new window in carbocatalysis. Carbon nanotubes, in its oxygenated forms, showed efficient catalysis for oxidative dehydrogenations e.g. conversion of n-butane to 1-butene [20]. In the catalytic hydrogenation of ethylbenzene to styrene, a process of high industrial relevance, CNTs perform better than activated carbon and graphite as catalysts. It was reasoned that the reactant molecules were first adsorbed on the CNT surface via π -interactions next to basic oxygen moieties, which facilitated dehydrogenation with concomitant formation of surface hydroxyl groups [19]. Taking advantage of surface modification techniques, various nanoparticle as well as molecular catalysts could be anchored on carbon nanotubes [21] (**Figure 1**).

2.1. Graphene oxide as a carbocatalyst

Graphene and other two-dimensional sp^2 -hybridized carbon scaffolds are expected to have large impacts in the area of catalysis, mainly because of their unique electronic properties

oxide surfaces can be reduced by heating at elevated temperature. Various heteroatoms such as N, B, P, Se, S, F, and Cl [24] can be incorporated into the lattice of graphene sheets. Several organic reactions can also incorporate acidic functional groups such as $-\text{SO}_3\text{H}$ groups onto graphene sheets [25].

GO and their chemically converted forms have shown broad spectrum of catalytic activity ranging from oxidation reactions and thermal decomposition reactions. Bielawski et al., first demonstrated catalytic activity of graphene oxide for liquid phase organic transformations [26]. Since then, a variety of organic transformations have been explored taking advantage of the functional groups present on the graphitic surface. **Table 1** summarizes a variety of reported reactions catalyzed by GO and chemically converted GO.

Further, the two-dimensional surface of graphene based materials can be used to anchor other active catalysts as well as biocatalysts. For example, the catalytic activity of several enzymes including cytochromes, peroxidases, myoglobins, and hemoglobins supported on graphene

Catalyst	Reactions	Active sites	References
	Oxidation reactions (promoted by molecular O_2)		
(BN)HoIG	Aerobic oxidation of amines	Doped N and B are active sites	[28]
GO	Aerobic oxidation of benzylic alcohols	Oxygen functional groups	[29]
	Oxidation reactions (promoted by other oxidants)		
rGO	Oxidation of pollutants (H_2O_2)	Electron rich oxygen groups	[30]
	Reduction reactions		
B, N or O doped G ribbon edges	H_2 dissociative adsorption chemisorption on G ribbon edge	Beneficial B doping	[31]
	Acid reactions		
rGO- SO_3H	Dehydration of xylose to furfural	$-\text{SO}_3\text{H}$ are active sites	[32]
	Base reactions		
rGO- NEt_3	Hydrolysis of ethyl acetate	Amino groups are active sites	[33]
rGO-PAMAM	Knoevenagel condensation	Basic sites of the catalyst	[34]
	Thermal decomposition reaction		
rGO	Thermal dehydrogenation and rehydrogenation of LiBH_4		[35]

Table 1. Catalytic reactions by GO and chemically converted GO. (B, N)-doped holy G [(BN)HoIG], reduced graphene oxide (rGO), triethylamine modified rGO (rGO- NEt_3), rGO functionalized with $-\text{SO}_3\text{H}$ (rGO- SO_3H) and poly(amidoamine)-modified rGO (rGO-PAMAM).

surface enhances several folds compared to the unsupported enzymes towards the oxidation reaction of pyrogallol [27]. The importance of oxygen functional groups on GO surface has been exploited towards several C–H activation and C–C coupling reactions. The carbocatalytic activity of graphene oxide has successfully been exploited by Ma et al. for the C–H bond arylation of benzene enabling biaryl construction. The oxygen functional groups in these graphene oxide sheets and presence of KO^tBu were demonstrated to be essential for the observed catalytic activity. Several model reactions and DFT calculations confirmed that the negatively charged oxygen atoms promote the overall transformation by stabilizing and activating K⁺ ions, which in turns facilitates the activation of the C–I bond. The π basal plane also greatly facilitates the overall reaction as the aromatic coupling partners are easily adsorbed on the 2d surface [36]. Transition-metal-catalyzed alkylation reactions of arenes have turn out to be a central transformation in organic synthesis. Szostak et al. developed the first general strategy for alkylation of arenes with styrenes and alcohols catalyzed by carbon-based materials, exploiting the unique surface property of graphene oxide to produce valuable diarylalkanes with excellent yields and regioselectivity. Remarkably, this protocol represents the first general application of graphene oxide to promote direct C–C bond formation utilizing oxygenated functional groups present on GO surface [37]. Recently, our research group have demonstrated the dual carbocatalytic activity of graphene oxide for the C–N coupling reaction towards the formation of α -ketoamides through a cross-dehydrogenative coupling pathway [38]. The presence of polar functional groups (e.g., carboxyl, hydroxyl, ketonic, and epoxides) on graphene oxide surface induce acidic as well as oxidizing properties to the material. This dual catalytic property of the material is explored towards the generation of α -ketoamides where surface acidity favors the initial formation of hemiaminal intermediate followed by oxidation leading to the desired final product. Several control experiments as well as thermal treatment showed that it is the oxygen functional groups, especially carboxylic acid group that is only responsible for the observed catalytic activity. The protocol could also be extended towards the synthesis of biologically important α -ketoamides. On the other hand graphene surface can also be used as support for immobilization of several metal/metal oxide nanoparticles and used for several electrocatalysis, photocatalysis and organic transformations [39, 40]. For example, Pd nanoparticle immobilized on graphene oxide gave remarkable turnover frequencies (TOF > 39,000 h⁻¹) in Suzuki-Miyaura cross-coupling reactions. Microwave assisted reduction of well-dispersed GO and palladium salt to form Pd/rGO [41] demonstrated outstanding catalytic activity for the Suzuki-Miyaura coupling reaction (TOF up to 108,000 h⁻¹) under ligand-free conditions, which was attributed to the high concentration of well dispersed Pd-NPs.

3. Current and future prospect

The carbon based nanomaterials have already demonstrated their enormous potential either as catalysts or heterogeneous catalyst supports. Graphene oxide with oxygenated functional groups on their surface could act as active sites for various acid catalyzed and oxidative catalytic reactions. Recent advancement of these graphene based materials shows that the modification of graphene surface by different methods leads to generation of holes which acts as traps

for reactive oxygen species for many challenging organic reactions [42]. Hence tremendous possibilities of these carbonaceous nanomaterials remain to explore in various fields including chemical synthesis, energy storage, fuel-cells, environmental remediation and organism degradation. Carbon nanodots are the recent inclusion to the nanocarbon family. The excellent photoluminescence properties of carbon nanodots have directed their application in different fields including sensing, optoelectronics, bio imaging, nanomedicine, etc. Although they are widely explored in sensing as well as bio-medical application, their inherent photocatalytic capability towards organic synthesis has not been explored much. So, the development of carbon nanodots towards organic synthesis may result in an important alternative to the traditional transition metal based catalysts. There are still huge scope towards (i) high performance carbon catalyst specific for desired products, (ii) development of chiral carbon nanomaterials for enantioselective synthesis, (iii) affordable methods for large scale synthesis, industrial scalability and economic viability, (iv) detailed elucidation of catalytic mechanism that can bring further improvements in catalytic activity and (v) stability of the catalyst to maintain excellent catalytic activity during recycling. Overall, development of carbon related catalysts with broader applications is imminent towards green and sustainable chemistry.

4. Conclusion

In this chapter, we have reviewed the inherent carbocatalytic activity of graphene oxide towards different organic transformations. The π - π^* network as well as oxygenated functional groups present over the GO surface both contributed towards the enhanced catalytic activity. The presence of π - π^* network on graphene surface helped the substrate molecules getting adsorbed over the catalyst surface and the oxygenated functional groups catalyzed the reaction. The oxygenated functional groups acted as the active site for several acid catalyzed as well as oxidation reactions. Further, the presence of various oxygenated functionalities on the surface of graphene oxide could be used for anchoring other active catalysts such as metal and metal oxide nanoparticles. The reducing capability of these nanocarbons could also be envisaged for reduction of metal ions to nanoparticles.

Author details

Biju Majumdar, Daisy Sarma and Tridib K. Sarma*

*Address all correspondence to: tridib@iiti.ac.in

Discipline of Chemistry, Indian Institute of Technology Indore, Indore, Madhya Pradesh, India

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